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## My Life with Polymer Science: Scientific and Personal Memoirs

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# My Life with Polymer Science



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## Acknowledgments

During my life I was associated with numerous persons and personalities who shaped my personal, scientific and professional life. I am indebted to all of them with full appreciation. They are mentioned throughout the book, in the list of co-authors and students.

In this acknowledgment I would like to thank those that were directly involved in my development: playmates in childhood, school friends, high school and college friends, mentors, colleagues, coworkers and students.

The early years of my life were spent in Traiskirchen, Austria, my birthplace. I had a nice childhood in a happy family, wonderful playmates and school friends at the Elementary School: Hertha Pezda, Rudi Kautz, Friedl Ferschner and I had a very dedicated fourth grade teacher, Olga Hermann, whom I adored. She spent many hours after school preparing me for the entrance examination to the Realgymnasium in Baden.

The Realgymnasium (middle and high school) provided new and trusted friendships for a growing adolescent: Heinz Wogrinetz, Leopold Stumvoll. Later Wolfgang Ulrich became my intellectual friend. How I admired my history teacher, Kraupp, and my chemistry teacher, Helpap.

Once I entered the University of Vienna I entered a new world. Again new friends became an essential part of my life. As the new generation of chemistry students we formed the "the group of '45": Karl Schloegl, Fredl Renner, Kurt Komarek and Liselotte Kuert.

During my thesis work I was in Galinovsky's group: We had the "left-overs" of Spaeth's graduate students - Tuppy, and Goldberger. We also had a postdoctoral visitor from Milan, Italy, who has been a close friend throughout my life: Giuseppe Bianchetti. Over all these activities my mentor and thesis advisor Friedrich Galinovsky kept a keen watch.

Upon arrival in the Unites States, I first went to the University of Michigan where I worked with Christian S. Rondestvedt and had as my laboratory partner Kathy Spackman. Then I moved to Princeton University, where I worked with Ted Taylor

with Tom Osdene as my laboratory partner. I remain grateful for all these people with whom I had close contact during the beginning of my career in America.

My scientific contributions to Polymer Science can be divided into three parts.

The first years were spent at DuPont, at the Polychemicals Department. There I appreciated the companionship of Herbert S. Eleuterio, William L. Truett, the Manager of the Delrin group, Carl Schweitzer and the Director of Research of the Polychemicals Department, Frank McGrew. At the Central Research Department, my lab partner for several years was Burton C. Anderson, and the Director of the Central Research Department; Ted Cairns played an important role in my life.

I am most appreciative for my academic career at the University of Massachusetts to Richard S. Stein, who seemed to have suggested me for the position of Professor of Polymer Science and to Roger Porter, Department Head, who subsequently hired me.

Over the years, how very much I learned from my close acquaintance with the giants in Polymer Science, Carl Marvel, Herman F. Mark, whose name was used later for the name of my endowed Professorship at the Polytechnic University and Junji Furukawa who opened for me the door for Polymer Science in Japan (and the Orient).

In my career I became closely associated with some older colleagues who had achieved a high distinction in the polymer community: George Smets, Bengt Rånby, Henri Benoît, Piero Pino, Teiji Tsuruta, Cristofer Simionescu, and Renyuan Qian. I am also grateful for their friendship and support.

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For over 45 years much of my scientific research involved work in the laboratories; it was necessary to be inventive and novel. I am indebted to my former collaborators, coworkers and students for their dedicated devotion Burton C. Anderson, David A. Tirrell, Ann Christine Albertsson, Eberhard Borsig,

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Part of my career was involved in professional politics, especially in the ACS Division of Polymer Chemistry. I was happy to be associated with Jack Elliott, Jesse Hwa, Joseph C. Salamone, and Stanley Israel in this activity.

My most important dedication of this legacy is to my parents Franz Vogl and my mother Leopoldine, née Scholz. They provided me with a wonderful childhood and guidance for my adult life that I believe is unparalleled. They provided me with love and encouragement to succeed in the world. My brother Leopold, older than I, was always available when needed. While I was a student in Vienna, he provided me with support in every possible way and later in life was an ideal Uncle to my children.

In Ann Arbor, MI as a postdoctoral fellow I met my future wife Jane Cunningham. She has been a wonderful marriage partner and mother of our children Eric G. and Yvonne. They, born and raised in Wilmington and Amherst, have achieved successful careers after their college years and have their own families.

As I said I had the privilege of being associated with outstanding colleagues, post doctoral fellows, coworkers and students and a supportive family. They provided inspiration for the ideas, and dedication for the success in my career and life and I thank them all.

## Preface

For some time I have been planning to write down my thoughts and the circumstances that have led to my scientific career and accomplishments. I never had any specific ideas of how I would write the story of 55 years of my professional scientific career resulting in about 630 articles including 465 scientific papers.

In October 1990 I met with Dave Tirrell, a former graduate student of mine, and then a Professor at the University of Massachusetts, in a restaurant in Tokyo. The restaurant was located in the Ocha-no-mizu section near the University of Tokyo. Dave is now the Head of Chemical Sciences Division at Cal Tech and at that time he was the Chairman of the U.S.-Japan Symposium on Polymer Synthesis, a conference that was the last in a sequence of Symposia that I had started with Professor Junji Furukawa of Kyoto University 20 years earlier.

When Dave and I started to talk about the accomplishments of scientists in chemistry whom we knew who had written their "life stories." Dave said, "why don't you write about your scientific career and how you arrived at where you are today?"

It was then that the idea of writing my "life story" was formed. Dave was and is very interested not only in science but also in science history the circumstances under which discoveries and accomplishments are made. He commented that he knew me very well but that there were many things that he didn't know about me.

I was intrigued by Dave's suggestion and because memories often pale as time passes, I decided I would begin as soon as time allowed. It was my intention to emphasize primarily science but also weave some other personal developments and thoughts into the picture where I believed it was necessary and desirable. Considerable research for background information from notebooks, notes, annual and

meeting reports from my earlier days which were not as well recorded was necessary. From the day I dictated the first draft of this undertaking, more than 10 years have elapsed and I have substantially changed my approach to the project.

For many years I have followed the accomplishments of my colleagues and especially admired those of my elders. Over the years such giants as Marvel, Mark, Smets, Rånby, Elderfield, Fajans, Palit, Kern, Staudinger, Blicke, Pacsu, Turkevitch, Roberts, and Everett Wallace had crossed paths with my career. I had followed their accomplishments and known them personally. Such connections are important and influenced greatly my own development and way of thinking. However, many other scientists have played significant and influential roles in my career. I would like to mention only a few; J. Furukawa, S. Okamura, C.I. Simionescu, E. Katchalki-Katzir, Murahashi, Oda, Fukui, Kern, H. Benoit, F. McGrew, C.C. Price, G. Natta, P. Pino, P. Corradini, T. Tsuruta, M. Takayanagi, W. Bailey, C.G. Overberger, G. Butler, G. Manecke. Dozens of other people, especially of my generation, have directly influenced my research and my thinking about science.

I realized that some events might appear more glorified and possibly quite different from the actual circumstances and impressions when they occurred. Some earlier events probably seemed more important at the time and later other events replaced them in importance. I will try to balance these memories now as they come to mind.

My "life story" will begin with my formative years, my childhood and student days at the University of Vienna, including my dissertation. It will be followed by my teaching appointment as an Instructor at the II. Chemical Institute of the University of Vienna. The urge to see other lands, learn other languages and scientific methods led to the Wandering Years that brought me to the United States. After three years spent as a Research Associate at the University of Michigan and at Princeton University I spent more than 13 years in an industrial career at the Du Pont Company in Wilmington. I returned to Academia when I received an invitation to join the University of

Massachusetts as Full Professor, a second academic career ensued; as an established scientist. I concluded the last part of my career as the Herman Mark Professor of Polymer Science, an endowed chair at Polytechnic University in New York and the first endowed chair in polymer science.

Each period of my professional life has had its own characteristics. In the formative years, I was dependent on others and guided by their interests. During my industrial career, I learned the importance of novelty, patentability and the drive for usefulness. In Amherst emphasis shifted to teaching, research, professional politics and complete scientific independence. As Research Professor in Brooklyn, my career was strengthened by addition of responsibilities of representation.

In the last two decades I became more and more involved in writing and scientific publishing. I retained my position as Editor-in-Chief of Progress in Polymer Science until the end of 2002. It was a fascinating and demanding position that I treasured very much.

I will present my scientific career not in an exactly historic way, but as scientific programs and projects developed. The content of the book covers the 55 years of my scientific career. I have worked and been interested in a number of areas of science. As a Professor and leader of a sometimes-large research group, I organized our research activities into a few thrust areas. We changed these areas when we felt we had made significant contributions. I wanted to expose my students and collaborators to a substantial part of Polymer Science, not just one important subject. I also wanted to be able to enter a new field in which we could make significant contributions.

I have now concluded my scientific career. This book is intended as simple reading material and does not pretend to be more than a life story that developed through circumstances, foresight, determination, and recognition of unusual relationships.

Amherst, August 2004

# I. The Formative Years

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## A. My Youth

I was born in the city of Traiskirchen, in the Karl Luydererstrasse Nr. 8, on November 6, 1927, as the second son of Franz and Leopoldine Vogl (née Scholz). Traiskirchen lies in Lower Austria about 20 miles south of Vienna and was a market town (Marktgemeinde) for centuries. It had been elevated, on June 30, 1927, to the status of a city, having, at that time, a population of about 6,500; it was divided into the townships of Traiskirchen. Möllersdorf and Wienersdorf. Today, Greater Traiskirchen also includes Tribuswinkel and Oyenhausen and the population has grown to 16,000. It is now the 8th largest city in Lower Austria and the 28th largest in Austria.

The land on which Traiskirchen is located was already inhabited in Roman times and actual remains of inhabitation can be traced to the 6th century. Several years ago the ruins of a village of the Awares, Asian conquerors that dominated this part of Europe during the 4th to the 7th century, were unearthed in the area of Traiskirchen proper.

The first official note of habitation in the location that has become Traiskirchen can be traced to 1082 when the bishop of Passau authorized the building of a church. The church was donated in 1113 by Duke Leopold to the Benedictine Abbey of Melk. This year is often used as the date of birth of Traiskirchen. This church became the mother church of churches serving a number of villages on the western part of the Vienna lowland south of Vienna. Melk had been the capital of the Babenbergs; a family of dukes who reigned over the land that was then called "Ostarrichi" and that ultimately became the country of Austria.

In 1319, Traiskirchen was elevated to a market town. It was devastated several times during the wars of the 15th to the 17th century. After the successful repulsion of the last Turkish siege of Vienna in 1683, the country of Austria prospered. Traiskirchen also prospered, especially in the late 18th and 19th centuries. The town was located only a day's travel by horse to/from Vienna on the southern trade route and almost exactly in the middle between the important town of Wr. Neustadt and Vienna. At one time the town had 30 inns providing food and shelter for horses and men. Traiskirchen was also, for over 100 years, the district capital and was the seat of the bishop.

I was actually the 5th or 6th newborn citizen in the new city of Traiskirchen, a "City Citizen." I had one brother, Leopold, who was several years older than I. For that reason I grew up for practical purposes as an only child, although in the later part of our lives my brother and I were very close friends. My father's ancestors came from Traiskirchen and surrounding towns, mainly Moedling, located on the edge of the Vienna Woods. My mother came from Velm and surroundings, about 10 miles to the East of Traiskirchen, toward the state of Burgenland. The legendary Franz Joseph I. reigned as Hapsburgian Emperor over the Austro-Hungarian monarchy, a country of about 55 million people.

I should probably relate some of the stories from my early youth. Many are probably not in my memory directly, but have been told or recollected. Not many stories were written down nor were pictures taken because photography was not common and not everybody had a camera.

I grew up in a small house that we rented from a certain Mr. Wanek, a tailor who lived in Vienna and had his business there, but who kept a room in his (our) house in the Luydererstrasse. As a consequence my father was one of the best-dressed men in Traiskirchen because he obtained his suits that were barely worn from Mr. Wanek. Mr. Wanek came once or twice a month for a weekend.

According to my mother, I was born on a Sunday at 1:30 in the afternoon shortly after Sunday dinner. When the time came, my father went to fetch Mrs. Hospital, the midwife in Traiskirchen who delivered me. The day I was born Mr. Wanek was in Traiskirchen and had lunch in town. He had to climb into his room through the window so as not to disturb the procedure of delivery.

The Luydererstrasse was and still is a very traditional street in Traiskirchen that connects the main square with the city park and has the style of a "Reihendorf" that is common in this part of Austria. Our house had a cast iron fountain, painted green with a stone basin. The yard was bricked, the middle part being dirt. This was very important feature because it provided a convenient playing area for us children. The house had a tile roof and a brick annex that had a hayloft and led to the stairs of the cellar. The cellar also had a dirt floor and stone steps leading down. It was always sopping wet and had no electric light. Near the front door was a shelf where a candle in a candleholder and matches were kept. Coal, and winter vegetables such as potatoes, carrots, cabbage and beets were stored in the cellar.

There was only one water spigot in the house, which was located in the annex. The annex had a brick floor; there were shelves for tools and a chest of drawers where smaller hand tools were kept. At the end of the yard were two species of gigantic walnut trees. The house had a garden with a gravel path that was edged with big round stones from the river. In one section of the garden, my father later constructed a small shed, which became the home for 3 brown chickens and 4 rabbit hutches. Father liked gardening and prided himself in his rose bushes. They were actually little trees, which he had specially grafted and trained.

In the middle part of the garden were 2 big trees, one apricot and one pear tree. We called the latter a trout pear tree. In Amherst, we live in apple country and pears are also grown and sold. Very recently I found in the market (after 60 years of looking for

this pear species) a pear that was called "Forelle" (trout) pear. It was exactly the same kind of pear with which I had grown up. There was also an old tin bathtub that was filled with water in the summer and (after a period of sunshine I used it for splashing.

The garden was surrounded on three sides with a 6-foot wooden fence. On one side of the fence, father had trained 2 or 3 espalier fruit trees. We had both red and white currants trained as small tree and 2 or 3 gooseberry bushes. On the other side toward the other neighbor we had a plum tree, a peach tree and Easter and fire lilies along the fence. There were two large lilac trees, one single white and one single purple. In the front of the garden, near the fountain there was a small double purple lilac bush hovering over a bed of lilies of the valley. In the corner where the neighbor's house met with our annex, there was a grape arbor.

Our family life included animals. When I was a baby I was allergic to cow's milk. In 1927, this was a serious matter. Since a "formula" as we know it today did not exist, hence my parents acquired a goat. In my first few years I was raised on goats milk. Perhaps this was the reason I felt later an attachment to goats. When I was a little older I often went to see the goats at the towns grazing ground, which was reserved for these animals.

As I indicated, it is very difficult to distinguish between actual memory in childhood and what had repeatedly been told and retold. But I do recall that when I was a little boy we had a dog whose name were Putzi; a regular dog, not a pedigree, just a plain dog with white short hairs and black and brown spots. My mother told me I that I had been very attached to the dog. I still am a dog lover, but now we have black Labrador retrievers.

A couple of years ago, on one of my visits to my hometown, I talked with a friend of my youth, Hans Stadlmann. We reminisced about what we had been doing, 70 years ago. I remembered that one of my first playmates was Hertha Staska. We often played together from the time when we were 3 years old, since our families were living just a

block away from each other. I still see Hertha about once a year when I visit Traiskirchen. I went to Elementary school with a number of playmates who still live in Traiskirchen: Rudi Kautz, Mitzi Raufer, Friedl Ferschner and others. We played together; games that children played at that time not organized games. Soccer or a kind of soccer with a ball we made of pieces of cloth and lady's stockings was a favorite; it was called "Fetzenball," a ball prepared from rags. Another special game was "Hudl Poelzen" a kind of baseball. It was relatively easy to find a few boys to play marbles, using mostly the cheap clay marbles. The few children from the few more affluent families had glass marbles. Those games were played on town's properties on the outskirts of town. We also played in each other's homes or yards.

I often think of the hours and days I spent with Rudi Kautz. The Kautz's had a farm at the south end of Traiskirchen, which Rudi took over when his father became older and ran all his life. It is now in the hands of his son. It was a paradise for us kids; the Kautzs' had cows and pigs which we liked to tease and play with; they were so friendly and such good companions. I also played with my friend Karl Gliederer. In the family's small farm we had the run of the den. What wonderful things one could find and did find in Ferschner's estate, an estate of 120 acres the largest farm in Traiskirchen. The Ferschner's were the most prominent farmers in town, gentlemen farmers. Was it fun to have a large piece of cake in the elegant kitchen!! Mr. Ferschner was the Mayor of the town when I grew up and Friedl, their son, was my close competitor in school. The Ferschner mill (the Ferschner estate was formerly a mill) was a little outside of the town and always a very dignified residence. To have the run of the house with Friedl was a special treat.

Later, in the gymnasium, I had friends from my class in Baden, Leopold Stumvoll and Heinz Wogrinetz were very close friends and we did spend many hours and days together. I "almost" learned how to swim in a swimming hole in the Schwechat River, but there was never any real instruction. It was customary that one was thrown into the deep water and one was expected to "dog paddle" to safety. In the swimming stadium

(100 meter pool) in Baden, I almost learned how to dive. Again, when my friends challenged me to jump from the 7.5 meter platform at the swimming pool (that had been constructed for the proposed world's swimming championships in Baden in 1938), halfway down I tucked and splashed into the water. For days I was in a great deal of pain - how stupid!

My Father's family was associated with the local band. One of the Vogl's of my Grandfather's generation was a respected local musician and bandleader and my grandfather played the violin. This I know because we had his violin, a clarinet and an ocarina in our glass cabinet in our home. My father frequently led the veteran's band of Traiskirchen.

It was no surprise that my mother decided that I should learn to play an instrument and it should be the piano. As I know now I did not have a special knack for music -- but I learned to play the piano. My early interest in the violin was a failure. My mother then sent me to Mr. Wanschura, the organist of the church St. Margarita whom everybody in town knew. This town church is a late Baroque, early Rococo building from 1752 where I had been baptized and attended mass every Sunday. Twice a week I went to Wanschura's 2-room apartment in the church compound to learn the piano. I still remember the oppressive atmosphere in his apartment full of cigar smoke - where I practiced and played. We did not have our own piano, so I learned and practiced on Wanschura's piano. He also tried me on the organ but it was a failure.

I learned enough from Wanschura to teach my own children piano for three years. We all made it to "Fuer Elise...." I still love to play the piano. It has become one of the most enjoyable past-times in my retirement.

I started Elementary School (Volksschule) in Traiskirchen in the fall of 1933 (September 14) in a rather large class with over 50 children, which was not uncommon in those days. This was possible because strict obedience was maintained.

The boys in my class were: Bertl Josef, Dauboeck Ludwig, Dokoupil Ludwig, Esterle Bruno, Ferschner Friedrich Geppert Eduard, Giesser Karl, Hoeller Josef, Kautz Rudolf, Leroch Franz, Micak Erwin, Neubauer Johann, Planner Ludwig, Rabong Anton, Seidl Friedrich, Scheibelreiter Alois, Schmid Johann, Schrammel Kurt, Schulz Alfred, Staudinger Franz, Vogl Otto, Wallner Leopold, Wilfling Friedrich, Zazel Johann. And the girls: Albasser Alice, Bachner Charlotte, Baumgartner Erna, Bowisch Marie, Glaser Leopoldine, Hagenhofer Anna, Hanser Franziska, Hanser Hedwig, Hanser Marie, Hecher Margarete, Hoeck Elisabeth, Juray Anna, Kalzig Rosa, Kraus Susanne, Kreiner Johanna, Kritschka Edeltraut, Osterer Helene, Pezda Hertha, Pocsay Hilda, Pfaffelmayer Elisabeth, Reisenberger Josefa, Rynesch Beatrix, Skoda Gertrude, Schieler Josefa, Schneider Marie, Schneidhofer Berta, Steinberger Anna, Traumueeller Leopoldine.

Mr. Josef Bundialek was our first grade teacher and the principal, but insisted in teaching the first grade himself. In religion we had Pater Conrad Mader. In the second grade, Mrs. Eugenie Klement was our homeroom teacher, assisted by Berta Madl for Penmanship and Singing, Margarete Stadler taught Art and Gymnastics and Pater Raymund Haid Religion. In third grade Maria Chledowski was our homeroom teacher, she was responsible for Math, Penmanship, Gym & Art. Berta Madl taught Social Studies, Language and Singing and Olga Herman taught workmanship (for girls), although Herbert Doletschek signed the final certificate. Pater Raymund Haid and Eusebius Katzelberger taught religion. From grades 2 to 4, Emil Suesser was the principal of the Elementary School. Olga Hermann, my forth grade teacher, had the greatest influence on my future. She concluded that I was a capable pupil and should pursue an academic career. Nobody in my family had ever attended a select school, or a school of higher education. In fact my mother had gone for her obligatory 6-year education (until 12) to the little village school in Velm that had two classes; it provided her with a solid education.

Mrs. Hermann paid a great deal of attention to me and devoted hours and hours

preparing me for the required entrance examination into the Realschule in Baden. After 4 years in the Volksschule of Traiskirchen, I entered the School in Baden. The School was officially called "Bundesgymnasium and Bundesrealschule." It was a special school for the district (county) of Baden and had 8 classes (grades). It was located in the county seat, Baden, Biondegasse 6. The school had two branches; the Bundesgymnasium was the humanistic or classic section while the more science and mathematics oriented section was the Bundesrealschule. Each of the two branches had one class per grade with about 40 students for each class.

The Bundesgymnasium and Bundesrealschule were preparatory schools for the University and had slightly different curricula. The Bundesgymnasium prepared the student for enrollment at the University in the Law, Theology, Medicine and the Humanities. The language curriculum of the Gymnasium required Latin from the first class on and classical Greek from the third class. Other subjects of the curriculum were also arranged slightly differently, with more emphasis on humanistic subjects.

In the Bundesrealschule French was the foreign language from the 1st (5th grade) class on and English or Italian later. The curriculum included more mathematics, biology and chemistry and from the 6th class on descriptive geometry. Several years later a new school system was created that combined elements of both school forms to the so-called Realgymnasium. French was required from the 1st class and Latin from the 3rd. I was educated in this system, with French from the first and Latin from the third but did not learn English!

In the Elementary School in Traiskirchen, as in many schools at that level, the homeroom teacher taught all or most of the subjects. In the Realschule, a specialist taught each subject. This was a substantial change and required some adjustments.

We were 40 students in the "first class" (the 5th grade): Auer Helmut, Beirer Arnold, Benesch Heinrich, Besler Harald, Brat Adolf, Braun Otto, David Erich, Englisch Siegfried, Feichtinger Ludwig, Fitz Gerold, Forst Gabriel, Gam Guenther, Goetz Johann, Gruenberger Otto,

Grundgayer Hans, Gschiegl Alois, Halm Friedrich, Hirschbrich Franz, Janisch Siegfried, Klein Hans, Massinger Heribert, Mazura Walter, Moritz Arthur, Nepp Othmar, Ranft Peter, Rappold Johann, Schackl Leopold, Schiefer Josef, Seiser Josef, Sitar Leander, Sladky Otto, Steigner Heinrich, Stoeger Josef, Stumvoll Leopold, Trattner Hans, Vogl Otto, Voglauer Karl, Wogrinetz Heinz, Pallas Herbert, Perger Gregor.

Franz Wressnig was our homeroom teacher and Sulzenbacher the principal. We had 11 subjects in the "first class" besides Crafts and Choir. Other subjects and teachers were: Religion, Josef Hlawati; German, Franz Wressnig; French, Franz Wressnig; History, Friedrich Gebert; Geography, Friedrich Gebert; Biology, Rudolf Spatschil; Mathematics, Ferdinand Helpap; Drawing, Robert Leitner; Penmanship, Robert Leitner; Music, Franz Valentin Damian; Sports, Hans Gerhold; Crafts: Alois Weissenbacher and Choir, Franz Valentin Damian.

Life in Austria changed drastically in March of 1938, when it was occupied by Germany and became the 17th province of Germany. The system in our School in Baden also changed; the two divisions of the schools were reorganized and the curriculum was also reoriented. In the Realgymnasium, French was still maintained as the first foreign language and Latin became the second language from the 3rd class. Thinking back, this was an excellent choice for me. However, English became the foreign language for the new class entering the fall of 1938.

My interest in languages, history and foreign travel received an important impetus in the summer of 1940. Together with one student of my age group from the Bundesgymnasium, I was selected to spend the summer vacation period in Hungary. It must have been based on some type of competition. This was then a tremendous event. The war had started; food was limited and we had ration cards. Hungary was not at that time involved in the war and the legendary Hungarian food was plentiful. I spent about 3 months in the outskirts of Budapest with a Hungarian family. They had a son a year older than I was, but the family Simon, especially the son "Joshi" spoke no German. The objective was that their son should learn German - actually I learned more Hungarian. Fortunately there was a neighbor, who spoke

some German, but it was still difficult and I learned what homesickness was. I had never been away from home before and I spend quite a few nights in tears of homesickness in the beginning. Fortunately, the family, the Simons could not have been nicer to me and the experience was invaluable. I learned to love Budapest and Hungary. Today I still have close relationships with a number of Hungarian friends.

Wressnik remained my homeroom teacher until the middle of the 5th. class. His position was taken over by Lewandowski for the 5th and 6th class. We were fortunate to have Oedendorfer for the 7th class as the homeroom teacher, the position that Semrad took over for the 8th class. In 1938, my second year in Baden, Germany had taken over Austria and also the school system. Carl Groiss became the principal. He was my Latin teacher for the first two years of my Latin education, which meant in the 3rd and 4th class. Unfortunately he was greatly politically oriented and a mediocre teacher. As a consequence I never excelled in Latin.

I adored my homeroom teacher, he was strict, and quite demanding, but I remember him as a very warm person. Weber to whom we were assigned for French from the 4th class was a different kind of teacher. He was excessively demanding and unreasonable. I did not like him and grades in French started to drop. After the first weekly school essay test, we anxiously waited for the results. One student obtained a grade B. I, who was always accustomed to A's with an occasional B, received a C. Two other students also received C's, the rest of the class D's and F's. It should be mentioned that the grading, after 1940 had been changed from the original grades 1-4 to grades 1-6 and one 6 or two 5's were failing grades. To receive a 6 or two 5's meant the student had to repeat the whole class. During the same period I also had an inspiring history teacher who instilled in me my lifelong interest and love in the classics and world history.

My interest in and fascination with chemistry began in the 5th class, when I was 14 years old. From the 5th class on for two hours a week, chemistry was part of the

obligatory high school curriculum. We had an enthusiastic and inspiring chemistry teacher, named Helpap. The gas laws were his specialty. I had already had Helpap in Mathematics in the 1st class and in subsequent classes. He was like Wressnik, an inspiring teacher without being excessively demanding. Helpap took a liking to me and encouraged me to come once a week in the afternoon to the laboratory and help him prepare for a simple laboratory course and clean up afterwards. Soon Helpap created in me a fascination for chemistry. I decided that, as soon as I had finished the Realgymnasium, I would study chemistry at the University of Vienna.

During my school years in the Realgymnasium I had a number of Teachers with varying personalities and qualifications, but they all provided me with an excellent education: Josef Biegler, Adolf Butz, Franz Valentin Damian, Viktor Dostal, Friedrich Gebert, Hans Gerhold, Ludwig Gränitz, Carl Groiss, Ferdinand Helpap, Josef Hlawati, Ernst Jirgal, Leopold Kastner, Rudolf Klose, Walter Kosmath, Josef Kraupp, Alexander Kuzmany, Franz Leitgeb, Robert Leitner, Josef Lewandowski, Ludwig Oedendorfer, Anton Pürchenfellner, Franz Schwarzmann, Walter Semrad, Rudolf Spatschil, Hans Weber, Alois Weissenbacher, Franz Wressnig.

I should also mention the students of the School Year 1944/45 Class VIII, in the Section Realschule we had 9 students: Gamauf Rudolf, Janisch Siegfried, Mazura Walter, Nepp Othmar, Rappold Hans, Stumvoll Leopold, Vogl Otto, Wogrinetz Heinz, Sitar Leander and 7 that actually belonged to neighboring schools: Brandau Klaus, Cech Franz, Hazuka Hermann, Medlin Herbert, Saltner Kurt, Zeiser Otto, Spatschil Franz. The Gymnasium section had 10 students: Ferschner Friedrich, Heidrich Leopold, Oedendorfer Heinz Petrasch Franz, Perider Erich, Satttek Hans, Schmid Helmut, Strobl Walter, Tauschek Kurt, Ullrich Wolfgang.

I have often been asked: How did you become interested in Chemistry and in Research. I have answered the first question, by pointing out the encouragement by my chemistry teacher, Helpap in Baden. Other subjects were just not as exiting. To

answer the second question requires also my comment that my teacher Kraupp instilled in me in history, and the importance of the family.

In my days, families did not move very much, children stayed in town or married somebody from the next town. In my case my father was from Traiskirchen. His father Anton had four children. The oldest was a girl; named Theresa born in 1884, for me she was the "Tante Resi," who married a Mack. They had 4 children, two boys and 2 girls. I am still in contact with Erwin, the son of the younger boy. He is now deputy county commissioner in the county of Muerzzuschlag in Styria.

Then came Mitzi, born in 1986 She had married Ferdinand Fuchs, called uncle Ferry. They had no children. My father Franz was the next child of my grandparents; he was born in 1989. The last boy, Josef, was born in 1992. He had one daughter who was my age but died when she was in her 20's.

Growing up in Traiskirchen I frequently visited my grandparents who had the only grocery store in Velm, a village of about 700 inhabitants. My Mothers family was larger. As I mentioned they had the local grocery store. I was always much closer to my Mother's family. Grandfather Anton Scholz was born in 1853 and his wife in 1863, they had 15 children, 6 of whom died in early childhood, two boys Karl (1984) and Gustav (1894) were killed in the First World War. The remaining 4 boys and 4 girls were: Josef (1887). Katharina (*Kaethe*) (1889), Aloisia (*Loisi*) (1890), Anton (1891), my mother, Leopoldine (*Poldi*) (1892), Wilhelm (*Willi*) (1894), Rosa (1899) and Hans (1903). I am still in close contact with Rosa's (Stichlberger) daughter Paula, who, as a lawyer, worked for the Austrian government in Vienna as a director of a division in the Ministry of Commerce and received, on retirement, the title of " Frau Hofrat." I am also in contact with Wilhelm's son Josef Scholz, who acts now, after I established the first family tree, as the "historian" of the Scholz clan.

When I was a boy I my mother used to tell me various tales about relatives of friends of

her family. They were located in the various towns around Velm. When I was 14, in the summer of 1942, I decided to trace and record our family tree. Velm is about 6 miles from Traiskirchen so I was able to use my bicycle to visit the surrounding towns that were separated by distances of 3-5 miles, connected by small country roads. Automobile traffic had not developed significantly. The common means of transportation were horses and wagons. The Catholic Church, the state religion in Austria, kept excellent records of births, deaths and marriages. Every child had to be baptized, have communion in first grade, when they were 6 or 7 years old, and young couples were married in the church. When people died, they were buried in the church cemetery. Consequently all the important entries of people's lives could be found in the relevant books located in the church office.

The project of tracing my family members was my first experience in research as autodidact. I learned to connect the entries of births, weddings and deaths to check, crosscheck and confirm. Spelling of names varied, it seemed that the priests or their secretaries had listened to the applicants rather looking carefully at documents that were presented. Also the handwriting and general spelling before 1800 varied considerably over one person's lifetime. In addition most people probably did not know how to read and write.

The priests in many local churches were very helpful, enthusiastic and surprised that a boy would begin such an undertaking in the hot summer's days. I was on my bicycle riding to Himberg, Gramatneusiedl, Ebergassing, Moosbrunn, Unter-Waltersdorf and Ebreichsdorf in some cases more than once. At that time, when the telephone was not commonly used on the countryside, I bicycled to the towns hoping to find the church office open or I had to make an appointment later.

By combining the entries from birth, marriage and death certificates, I could come up with the family tree. The oldest entry was a death certificate of one of my ancestors, who died in 1638 at 104 years of age - he must have been born in 1534. But were the

records correct and was the man really 104 years old when he died???

Father's family in Traiskirchen was easier to trace, because Traiskirchen was the seat of a bishop until 1688 and some of the documentation was better. Part of his family came from Moedling, also a large and important parish.

There was one big problem that could not easily be overcome. Sometimes one of the books (register) was missing. I could sometimes recreate the lineage and continue with an earlier register, but sometimes the connection to the earlier times was lost. Some earlier ancestors came from places farther away from Hapsburgian possessions, from places that would not reply.

This part of Austria, east of the Viennese Forest, was the battleground of various wars, raids, and 2 major Turkish invasions that led to the sieges of Vienna. It was not uncommon that a policy of "scorched earth" was instituted, whole villages and churches were destroyed and records were lost. My family tree, especially on my mother's side, could no longer be created because at the end of World War Two, in 1945, this part of Austria was war zone and many records were destroyed.

The creation of the family tree was a fascinating undertaking and taught me logical thinking, creative combinations and the importance of keeping accurate records and perseverance.

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## **B. The Student Years**

On March 31, 1945, I graduated from High School and received my High School Diploma. I really did not quite know what to do. Fortunately I had an older friend, Ernst August Schneider, who was then the Administrative Director of the State Opera of Vienna. I went to see him and sought his advice. What should I do? Should I try to find

a job? What kind of job? There were few available for young people without skills, other than a High School degree. I did not have not much money and I could see it rapidly disappearing Ernst said "Study, go to the University!" You have your High School diploma; this degree together with your solid education and determination will be sufficient to succeed. If you become a student you are entitled to a special ration card (a worker's card) that will provide you with access to a little more food than the regular 800 cal/day, which everybody had for the next year.

With this advise my plans were set to enroll at the University of Vienna with the intent to study chemistry. The war had finished a few weeks earlier; Vienna was still in shambles, the central part of the City within the Guertel (belt-way) was substantially destroyed and the Red Army occupied the City. Life in the city was dismal and everybody struggled to survive. Disabled vehicles, both civilian and military and debris and rubble were still left in many places. The transportation system in the City of Vienna was destroyed and was being "recreated"; a few trams were running, tram cars without windows, of course.

A general feeling of optimism and enthusiasm were evident in the minds and hearts of people, especially young people. The future was seen as being bright. The war, the destruction and oppression were finally over and we could start looking forward to a happy future, our future.

I had settled with one of my aunts, a sister of my mother, Aunt Kaethe, who had an apartment not too far from the University. Soon thereafter I was able to arrange to take dinner with another aunt, a sister of my father. She lived on the same tram line, # 46, and three miles away. My parents had left Traiskirchen as many people did, and were hopefully alive and living somewhere in the Western part of Austria.

The University had announced that the summer semester would begin on May 29, 1945. The University especially the Main Building had been significantly damaged; it

had been hit by dozens of bombs. Most of the windows were broken; staircases were destroyed and led to nowhere. Some rooms were usable and the University offices started to function. I consequently stood in lines and there were many lines because everybody wanted to start to study or continue their interrupted studies. At the office of the Dean of Philosophy I received the official admission to study at the University.

Indeed, on May 29 the lectures began and I still remember the first lecture of the famous Professor Ernst Spaeth. He was then also the President of the Academy of Sciences, an excellent scientist, and a giant of a personality as well as an excellent lecturer. Since it was a summer semester, only a few courses were offered, but not in the right sequence. I took all the courses that were available: Chemistry II (Organic Chemistry) with Spaeth, Experimental Physics, with Seidl and even Radiochemistry and Nuclear Chemistry with Karlik. I could actually register for the course the next Semester, after I had passed the course. I saw Professor Karlik last year just before she died at a meeting of the Academy of Sciences; she was then 86 years old. It was interesting to reminisce with her. We had been in continued contact off and on and as a consequence she remembered very well those days and the few young students that came to her lecture in 1945. She did not believe an atomic bomb could be built or was in the making. Two weeks later the atomic bomb was exploded in New Mexico I still remembered her showing us a crust of radium bromide in a 5 Liter round bottom flask that apparently she had rescued from somewhere at the end of the war. There were no particular precautions taken for the radiation from radium bromide but Bertha Karlik lived to a ripe age in good health. She must have received quite a radiation dose over the years.

Two more courses that I took during my summer semester were very important for the advances of my studies. Docent Sirk, a curious fellow, gave one but he gave a course unique for me: Introduction to the Mathematical Treatment of Sciences for chemists and pharmacists. I loved his lecture, he was so sincere and he provided mathematical problems of a degree of difficulty needed, not more not less to handle problems that

would come up later in physical chemistry and chemistry. I still see him even now in his black worn cloak covered with white chalk marks. He was committed to provide the student with what they needed with kindness. Sirk was a great teacher; I learned from him mathematics that I could use all my life. He was also a supporter and proponent of the Esperanto movement, a movement that wanted to create an unnatural, artificial language composed of Latin, Germanic and Slavic portions in a uniform language. Latin had been, for centuries, millennia, and the language of choice. It ultimately failed as a permanent universal language, as had French before. Esperanto was believed to be a possibility as a universal language. It was not a truly spoken, "living," language and had no chance to survive. How long will English, in the computer age of computers, last as the universal language?

This was interesting to me because I was intrigued by languages. In fact, in the fall of 1945 I had found some time to study French for one semester at the Vienna branch of the Sorbonne, the University of Paris. The Sorbonne had an official chapter in Vienna and taught French on various levels. This was quite convenient, because I had had French in high school for 6 years and was able to revive my knowledge and even improve it in a more colloquial form. This knowledge was vital later on for my teaching at the University of Strasbourg 30 years later when I had to lecture in French.

The first semester was not my best semester in my studies at the University. Everything was new and awe-inspiring: the new life in Vienna, a large city, the life at the University, and my daily life. I had to spend much time finding the necessities of life. This was a period that each university student had to go through. In 1945 it was particularly complicated, because nothing or very little was available.

Most important was the survival on a limited diet. There was not much to eat in Vienna then. Ration cards provided the population with 800 calories per day. At the Mensa (student cafeteria) there were extra rather simple meals with no meat or fat, available when food was delivered, which was not the case every day. As a consequence, I tried

to find a way to survive the summer 1945 and find something to eat. I remembered a school friend from my high school in Baden. His name was Hans Rappold and he lived with his parents who had a farm in Alland about 25 miles south of Vienna, in the Vienna woods. I wrote to him and his parents and inquired: Is there any possibility for me to spend the summer with you and could you use an extra pair of hands? Of course, I would do the normal work of farmer or a farmer's son. Happily I received an answer rather promptly. It said that I could come during the summer vacation of the University and work on the farm.

In July I arrived in Alland and had the first substantial meal in over three months. It was a farmer's meal so it also didn't have much meat but it was important for a boy not quite 18 to have enough to eat. The next two months I spent doing farm work. Every day I rose at 4:30 in the morning taking the horse and wagon and gathering the fodder in the fields for the animals. It meant learning how to treat the horses and how to use the scythe. I also had to milk the cows although I have subsequently never used these skills. I think of this time very fondly because this period probably was essential for my well being in the next few years and access to a healthy food at this age probably saved my life.

Back at school, the University affairs were now much better organized and lectures that were normally in the programs were available. The chemistry curriculum at the University then was arranged by a sequence of laboratory courses rather than by lectures. No more general courses were required as the general education had been accomplished at the gymnasium level

The laboratory courses (called Practicum) consisted of Qualitative Analysis (Chemical Experiments for Beginners), Quantitative Analysis (Chemical Experiments for Advanced Students) and the very important laboratory course in Organic Chemistry (Chemical Experiments for Organic Students). In addition, a laboratory in Physics (Physical Practicum for Beginners) (half semester) and in Physical Chemistry

(Experiment in Physical Chemistry) (half semester) was required. Practical for Microanalysis and Gas Analysis and High Vacuum Technique were also available. They could be taken between semesters because spaces in these laboratories were limited. On the other hand, since the Instructor positions were full time positions they were also available during the Semester breaks.

The laboratories were open from 8:30 a.m. to 6 p.m. and the laboratory course was completed when all the tests were successfully carried out and other obligations were completed. At the beginning of the Semester the student taking one of the major laboratory courses was assigned a laboratory space and he or she could use this space for their experiments whenever they wished. There were always 3 Instructors on duty for about 56 Students. At the beginning of the laboratory course (which did not have to be the beginning of the Semester) the student had to pass an oral given by the Chief Assistant or Docent and again at the end of this specific laboratory course. Sometimes we also had a less formal examination. As I discussed, the examinations were oral, even the final examinations of lectures, called "colloquium" were oral. Not all lectures required examinations, because they were superseded by more formal examinations conducted by the Head of the Institute.

Professors and Docents presented their lectures during the day in the Institute or neighboring Institutes. The laboratory courses were "open laboratories," students could leave, attend the required lecture and return to the laboratory to continue their experimental work. There was a considerable amount of freedom in the timing of examinations. They could be taken right after the lectures were completed or in a second period after the semester break. This system allowed a great deal of flexibility for different kinds of study habits.

Now back to my second semester at the University, the winter semester 1945. I registered for the most important lecture Chemistry I (Inorganic Chemistry I) (Spaeth), Analytical Chemistry I (Qualitative Analysis) that was inorganic analysis (C.C. Mary).

These lectures that were mandatory, but I also took Aliphatic Chemistry III (Wessely), and Experimental Physics (Seidl), also necessary, Optics (Seidl) and Fundamentals in Biochemistry.

. In the winter semester, I also took a course from Galinovsky in Quantitative Analysis. Galinovsky substituted for the professor who held the chair of analytical chemistry. It was an important course, and I had the opportunity to know the person as a lecturer who ultimately became my thesis advisor. I also attended a course from Professor Klemenc who was not an important personality in the chemistry program but he was teaching a needed subject.

When the winter semester began, the teaching laboratories were not functioning. Vienna had a limited supply of gas and water. The laboratories finally opened in the middle of November. There was no glass in the windows or they were covered with thin sheets of plywood; heat was non-existent. Gas was available only for two hours during the day, from 11 a.m. to 1 p.m. Life that depended on gas was dangerous, because the gas was City gas from the gas cooker and contained a considerable amount of carbon monoxide. Also, the gas valves had to be closed in the "off-hours" because open gas valves could cause explosions when the gas reappeared for the next "gas period." It was difficult to work in freezing or near freezing temperatures. Winter clothes and gloves were essential, while working out the prescribed tasks in the laboratory. Particularly, the cleaning of the test tubes in cold water was demanding and soon frost bites appeared on the upper parts of the fingers. We were working with old gloves that had their tips cut off.

The few students that actually lived through that period, perhaps 20% of the total who had assigned places, were working in the labs at the time. Those that were there became very close friends in the misery of the circumstances. The group that worked vigorously and together included Kurt Bachmayer, Fredl Renner, Elfriede Binder, Max Poehm, Robert Weiser, Gottfried Giesser and a number of others. The head of the

laboratory was Dr. Ballczo with Goldberger and Gerald Kainz as the Instructors

As soon as I could, I took the "entrance" examination with Ballczo and performed my 39 experiments of qualitative inorganic analysis. The program was designed to be completed by the fastest (top) students in one semester. I soon learned from experience that this system of studying chemistry favored the fastest and, in my future activities, I followed this theorem.

In January 1946 Europe, including Vienna, experienced one of the coldest winters ever seen. The Danube was frozen over and rumor had it that Russian (Vienna was in the Russian occupation zone) T34 tanks could drive over the frozen river.

I should mention and emphasize that Chemistry was divided into two Institutes, located in 2 different buildings: The Director of the I. Chemical Institute of the University Vienna was Professor Ludwig Ebert, a Professor in Physical Chemistry. Inorganic Chemistry was a division of the institute and had an Associate Professor as its Head. The Director of the II. Chemical Institute was and had been since 1930 Professor Ernst Spaeth a Professor of Organic Chemistry and Professor C.C. Mayr an Associate Professor and the Head of the Analytical Division.

I was in the fortunate situation of being selected to take the Short course of Microanalysis in February 1946 during Semester break. Other hurdles had to be overcome, however. One that was particularly interesting was the micro-chemical Laboratory, which consisted of several gravimetric micro-analytical tests in carbon hydrogen and nitrogen analysis and a molecular weight determination. Only four students could take this laboratory course at each period that took between two to four weeks. There was still no permanent gas supply at the university. As a consequence, we had to go several miles to refuel the gas tanks in the Gas Works of the city of Vienna and all four of us had to carry out our combustions from one gas tank. If one person did something slightly incorrect all three analyses had to be abandoned and

repeated and even the next analyses were questionable. As a consequence, true friendships and cooperations between most students developed in this cold winter leading into 1946. Looking back now it looks as if everything was incredibly difficult. During our working period, there was only one serious mishap. One day, the girl friend of one of my colleagues visited him in this laboratory. She stepped accidentally and unknowingly on the gas line, and the analyses of all four students were ruined. It took a whole day to bring again order into the system.

I was one of the few students who finished the laboratory course of qualitative analysis in one semester. I took the final exam with Ballczo and the entrance exam with Galinovsky for the Chemical Experiments for Advanced Students (Quantitative Analysis), which was the key course for my 3rd Semester.

I also took a number of additional lecture courses in the Spring Semester: Analytical Chemistry (Quantitative Analysis) (Mayr) and the Important Introduction to Physical Chemistry (Ebert). In addition Selected Chapters of Inorganic Chemistry (Klemenc) and Theoretical Fundamentals of Organic Chemistry (Galinovsky). I rarely attended the lectures of Seidl: Acoustics and Heat as I was loosing interest in Physics. The lecture by Mueller entitled Gas Analysis and High Vacuum Technique with the Experiments was much more interesting.

The next semester, the Practicum Chemical Experimentation dominated the spring semester in 1946 for Advanced (Quantitative Analysis) and the Section head was Docent Friedrich Galinovsky. He was a kind, personable character, about 40 years old. I can see him in his black lab coat and short haircut, always ready to help the students. After the obligatory exam we dove into the prescribed experiment: first the simple quantitative determinations, and later the titrations, the minerals and alloys. I still remember the sodium potassium separations in the big platinum crucibles and the calcium/magnesium separations of the magnesites. The Institute had a fine collection of accurately analyzed ores and alloys of different compositions.

Although I had registered for the physics laboratory in the Winter Semester, I actually did not take it until the 3rd Semester. Professor Haschek headed the laboratory of physics; his laboratory assistant was Dr. Karl Lintner. I did not do very well in the physics Practicum and certainly was not at the top of the class. I met Karl Lintner not too long ago at the meeting of the Academy of Sciences in Vienna. He had become not only a highly respected and recognized Professor of Physics but also the Secretary of the Academy of Sciences.

I decided to take Chemistry II (Organic Chemistry) for credit with Spaeth under less pressure and in a more leisurely way having had now more experience. I had not done well in Spaeth's colloquium in the first Semester because I intended to ask him if he would be willing to be my thesis advisor. When I started to study at the University I was overwhelmed by the novelty and the excitement of living, working and studying in Vienna. In time I realized that my basic interest probably was in organic chemistry.

I had already decided that I would aim to become a graduate student of Professor Spaeth. However, a tragedy struck in May 1946 when Professor Spaeth died of a stroke at the age of only 60 after visiting his daughter in Sweden. His lecture had to be completed by his Assistant, Dr. Schlaeger. Schlaeger was an excellent lecturer; I also did very well in his examination. Consequently my career plans to get a degree in organic chemistry (but with another thesis advisor) were set.

In the Spring Semester I also took Analytical Chemistry II (Quantitative Analysis II) (Mayr), Introduction to Physical Chemistry (Ebert) and Gas Analysis and High Vacuum Technique with Experiments (Mueller). The schedule was completed by Theoretical Fundamentals of Organic Chemistry (Galinovsky) and Selected Chapters of Inorganic Chemistry (Klemenc). I rarely attended the lecture on Acoustics and Heat (Seidl)

In the fall of 1946 and spring of 1947 I took the laboratory courses in physics and

physical chemistry. These courses were taken students from the I. and II. Chemical Institute. Consequently I became acquainted with many more students, and also became better acquainted with the other students from our institute especially the group of Docent Willy Gruber. Gruber had a good group with Horvath, Gerhard Proske, Karl Schloegl and Hertha Renner. Schloegl and I developed a close friendship, ongoing throughout our lives to the present time.

Most of the important lectures had by now been completed and I was able to concentrate on special lectures in organic chemistry, in inorganic chemistry, mathematics and physics.

In the 4th semester I entered the field of organic chemistry, Chemical Experiments for Organic Students. I registered for 2 semesters for this laboratory course. This was longer than normal for me but it was the laboratory, which would be the basis of my dissertation. The organic laboratory course consisted of two parts, one for the official laboratory tests like those that are described in, for example, Organic Synthesis. 20 Such experiments were required, which were taken from the famous organic chemistry laboratory textbook Gattermann. It also required an apprenticeship overlooked by a graduate student. We called it "coolie" work, because we had to synthesize compounds that a selected graduate student needed as a starting material for his thesis work. Since there was no "Aldrich" catalogue in 1946 from which one could order needed chemicals, every intermediate and starting material had to be synthesized. The student was assigned to a graduate student and made special preparations based on literature descriptions, in other words, literature preps that had not been tested. This normally allowed the student to work during the vacation to complete the requirements.

Organic chemistry would not be the only interest that kept me alert. It was the Physical Chemistry taught by Professor Ludwig Ebert that caused a great deal of concern for me. I had difficulties to understand the subject although the best possible teacher taught it. It turned out that in my later research career I published an considerable

number of papers on physical chemistry.

In this semester I also took also Theoretic Fundamentals of Organic Chemistry (Galinovsky) Chemistry of Heterocyclic Compounds (Mueller) and Chemistry of Benzene Derivatives (Schmid). Although his family came from my hometown of Traiskirchen, his lectures were uninspiring. Years later he taught food chemistry. I also rarely attended the lectures Fundamentals in Biochemistry (Brunner) and Mechanics (Przibram)

Very soon I found that certain other interesting subjects like advanced math with E. Hlawka and advanced physics was not for me and I concentrated more on the lectures on specialties in organic chemistry.

The fifth semester and the last semester before I started my dissertation I had few special interests. In this country we would have called it the semester before graduation from college. I finished the formal registration for Chemical Experiments for Organic Students and the more difficult and required lecture on Physical Chemistry II (Ebert). I attended other lectures of interest: Theoretical Fundamental of Organic Chemistry II (Galinovsky), Chemistry of Benzene Derivatives II (Schmid), and Fundamentals in Biochemistry II (Brunner).

In the spring of 1946 the second part of the Organic Laboratory became for me very important. It was the practical training in my "undergraduate" program that prepared me for my thesis work. Experimentation still had limitations because some functions necessary for top of the art laboratory work was still not available all the time. Laboratory equipment was available only in limited amounts. When glassware was broken it could sometimes not be replaced. The chemicals that were available were frequently impure and had to be purified. This laboratory course was under the direction of Docent Matthias Pailer, a feared but knowledgeable teacher. The examen at the beginning of the organic laboratory course was essential and important because

I had planned to work on my thesis in organic chemistry.

An important and required laboratory course was the Practicum of Experiments of Physical Chemistry. It was headed by the cynical Docent Wolfgang Breitenbach, a student of Professor Mark. Mark had been the head of the Institute of Physical Chemistry, the I. Chemical Institute of the University, from 1934-1938 before he was forced to immigrate to North America.

While I was at the University, the Director of the I Chemical Institute was Professor Ludwig Ebert, an excellent teacher, who was able to make physical chemistry understandable. I struggled with physical chemistry during my student years, but later in my scientific career, I published numerous papers on the subject.

The physical chemical laboratory course thought by Docent Breitenbach; he assisted by Dr. Christl Schneider and Dr. Hans Peter Frank. They provided a very collegial spirit and instilled in us how to measure accurately and how to interpret the data. Still, the physical chemical laboratory was not easy for me.

I knew Frank better in later years when we played soccer together and even later when I came back from the U.S. and visited my friends, and Hans Peter was research director of the Polyolefin Co., PCD in Linz.

The 5th Semester and the summer of 1947 was again a period of decision-making.

1.) I had to select a subject for the physics minor examination. I selected Mineralogy and Meteorology. It did not require more than to enroll in the key lectures:

Crystallography and Crystal Chemistry (Machatschki) and Meteorology (Ficker).

2.) Our degree at the University of Vienna was a degree of doctor of philosophy. That meant that we had to register for 20 hours of prescribed lectures in philosophy and psychology, and we had to take a final (rigorous) examination in philosophy as a minor to chemistry. Fortunately, only registration was required for these courses. They were

the prerequisite for the final exam but attendance was not required. The philosophy and psychology professors had written books based on these courses and it was sufficient to study (and buy and show) these books. Consequently I registered for: Pedagogical Philosophy (Meister), General Psychology (Rohracher), General Psychology II (Rohracher), General Psychology (Rohracher), Introduction to Philosophy (Kraft), Philosophy (Dempf)

3.) I had to make another preliminary decision. In 1947, the job situation was dismal. We had few options: a.) University career; (looked very unlikely); b.) Industry (the prospects for industry openings for 1950, the year of my receiving my Ph.D. were minimal) c.) Position as a high school teacher in chemistry, a state position.

I decided to enroll in all courses that were necessary to undergo the "Lehramtspruefung," in other words to prepare for the final examinations. There were no "in-between" examinations required. As it turned out I went to few lectures but was somewhat conscientious about the mathematics of Hlawka and Radon, and actually took the Exercises. I could have saved myself the time. I have never needed higher mathematics in my professional life.

Here are the obligations that were required for the "Lehramt", and in which I enrolled: Kammel: History of the Austrian Education System, Meister: Theory of Education, Machatschki: Reserves and Distribution of Raw Materials, Ficker: General Meteorology, Przibram: Electricity, Przybram: Heat and Molecular Physics, Radon: Differential and Integral Calculations Exercises, Hlawka: Analytical Geometry Exercises, Lewandowski: Fundamental Mathematics, Hofmann: Descriptive Geometry, Machatschki: Special Mineralogy, Przybram: Optics, Radon: Differential and Integral Calculations, Hlawka: Analytical Geometry, Lewandowsky: Fundamental Mathematics, Hofmann: Descriptive Geometry (2); Exercises, Springer: General High School Pedagogy, Sternhagen: Strategy in Special Education: Chemistry, Prommer: Strategy in Special Education: Physics, Dintzl: Strategy in Special Education: Mathematics, Machatschki: General Mineralogy, Hofreiter: Algebra, Hofmann: Descriptive Geometry,

## Exercises.

It turned out that one of the teachers in the "Lehramt-curriculum" was Josef Lewandowski. He had been my mathematics teacher in High School, and I knew he was an excellent mathematician. In the post war period when docents for teacher training were needed he had been promoted to Docent and recruited to teach at the University.

Another observation should be permitted. Why would high caliber University Professors teach subjects for high school teacher training? This was an interesting observation, but seems to be understandable. The lecturer was paid by the lecture, and the number of attendees. Sometimes he could send a substitute, an assistant who also needed the money to present his lecture.

The "Lehramt" was not for me. I knew that I would probably be appointed an Instructor at the Chemical Institute the next year and jettisoned my potential high school teaching career for a University career.

I was relieved that I had made this decision. Often do I think what would have happened if I had passed the "Lehramtspruefung" and had obtained a High School position? I remembered this problem last year when I visited "my" Realgymnasium. I visited the 8th class in chemistry and the teacher. He wore a white lab coat was discussing "acetone." Would I have liked to discuss acetone?

I now could concentrate on the next hurdle, the qualifier to allow me to start with my thesis. After these series of laboratories were successfully completed, students were required to take a summarizing examination, the so-called "Doctorandum". This was a sequence of oral qualifying examinations. It was the prerequisite for the student for working on the doctoral thesis. I would rank it as the equivalent of a degree in this country somewhat between B.S. and M.S.

I took the qualifying exam on October 1, 1947, with my friend and colleague, Karl Schloegl. University regulations required that this examination was done in one day. I still remember it very clearly. We took the examination in organic and inorganic chemistry by Professor Galinovsky and passed. In the afternoon, at 14:00 we arrived for the physical chemistry in front of Professor Ebert's office. It was a rather warm afternoon and it was very quiet. Karl and I were sitting on a bench trying to remember all the things that we had studied, and trying to help each other. Karl took the examination first; after all he was senior to me. This meant additional 45-50 minutes of worrying. We both passed with flying colors. All of a sudden, we felt that we were graduate students. For us it was a historic event because now we were ready for our scientific career.

I had hoped to work with Professor Ernst Spaeth, but fate had decided otherwise. Consequently, I had to look for another "doctor father." The obvious candidate was Friedrich Galinovsky, only just 40 years old but had the competence that I was seeking. Galinovsky had been selected by a number of "left over" graduate students from Spaeth, his best students that had not quite finished at the time of his death. Among them were Heinz Goldberger, Gerald Kainz and Hans Tuppy who later became President of the University of Vienna, President of the Austrian Academy of Sciences and ultimately Federal Minister of Arts and Research.

I was ready to start on my research. I had already been in contact with Galinovsky and he was willing to take me as a graduate student. After many years of studying and taking exams, there were no more exam hurdles in my way. Successful experimental work and the writing of the thesis were the goals to be achieved for the final doctoral examination.

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## C. The Dissertation

The time was ripe for me to begin work on my thesis. Galinovsky, who had received the title of a Professor, had accepted me as a graduate student. A titular Professor was not a full professorship but an honorary recognition.

Galinovsky's responsibility was the laboratory for quantitative analysis on the third floor of the II. Chemical Institute. The inorganic analytical teaching laboratory was located on the second floor. I moved into the end office/laboratory, beautifully located, which was designated for graduate students under the guidance of Galinovsky. In 1947 we didn't have many chemicals other than the most common ones that had been there since the war but could not be replenished. The glassware and cork stoppers that were used had to be provided in part by new graduate students from their own money.

I joined the group, Galinovsky had had one graduate student, Erika Stern (his wife) who had finished her thesis and received her doctoral degree. A graduate student, Hilde Mulley had started her thesis about one year before. Galinovsky also had inherited 2 graduate students from the late Professor Spaeth, Heian Goldberger and Hans Tuppy.

1947 was still the period of the "interregnum" at the II. Chemical Institute, no new Head of the Institute had been appointed. The day-by-day operation of teaching and also research were in the hands of young assistants and associate professors. The overall responsibility as Acting Head of the Institute was in the hands of Professor Ebert, the Head of the I. Chemical Institute. He signed all the papers and took care of the "important" examinations. It was not until the beginning of 1949 that the new head of the institute was actually appointed.

In his early 40,s, my new thesis advisor Galinovsky had worked on his first independent research project, the bromination of cholesterol and androstenol-5-diol-3,17*t*. By bromination and dehydrobromination with collidine, he had obtained the

unsaturated ketones, cholestenone and testosterone in high yields. Galinovsky, through some of his student friends had some connection with the company Chinoine. This company was located in Budapest and traded in steroids Chinoine's entry in the steroid business was by utilizing cholesterol as their starting material. They used the Ruczicka chromic acid oxidation of cholesterol dibromide to make intermediates for hormones, both male and female hormones (the Ruczicka oxidation gives yields of 2-3% of starting materials of the desired products). Chinoine was the mother company of the now famous Syntex Company in Mexico. With his connections, Galinovsky had received a large sample of cholesterol, a small amount of testosterone.

Galinovsky thought I was capable of taking on this rather difficult steroid project. He asked me to look into the bromination and dehydrobromination of cholesterol to 7-dehydrocholesterol. I accepted enthusiastically. We had about one kilo of cholesterol as a starting material for our work. We had to be very careful because there was no possibility of getting more starting material.

At the time I started with my thesis, calciferol (7-dehydroergosterol) had been recognized as the provitamin of vitamin D. UV irradiation of calciferol yielded vitamin D. 7-Dehydrocholesterol the provitamin of vitamin D<sub>2</sub> was found to be the side chain hydrogenated product of calciferol.

In 1942 (the literature did not become available to us until 1946) a new reaction had been published which described N-bromosuccinimide (NBS) as a new selective brominating agent. It could brominate, as one example, the methylene group alpha to a double bond. We had some succinimide in the stock room and I started preparing NBS by brominating succinimide. We decided to attempt to brominate cholesterol esters, the acetate or benzoate esters, but also free cholesterol with NBS. 7-Bromocholesterol esters were obtained and isolated or the bromination mixture was immediately dehydrobrominated. Dehydrobromination was carried out in boiling collidine as the dehydrobromination agent. Collidine was then the most commonly used hindered

amine dehydrobrominating agent. It gave only  $3\beta$ -cholestadienol-4,6, which is equivalent with 6-dehydro-allocholesterol, and not  $3\beta$ -cholestadienol-5,7. However, a shoulder could be noticed in the ultraviolet spectrum of the raw dehydrobromination product indicating that 7-dehydrocholesterol also had been formed.

We spent much time optimizing reaction conditions to obtain 7-dehydrocholesterol but without success. We had indeed been on a very difficult but promising subject because within one-year five research groups described the synthesis of 7-dehydrocholesterol by exactly the same route. These groups worked on variations for the dehydrobromination and successfully used milder dehydrobromination conditions. Some of the reports came from industrial companies with much more experience and skill on this rather difficult problem.

As a consequence, we abandoned our original project and concentrated on simple reactions of the unsaturated steroid alcohols. My objective now became the doubly unsaturated steroid alcohols, the characterization and the reactions of 4,6 unsaturated sterin alcohols (2) (Figure 1).

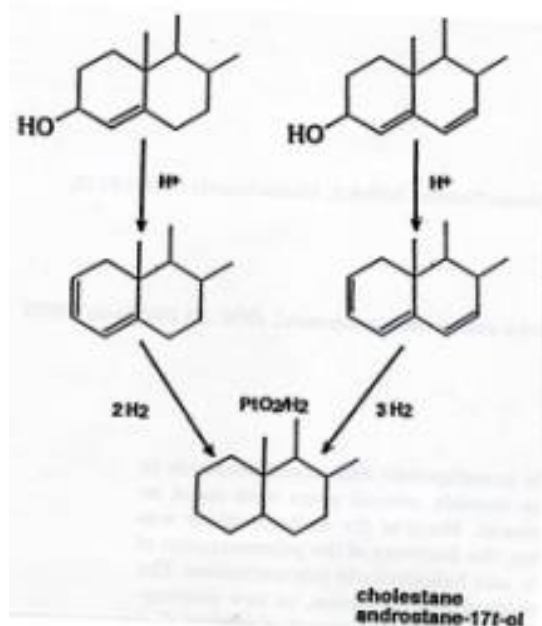


Figure 1: Highly Unsaturated Sterin Alcohols; Reaction on Steroids

$3\beta$ -Cholestadienol-4,6 was found to be stable to alkalis but was readily dehydrated with

acids to cholestatriene, most probably 3,5,7-cholestatriene. It was isolated, hydrogenated, took up 3 moles of hydrogen and gave cholestane with the *trans* linkage of the steroid A and B ring, not koprostane that has a *cis* A and B ring linkage. Allocholesterol, 3 $\beta$ -cholestenol-4, was dehydrated with acids to 3,5-cholestadiene and hydrogenated with 2 moles of hydrogen also to cholestane. For the first time the epimer of the 4,6-dienol, 3 $\alpha$ -cholestadienol-4,6 were synthesized. It was also readily dehydrated to cholestatriene-2,4,6.

In the early stages of my thesis work it was often necessary to reduce steroid ketones using the Meerwein-Ponndorf reduction using aluminum isopropoxide and isopropanol (since lithium aluminum hydride (LAH) as reducing agents for ketones to alcohols was not known then. Oxidation of the steroid alcohols to the corresponding ketones by the Oppenauer oxidation reaction, the reverse of the Meerwein-Ponndorf reduction using the same type of catalyst was commonly used.

Some compounds of the cholesterol series, such as ketones or hydrocarbons with the aliphatic side chain in the 17 position, when they are not very pure, have the tendency not to crystallize readily. Separations on alumina column, the Tsvett technique, were common techniques to improve the purity of such compounds. Over the years during my thesis work I carried out many chromatographic separations. They were all done manually at that time, which was very labor intensive and time consuming and required constant attention.

It became clear that one could easily separate various cholestane derivatives by chromatography. Hydrocarbons were eluted with petroleum ether while intermediates with more polar groups were eluted with more polar solvents such as benzene. The sterin alcohols could be extracted from the alumina in a Soxhlet extractor with ether.

We were able to establish general rules for such separations of cholestane derivatives. A blue trichloro acetic acid reaction was typical for trienes, a red color reaction for

dienes.

Spectroscopic characterizations in those days were very difficult to obtain; no infrared facilities were available. The ultraviolet spectrum had to be determined by exposing the sample at various wavelengths, taking the picture at the wavelength and developing the individual glass plates and constructing the ultraviolet spectrum graphically. It was still two to three years before the first Beckman UV spectrometer appeared and even one or two years until the single beam infrared spectrometer became available.

Having had moderate success in Tsvett type chromatography, Professor Galinovsky recalled a paper by Christiani who had reported in 1941 that 5-cholestanol, the 5-*trans* compounds, and koprostanol, the 5-*cis* compound could be separated by chromatography. Galinovsky ask me to try to see if we could separate the 3-isomeric cholesterol alcohols. I started to think how I could separate the 3 $\beta$ - from the 3 $\alpha$ -alcohols (also called the epi-alcohols). My overall plans were to separate cholesterol from epicholesterol, cholestanol from epicholestanol and koprostanol from epikoprostanol. The problem was quite different from Christiani's work. Christiani's separation relied on the stereochemistry of the hydrogen atoms (*cis* vs. *trans*) in 5 position. This hydrogen atom is attached to one of the carbon atoms, which are common to the cyclohexane rings in ring A and B. The separation of the epimeric 3-alcohols was expected to rely on the difference of the stereochemistry of the hydroxyl groups in 3-position. The 3 $\alpha$ -group has the stereochemistry in axial, and the 3 $\beta$ - the hydroxyl group in equatorial position.

In order to do this it was necessary to synthesize the 6 alcohols. With the exception of cholesterol, the alcohols were not available and I had to synthesize them. The direct epimerization of cholesterol could not be achieved and the synthesis of the epialcohols was actually quite difficult although, it turned out, they were the epimeric by-products of in the Meerwein-Ponndorf reduction. It was quite fortunate that we had to carry out the Meerwein Ponndorf to synthesize the alcohols from the ketones because it produced

about 30 % of the epi-alcohols, the  $3\alpha$ -alcohols.

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All my steroid work relied largely on chromatographic purification and separation of individual compounds on aluminum oxide. We indeed found out very soon that it was possible to separate steroid alcohols from steroid hydrocarbons and/or ketones by passing mixtures through the columns with hexane as the carrier solvent. Alcohols stayed on the column.

Around that time there was a paper, published by Christiani, that described the chromatographic separation of cholestanol and koprostanol. It occurred to Galinovsky that it should be possible also to separate sterin alcohols that had the 3-OH-group in either  $\alpha$ - or  $\beta$ -position, the former also called epi-steroids (3) We know now that the a-position is axial and the b-position is equatorial. Cholesterol itself is the  $3\beta$ -cholestene-5-ol.

We could, indeed, demonstrate that the epi-alcohols could be eluted from the chromatographic column with benzene-petroleum ether mixtures and once the epimeric alcohols had been eluted from the column, the remaining regular or  $3\beta$ -alcohols could then be extracted from the column

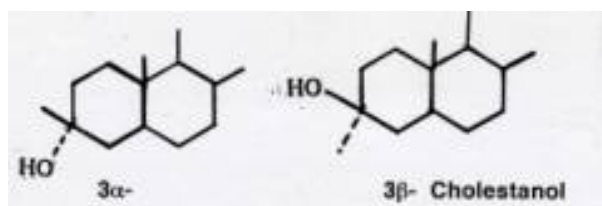


Figure 2: Chromatographic Separation of  $3\alpha$ - from  $3\beta$ - Sterin Alcohols

with ether (Figure 2). The success of the chromatographic separation of epimeric sterin alcohols was a significant boost for my ambitions in science. Separation of epimeric alcohols allowed the separation without the digitonine precipitation of the  $3\beta$ -alcohols that was the customary isolation technique of the b alcohols from mixtures. The

digitonine method although elegant and selective was good for general and robust  $3\beta$ -alcohols however there was always a question of decomposition of the compound while the digitonine adduct was decomposed into the actual compound and digitonine itself.

Incidentally when a mixture of cholesterol and allocholesterol (both have the hydroxyl group in  $3\beta$ - position) were heated with acid, allocholesterol was quantitatively converted into 3,5-cholestadiene which could be separated from cholesterol by chromatography. Cholesterol remains unchanged and could be extracted from the column with either. Cholestadiene-3,5 again could be hydrogenated with 2 moles of hydrogen to cholestane.

The final part of my thesis work turned out to be very interesting but also very delicate. It was a parallel work on the dehydrobromination in the cholesterol series. It should be mentioned that two discoveries became popular at this time. The discovery of NBS for the elegant and selective brominations in activated carbon-hydrogen links in organic molecules. The second discovery was the discovery of lithium aluminum hydride (LAH) as a mean of reducing quantitatively keto compounds to alcohols. Since this reaction was a reaction at room temperature it allowed many ketones and acid derivatives to be reduced under mild conditions quantitatively and without side reactions. In the series of steroid ketone reductions it always gave quantitatively  $3\beta$ -alcohols of equatorial configuration.

It was required at the University of Vienna for a graduate student to give two seminars on the subject of his choice but it was required that the subject had to do with recent developments. As the subjects of my seminars, I selected the bromination with NBS and the reduction of carbonyl and acid derivatives with LAH. Brominations with NBS were important for me in my work on cholesterol derivatives. LAH reductions became very important for my second thesis part the work in the androstane series.

It was fortunate that LAH did not become available until the second part of my thesis. I probably would have carried out all my reductions of ketones with LAH and not by the Meerwein-Ponndorf reduction and would probably never have gotten involved in the separation of epimeric steroid alcohols because LAH reductions are very specific. They give only the  $3\beta$ -, in other words, the regular alcohol with equatorial hydroxyl groups and no  $3\alpha$ -epialcohols.

The work on the male hormone testosterone taught me another entirely new way of thinking--thinking in small quantities. For the entire work Galinovsky had about 0.3 g of testosterone available; he handed it out in very small amounts. As a consequence, reactions had to be carried out in amounts of 50 mg to 100 mg, micro-hydrogenation with 8 to 10 mg, which still allowed the sublimation of the product, crystallization, carbon-hydrogen analysis and melting point and mixed melting point determination if needed and when possible.

This way of thinking has helped me in my entire career, even later in polymer chemistry and polymer synthesis. It emphasized the importance and need of the purity of compounds and what was even more important how much influence these impurities might have on the ultimate objectives.

The remainder of my thesis work consisted of work in the androstanol- $17_t$  family.

Androstene-5-diol- $3,17_t$  was brominated with bromine and the dibromide dehydrobrominated with collidine. It yielded testosterone, but also androstatriene 3,5,7-ol- $17_t$ . The three double bonds of the triene were quantitatively hydrogenated with three moles of hydrogen to androstanol- $17_t$ , which was also prepared from testosterone. The keto group in 3-position of testosterone was reduced with LAH to

androstene-4-diol-3,17 $t$  which was dehydrated with acid to androstadiene-3,5-ol-17 $t$ .

Quantitative hydrogenation gave under absorption of two moles of hydrogen androstanol-17 $t$ .

Testosterone was also transformed with acetic anhydride to the enol acetate 17-acetoxytestosterone acetate. LAH reduction gave androstadiene-4,6-diol-3-17 $t$ , which on dehydration yielded androstatriene 3,5,7-ol-17 $t$ ; this compound was hydrogenated with 3 moles of hydrogen to androstanol-17 $t$ . Androstadiene-3,5-diacetate 3,17 on bromination gave 6-bromo-17-acetyl testosterone, which was dehydrobrominated to 6-dehydrotestosterone. 6-Dehydrotestosterone was reduced with LAH to androstadiene-4,6-diol-3,17 $t$ , which on dehydration yielded androstatriene 3,5,7-ol-17 $t$ ; it was also hydrogenated with 3 moles of hydrogen to androstanol-17 $t$ .

The same products could be obtained by hydrogenation of androstadiene-3,5-ol-17 $t$ .

Androstane derivatives were much easier to handle than the derivatives of the cholestane series because these compounds are relatively high melting (because of the hydroxyl group in 17 $t$  position) and could be sublimed in high vacuum at  $10^{-3}$  to  $10^{-4}$  mmHg. It should be pointed out that the vacuum sublimations were carried out with mercury diffusion pumps. Oil pumps were very rare in those days and the quality of the high vacuum oil was not sufficiently good to reach vacuum approximating that of the mercury diffusion pumps. By the end of 1949 the experimental part of my thesis was completed and the thesis had been written.

### ***i. Examinations and other activities as a graduate student***

A few comments should be made to explain the examination procedure to obtain a Ph. D. degree at the University of Vienna in 1950. Since the degree was in philosophy, it was required to have 20 credit hours in philosophy and in psychology and to take a final examination in these subjects. It was permissible instead of psychology to take

subjects such as meteorology but it was customary to take psychology with philosophy. Although I had completed and written my thesis by the end of 1949 it took another 5 months to study for all the final examinations (*rigorosa*). It was not unusual that the preparation for philosophy and psychology took 6 weeks and for the major, chemistry and minor, physics 4 months. The chemistry combination included inorganic, organic, analytical and physical chemistry. The three examinations had to be taken in a 24-hour period. The examinations in inorganic and organic chemistry were by the Head of the II. Chemical Institute, Professor Wessely. The "Rigorosum" in physical chemistry and analytical chemistry by the Head of the I. Chemical Institute, Professor Ebert. I took the physics exam with Professor Przibram.

I chose to take the philosophy *rigorosum* first with Rohrer in Psychology and then with Kraft in Philosophy. The dean of the faculty of philosophy assigned two philosophy professors as examiners for the candidate and the candidate could not choose his examiner. I was fortunate to have had Professor Kraft rather than Professor Kainz as the examiner. Kraft had changed from his professorship of physics to philosophy. This was not an uncommon phenomenon. Kraft had a great deal more interest in the philosophy of natural sciences than in a "pure" philosopher which Kainz represented.

I had studied intensively with my friend Fredl Renner (who later became a director of Ciba-Geigy, Switzerland) and was a graduate student of Breitenbach (who had now become a Professor. On several long weekends we locked ourselves up in my office in the Institute, ate, slept and worked. I studied philosophy and he wrote and completed his thesis.

Professor Kraft's exam worked out well. I received questions that I had studied well. It covered the Greek Stoics, Descartes and his own (Kraft's) philosophy. The two parts of the philosophy examination also had to be taken in one day. I began at 8:00 o'clock with Rohrer. It was initially a very threatening experience, as I could not answer the first three questions at all; but then it went very well especially since we

touched on his favored subject the Interpretation of Dreams. It was traditional that Rohrachner gave 10 questions and I was surprised that I walked out with a Grade A and with a pat on the shoulder. Rohrachner said: "Well, every student has a shock period in the beginning, your shock period was longer than most but I do not consider the shock period as part of the examination".

Kraft's examination followed an hour later and was equally nerve-racking. Kraft had a graying goatee and during my examination he had his mid-morning snack: a slice of dark bread from a round loaf, "buttered" with lard and an apple. He enjoyed it very much, although it was only about 9:30 in the morning, for me it was unnerving. Again the philosophy examination went surprisingly well for me, I survived it and I left with a Grade of A.

The Rigorosum in the major subjects, chemistry and physics were much more difficult. It was customary to appear for the examination in a dark suit. I had first my examination with Professor Wessely who was then the Director of the II. Chemical Institute. The main question of the examination in inorganic chemistry was the technical synthesis of mercuric chloride from mercury sulfate and sodium chloride. The first question of the organic part of the exam was the Prelog synthesis of adamantane. Wessely continued the exam by asking for the synthesis of the female hormone diethylstilbestrol. The examination in physical chemistry by Professor Ebert was rather less nerve wrecking and the physics examination under Professor Przibram was relatively easy. One point still comes to mind when I recall this examination. Professor Przibram was an expert in the blue color of rock salt and I had studied very carefully and knew all the details of his work. He asked only which physical methods I had used during my thesis and we discussed optical activity in great detail. In addition, he asked for the Maxwell Equation, which I knew very well but when he asked for details and fine points of the equation, I faltered. I still received an A and a pat on the shoulder from a very kind old gentleman. There were one or two other examiners in physics, which I could have had: Professor Ehrenhaft and Thirring. They were considered very

dangerous examiners, but I was lucky again and had Przibram, the best possible choice.

This examination was on May 10 and my graduation was scheduled for May 29. About 20 to 25 students of philosophy were invited for the official presentation. We received our doctoral degree and took the academic oath (in Latin) for truth and the glory of the University. Now with this new degree I continued to work at the University still under the direction of Professor Galinovsky.

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## **D. As Instructor at the University**

Before I completed my Ph.D., I was appointed an Instructor at the II. Chemical Institute (on October 1, 1948). It came just in time because it guaranteed my financial survival. Today when I think back it is hard to realize how I struggled from 45 to 48 with very little money. However, at that time living costs were relatively cheap in Vienna, tuition at the university was free. I had concluded half of my experimental thesis work.

In 1948 all my resources had more or less dried up and something had to be done. I had hoped to receive a position of Instructor. However, at the Institute we were still in the period of the interregnum after Spaeth's death and no successor had been appointed. No appointments of staff positions could be made until the new director of the Institute had been appointed. This happened by the middle of 1948 when Professor Wessely, the new director, came to interview me. Soon I was informed that Hans Tuppy and I had been appointed as the new instructors of the Institute as of October 1, 1948. Hans Tuppy continued to work for the organic teaching laboratory under Dr. Pailer and I was assigned to Galinovsky and the quantitative laboratory on the third floor.

We were three instructors in the quantitative laboratory, in the order of seniority (and

seniority counted): Goldberger, Kainz (no relation to the philosophy professor Kainz) and myself. My teaching responsibilities were 1/2 day per day for the 6 days of the week. During the remainder of the time I was expected to carry out experimental work for my thesis. Later on, after I had obtained the doctoral degree, I was expected to do scientific research still under the guidance of the mentor, in my case, Galinovsky.

We had to supervise 56 students in the laboratory course. Galinovsky gave the entrance and final examination of the laboratory course and the three of us gave only laboratory quizzes of a simple nature.

The starting salary of a young instructor was 285 Austrian Schillings per month at the exchange rate of 10 Schillings per Dollar. This meant that my salary was about \$28/month. The tramway fares then was 35 Groschen, but almost free for University students and lunch in a small restaurant was about 2.50 Schillings. Sunday dinner was perhaps 5.50 or even 6 Schillings. I did not have to pay my aunt for living with her and her husband. With my first salaries I was able finally to buy myself a new hat, gloves and a coat the next year followed by a new suit. I needed it for the doctoral examination and the formal graduation. The fall of 1948 concluded another important period in the history of Vienna. The ration cards were eliminated over night, which also eliminated substantially the black market. Prices of products increased rapidly; at the same time the stores were full but few people could afford to buy. All this happened at the same month as I received my first salary. Within half a year some of my other friends Schloegl and Michl, also became Assistants (Instructors).

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During the period of the work on our theses and shortly thereafter long-lasting friendships were formed between us from the II. Chemical Institute and the I. Chemical Institute. Since money was still limited the activities were also limited to less extravagant events. A few persons who lived at home, could afford a motor scooter. We had parties, Institute parties and student parties, Christmas parties. We also attended with enthusiasm, during the "Faschings-period" - balls, balls that were

associated with academic organizations.

Across the Institutes, in the Sensengasse, there was a sports complex and on Wednesday mornings, we gathered to play soccer and handball, either between "pick-up" teams, or frequently on a more formalized basis, like I. Institute against II. Institute. I think of my friends that played on our team like Anton Preisinger, Hans Peter Frank, Gustav Purth, Sepp Pesl, Fredl Renner and others. We participated with a chemistry team on the University championships. Teams came from various places at the University: Veterinary Medicine, General Hospital, Agricultural University and Dentistry. Assistants, Instructors, graduate students and even technicians could play. A few of the teams played even with players from the major league. In these cases we usually lost by significant scores. I played for two seasons for the chemistry team the position of center half, which was at that time and system like a quarterback. This training helped me later when I was at the University of Michigan to become easier incorporated in the American University System.

For two years I acted as an Instructor in the quantitative teaching laboratory. The research group of Galinovsky consisted of Hilde Mulley, Max Poehm, Robert Weiser and myself. We were located as the end laboratory of the second floor.

It was a most interesting period and I had a great deal to learn, how to deal with students and how to deal with colleagues. They were all older than I, because when I began my teaching career I was just 20 years old and at that time the laboratories were occupied with students that were much older because they had just returned from the war from being POWs. Many students were as much as 8 years older than I, and had lived a difficult life, which made my position sometimes complicated.

Galinovsky's first graduate student was Erika Stern, after the war, she became Mrs. Galinovsky. By the time I arrived in the group in the fall of 1947, she had finished her degree. I mentioned earlier that Galinovsky had also the duty and responsibility to help

the three graduate students of the late Professor Spaeth to complete their thesis requirements. When I joined Galinovsky's the only graduate student was Hilde Mulley. Max Poehm and Robert Weiser soon followed me. Thereafter came Anton Wagner, Helga Zuber and Walter Moroz. In 1952 we had an exotic addition to our group, Dr. Giuseppe Bianchetti from Milan as a post doc. Later Ronge, Hans Nesvadba, and Knoth joined our group

In the summer 1950, after I had received my degree, the Institute was reorganized Professor Galinovsky was asked to take over the qualitative teaching laboratory on the first floor. I was reassigned with Karl Eiter the senior Instructor of the laboratory and Heribert Michl. The quantitative laboratory, which was formerly the responsibility of Galinovsky, was taken over by the newly appointed Head of the Department of Analytical Chemistry, Professor Hecht.

This work was also interesting, because we had to deal not only with first semester chemistry students but also with pharmacy students that were required to take this course.

I should probably mention that during the thesis period I worked with the graduate students of Professor Galinovsky, Max Poehm, Robert Weiser and Hilde Mulley, Kainz and Goldberger were almost finished by the time I started to work actively for my thesis. Long-lasting friendships developed with the colleagues in Galinovsky's group. Docent Gruber's group, Karl Schloegl, Horvath, Gerhard Proske and Hertha Renner played a more social and personal role when I was a graduate student. I also developed close relationships with graduate students at the I. Chemical Institute, particularly the group of Professor Novotny, the new Professor and Director of the I. Chemical Institute: Kurt Komarek, Pesl, Purth, Kurt Bachmayer, Kromer and Fredl Renner.

As was customary at the University of Vienna, after receiving my Ph.D., I was required

to continue my scientific work with my mentor Galinovsky. Galinovsky had research interests in natural products, other than steroids, specifically alkaloids. We agreed that I should change my research activities to alkaloids, alkaloids of golden rain (*Cytisus laburnum*) (5. 9. 10. 13. 14), and later on pomegranate (*Punica granatum* L.) (4. 7. 12. 15) (Figure 3).

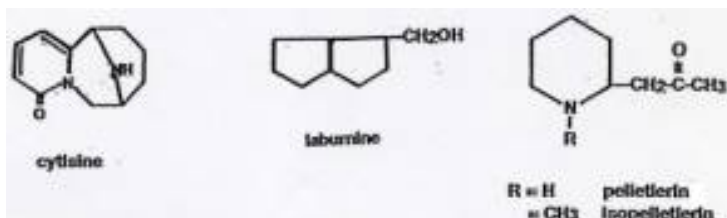


Figure 3: Alkaloids of the Golden Rain (*Cytisus laburnum*) and pomegranate (*Punica granatum* L.) Tree.

I had moved into a laboratory/office at the end of the corridor with a view on the Boltzmanngasse and the statue of Auer von Welsbach who is credited with the discovery of rare earth metals and the gas lamp. My office was also close to the teaching laboratory and I was ready to start on the alkaloid project. Galinovsky had assigned one graduate student, Walter Moroz, to work under my direct supervision. We worked on the cytisine project and had a good but not a special personal relationship. The second graduate student, Hans Nesvadba, was something quite different. We developed a close relationship that is still in existence today and I cherish it very much. I consider him as my first graduate student. We worked on the residual alkaloid of *Cytisus laburnum*, and Hans isolated in amounts of 2-3 % of the total alkaloids, a new alkaloid, and laburnine and determined his structure (10, 13).

Golden rain was known to have two alkaloids in the base fraction. We commonly extracted the seeds with methanol. The 2 golden rain alkaloids were called cytisine and N-methylcytisine. It was known that the structure of cytisine had three fused rings with 2 nitrogen atoms. Ring A was a pyridone ring and rings B and C were saturated with a secondary nitrogen atom common to both rings. N-Methylcytisine was

methyalted on the secondary nitrogen atom. Although the structure of cytisine had been established, we decided to synthesize cytisine, which was commonly done in those days to confirm the structure of a natural product.

Cytisine has three asymmetric centers with possible 4 racemates. We chose a 2-prong attack: First, to synthesize the basic three ring system, tetrahydrodeoxycytisine and dehydrogenate tetrahydrocytisine. The ultimate goal would have been to oxidize tetrahydrodeoxycytisine to tetrahydrocytisine, in other words to transfer the methylene group next to the tertiary nitrogen atom in Ring A into a lactam group. We could readily prepare tetrahydrodeoxycytisine from tetrahydrocytisine by reduction with LAH. Tetrahydrocytisine could be obtained by hydrogenation of cytisine. Dehydrogenation of N-acetyl-tetrahydrocytisine with Pd gave N-acetylcytisine, which was deacetylated to cytisine.

The first two objectives could be readily accomplished. The synthesis to tetrahydrodeoxycytisine gave a mixture of the desired tricyclic diamines with two racemates, which were separated via their picrates. The correct racemate was separated in the form of the tartrate into the desirable enantiomers (5).

Dehydrogenation of tetrahydrocytisine to cytisine was also accomplished (14). The only step left for the synthesis of cytisine was the introduction of the lactam oxygen atom in ring A. However, in all our efforts for our projected synthesis of oxidation of tetrahydrodeoxycytisine, the oxygen atom was always introduced into ring B and we did not obtain tetrahydrocytisine.

In the meantime one of our competitors, van Tamelen, succeeded in the synthesis of cytisine by a different route. He left the ring A as aromatic pyridine ring, which directed the oxidation into ring A.

During the work on cytisine we also isolated a new alkaloid from *Cytisus laburnum*,

laburnine (10,13) and established its structure and stereochemistry Laburnine is a derivative of pyrrolizidine, 3-hydroxymethylpyrrolizidine with the pyrrolizidine junction in *cis* -configuration. The pyrrolizidine ring structure was completely different from the structure of the other cytisine alkaloids, but is quite common in the alkaloids of the *lupinus* family.

The second objective in my research activity on alkaloids was the investigation of the alkaloids of the pomegranate (*punica granatum L.*) bark (7,15). We established that the structure of the formerly called pelletierin as piperidylpropionaldehyde as N-piperidyl propionaldehyde was incorrect. Piperidyl propionaldehyde is not an alkaloid of the pomegranate bark. The actual structure of pelletierin 2-piperidylacetone and N-methylpelletierin is N-methylpiperidylacetone. The synthesis of N-methylpelletierin was accomplished from N-methylpyridone by partial reduction with LAH and condensation with acetoacetic acid.

Pelletierin and N-methylpelletierin racemized frequently which caused a great deal of consternation. We soon recognized that the two alkaloids were stable under acid conditions but racemized in even slightly alkaline medium. We investigated this interesting behavior and worked out the mechanism based on enolization of the ketone followed by the formation of a cyclic enolate that allows the proton on the asymmetric carbon atom to migrate, which causes racemization (12).

With our interest with the then newly available LAH a challenging problem presented itself. My friend Max Poehm had started to work for Waldheim Co. He worked on muscle relaxing drugs to facilitate baby delivery, to suppress labor pain. Some such drugs or potential drugs were based on derivatives of lysergic acid. Naturally occurring derivatives are lysergic acid amides of amino acids or oligomer amino acids. There was a need to produce optically active amino alcohols of high optical purity.

Karrer had published an article describing the reduction of optically active amino acid

esters with LAH to the amino alcohols without racemization. There was one problem. During the esterification process of the amino acids the carbon atom holding the 4 substituents readily racemized, which made this path way to the amino alcohols unattractive.

We thought the simplest way would be to reduce the amino acids directly as amino acids without attempting esterification by adding them as solid powder to the LAH suspension in THF. It worked (6, 11). Optically active amino alcohols were produced in high yields without racemization.

I still do not know why optically active amino alcohols were desired for the synthesis of amides of lysergic acid and I have never been told what kind of physiological activity these lysergic acid amides from our amino alcohols had produced. I only know that we never made the diethyl amide of lysergic acid and consequently missed the entire business of LSD.

As we were supervising the laboratory of qualitative analysis we became involved with a problem that was facing us when it came to the Ni/Co separation. The two metal ions were commonly precipitated or co-precipitated as sulfides, but they were always obtained in a colloidal form that could not easily be filtered. Eiter, our senior instructor had found out that a new ultrasound apparatus had become available in the laboratory of one of his friends in the physics laboratory of Professor Seidl. Eiter, Michl and I decided to undertake the study of the effectiveness of the assistance of ultrasoneration on this sulfide precipitation. Initially it did not work because the type of reaction vessels did not allow the ultrasound to penetrate the cavity. We finally found that a condom was the perfect reaction vessel for the ultrasound-assisted precipitation of Ni and Co sulfide (8). We found it difficult at that time to justify the reimbursement for a box of condoms from the petty cash of the Institute.

One of the most interesting experiences that I had in my scientific career was based on

a very curious accident that happened - again - in our teaching laboratory. Again it involved Eiter, Michl and myself. This time I was the lead person of the team, but Eiter as the senior assistant and about 10 years older recognized the ultimate possibilities and ramification of the problem.

Among the tests that had to be performed in this laboratory course was a test for anions and the identification of anions in mixtures. It was customary to hand out to the students a mixture of sodium or potassium salts of anions as solids. For some reason I had chosen to give out a combination of nitrite, cyanide and iodide. Normally the students would dissolve the solid samples in water and carry out the determination of the individual anions, by tests or by separation of anions followed by tests.

For some reason the student that I had given the test example chose to heat the samples dry in a test tube over the Bunsen burner. Fortunately he used only a small amount of the sample. When the student heated the sample, a detonation occurred with the destruction of the test tube. Eiter (Karl) and I were close by and could readily handle the situation and contain the excitement. We immediately went to the literature, to check if this unexpected reaction had any previous recording in the literature and how this violent reaction could have been prevented.

As we expected initially we found nothing. Karl E. and I went to our own laboratory to check out experimentally what was going on. It was soon clear that iodide was an inert component and indeed nitrite and cyanide mixed in about equal amounts and heated gave a highly detonating material. The mixture melted first and then detonated. It was clear that an alkali fulminate had been formed as an intermediate before the explosion. As a consequence, we very quickly looked at all possible combinations including using mercury cyanide because it is known that mercury fulminate is one of the most important detonators used as an initiator for gun powder and other high explosives.

Karl decided that we may have more than just a chemical discovery. With some of his

friends (and he had many) -he checked into the possibility of developing a safety explosive. In the early 50's when Austria was still occupied by the four postwar allies it was not the time to develop explosives.

On one occasion in the II. Chemical Institute, we were visited by the allied police, comprised of all four representatives of the post war occupation: American, British, French and Russian in the Chemical Institute. A graduate student had placed a hot Carius tube on the windowsill for safety reasons in case the tube exploded. The Carius tube did burst violently and sent the tube contents out of the window. The projectile landed in the small park in front of the II. Chemical. Institute. Although chemistry does produce sometimes-unusual results and unusual- reactions, even violent reactions, these reactions were very difficult to explain to the Allied Military Police.

The possible development of a safety explosive had to be undertaken with great care and in secrecy. Down in the third basement of the II. Chemical Institute, with a pile of sand to protect the possible violent results of our investigations, we checked out - now in larger amounts - the behavior of a mixture of nitrite and cyanide when heated. We found indeed that we could produce violent explosives reliably with increasing power as the amount of the materials was increased. Naturally these experiments were carried out in the evenings or on weekends to avoid any interference from well-meaning and not so well meaning on-lookers. Before too long it was clear that the reaction that I had discovered by handing out the test sample to a student, on heating, caused indeed a thermal rearrangement of the chemical structures to form fulminates which immediately exploded.

It was then time for the scale-up and the actual test. Eiter made arrangements with the mechanical shop to have a steel tube prepared with a screw top that had a hole in the top through which we could introduce the proper and commercially available fuse. He also had some friends from whom he was able to obtain a fuse that was used in practice. This sample tube sufficient to contain about 100 grams of our mixture of the

proposed safety explosive. One weekend in February Eiter, Michl and I set out to carry out the actual experiments with two samples planned. Eiter had the mixture in the two containers and I had the fuses and the detonator, which Karl (Eiter) had obtained.

We decided that the experiment should be done in Styria, in the British occupation zone. I should remind you that Austria at that time was occupied by the four Allies as well, the Americans, British, French and Russians. All four Allies occupied Vienna. Each of the Allied powers had their own zone. The Chemical Institutes of the University of Vienna were in the American zone. However, it was necessary to go through the Russian zone to get to the British zone at the Semmering Mountains about 100 miles south of Vienna. As I mentioned, on this Saturday in February we were ready to go, equipped with mountain shoes, normal mountaineering equipment and knapsacks. We had to go to Gloggnitz, leave the train and cross both the Russian and the British checkpoint on foot in order to reach the mountain chain where we intended to carry out our experiments. It was then 1951 and much of the political situation in Europe had relaxed, at least in Austria. Still, having in possession unregistered firearms, explosives and the like was strictly prohibited and if found out subjected those involved to severe penalties by the Allied forces. It could have caused automatically jail sentences of several years.

The three of us took the train. I carried the fuse and the detonator, Karl the two containers and Michl the "substance" in a brown bottle for chemicals. We even left the original label on the glass bottle. We walked to the border crossing, crossed the border only to find out (after a mile or two after crossing the British checkpoints) that the fuse, the line that carries out the incendiary charge had been sticking out of my knapsack by about two feet; nobody had noticed it fortunately. This was very scary incident. After recovering from our shock we continued and marched our three or four miles into the mountains up to about 3,000 feet. Snow was heavy; in the higher elevations it was one to two feet deep and we set out on our mission for our two experiments. We had never carried out the experiments with an actual commercial fuse. All our experiments had

been concerned only with melting the materials together in small amounts to be sure. This time with the proper fusing we could check out, if our experiments could be used on a practical scale. We were still worried about what would happen if the experiments were not successful because it would have been very dangerous to get close to the failed experiments in case there was a late detonation. Fortunately and with great relief both experiments were a tremendous success. I still remember the roars that went up and down the mountain as the fuses were lit and the incendiary device set off the "chain reaction."

Having finished our experiments we then returned back to Vienna much more at ease. We were ready for the filing of a patent application of our invention at the patent office. The patent was applied for in December 1951 it was issued in late 1953 and it read as follows: A Safety Explosive characterized that metal cyanides even as complexes are mixed and used together with the salts of nitrous acid and it specifically said that by mixing metal cyanides also in complex form with a salt of nitrous acid are mixtures which detonate upon heating. When used with general or induction fusion the mixture can also be detonated when ignited with general or induction fusion. The explosive is characterized as compared to known safety explosives because of its extraordinary safety and stability against moisture and other mechanical uses as well as of the ease of accessibility of the starting materials. The patent gives sodium nitrite and potassium cyanoferrate or mercury cyanide and sodium nitrite, and finally sodium cyanide and barium nitrite as the examples (16).

This example of an application caused a considerable problem in the patent office because no patent for an explosive had been applied for since before the take-over of Austria by the Germans in 1938. We were visited two or three times, by investigators of the patent office. They tried to discourage us and said, "go away", "why don't you withdraw the application, it is of no use". The latter statement ultimately proofed to be correct. Nobody was really interested in this kind of safety explosive.

It was exciting for us to see that some research could be done under the most complicated and difficult circumstances even if the outcome was for practical purposes useless.

As 1952 came around, I decided I should probably have some experience abroad. Some of my colleagues had tried Germany and even England, but the most recent trend was to go to the United States. One or two people who had been instructors at the Chemical Institutes, Hans-Peter Frank and Helmut Merten, had gone to the United States. I was convinced that my destiny would be across the Atlantic and I started a campaign to find a postdoctoral position in the United States.

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## II. The Years of Wandering

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### A. At the University of Michigan

I have described the circumstances under which the University functioned after the war. What I did not mention was that the contact with other institutions was limited. One day a visitor arrived in the Institute and I happened to be near the entrance I greeted him, he was an American who could speak some German. It was William Mosher, a Professor of Organic Chemistry from the University of Delaware. He was staying at the Graben Hotel and wanted to see the Institute. I showed him around and brought him to the appropriate places. He was the first American professor that I encountered. He was an inspiration for my decision to go to America

Mosher also pointed out another former Austrian, a former Instructor if the II. Chemical Institute, Erich Mosettig, who had emigrated to the U.S. He had left Vienna before the war, and worked at the National Institute of Health. When I was in Wilmington at DuPont, I visited him once in Bethesda. I saw Bill Mosher later frequently at ACS Meetings.

A considerable amount of effort and luck was needed to ascertain a position in the United States. First I checked in the literature for potential prospects whose research interests were in my field of organic chemistry

I collected a list of names, mostly of younger Professors that I decided to approach and ask for an opportunity to work with them. Even then my principle was; if someone likes me and thinks he could use me, based on my background and my potential, he might make an offer. I am saying he because at that time there was no she that could have

offered and paid a postdoctoral position. I have followed the principle all my life that one should go where one could fulfill a need and where one is wanted.

When I had decided to proceed with this undertaking, my English was nonexistent. I had a reasonable knowledge of French, Latin and even some Italian, but no English. On one occasion I met an American who was willing to help me compose and write my letters. I wrote more than 25 letters and received one positive answer from Dr. Christian S. Rondestvedt, Jr., a young Assistant Professor at the University of Michigan who had some funding to support a post doc to study "Radical Arylations." I was very happy and accepted the position immediately. Two weeks later I received a cable from Professor Roger Adams of the University of Illinois inviting me to work as a post doc on alkaloids with pyrrolizidine structures, Senecio alkaloids.

In Galinovsky's group, we had found the same pyrrolizidine structure in laburnine the minor alkaloid of the Golden Rain. Although I would have liked to work with Adams who was a giant in his field and in chemistry in the United States I declined. I gave this offer to my colleague and friend, Reifschneider who accepted this position. He worked for two years at the University of Illinois and later at Shell Agriculture in California. Roger Adams would probably have been a mentor that could have opened every door for my future career. However. I had given my word and had committed myself to go to Michigan, which was in many ways advantageous.

I took a leave of absence from my position at the University of Vienna, sold my piano, a 3/4 grand piano, to my friend Fredl Renner. I bought a ticket for the student ship "Zuiderkruis" a ship of the Holland-America-Line and took the train to Rotterdam. After one day sightseeing in Delft and The Haag I boarded this ship ready to sail to New York. I had helped to secure Reifschneider a position in Illinois. He quickly married and the couple joined me on the ship to New York. Another colleague, Strohmaier, had secured a post doc position at Washington University in St. Louis with Professor David Gutsche and was also on the "Zuiderkruis." At this time none of us had traveled much,

traveling was expensive, and during the student years we did not have much time and money.

The cost of the transatlantic crossing was \$ 140. We slept in 8 man cabins. The ship was a rebuilt 10.000-ton Liberty ship and had an Indonesian crew. Everything we saw was new. The languages that were spoken on the ship, Dutch, English and various Indonesian dialects (spoken by the crew) were different from those languages that I could understand. But we learned quickly to adapt.

After a 10-day trip on the student ship from Rotterdam we were in New York. Strohmaier and I stayed the first night in New York at the Hotel Martinique for \$ 7.50 for two. Today the Martinique is a run down refugee Hotel. In 1953 it was older, conformable, respectable Hotel. The first (and only) day in New York was fascinating; we even went to Chinatown. We were so exited we did not know what to do. Next day I went to Idle wild Airport (now JFK) and took a DC-4 to Detroit.

My new advisor, Chris Rondestvedt, met me at the Willow Run Airport in Detroit. This was very fortunate because I had only 75 cents left in my pocket by the time I arrived in Detroit. Chris helped me to find living facilities and we found a room at the Atwoods house, on Cambridge Street in Ann Arbor. Professor Atwood was the chairman of the Electrical Engineering Department of the University.

After I had settled into my room at the Atwoods, Rondestvedt found a laboratory space for me. It in the basement of the Chemistry Building. The lab was actually in the annex, a post war addition to the chemistry building. Along the short corridor there were 5 or 6 two men labs each had windows near the ceiling. I was the only post doc's in this part of the building, the rest were graduate students belonging to several different professors. John Clegg and Anton Antoniadis were my lab partners and I shared my desk with John. Kathy Spackman and Seyhan Ege occupied the next lab. Kathy came from a prominent Pennsylvania family who had an estate near Philadelphia, and as

Mrs. Andersen lives now in Wilmington, DE. Seyhan Ege, of Turkish origin now a Professor at the University of Michigan, is dedicated to undergraduate teaching. Other student in this flights of laboratories were Jack LaRochelle, George Grenier and Bruce Wark. Very soon I became part of the group and learned how to play cribbage. Almost every lunch hour at noon we played cribbage in Bruce's lab using the dry-ice chest as the table.

The atmosphere at the University of Michigan was excellent for research and my further scientific development. I had the opportunity to meet such giants in chemistry as Bob Elderfield, Kasimir Fajans, Willard, Blicke, Phil Elving, Brockway, and a number of the younger and already outstanding scientists at the University of Michigan.

I was assigned by Rørdedstvedt to study the mechanism of the Meerwein reaction also (Figure 4).

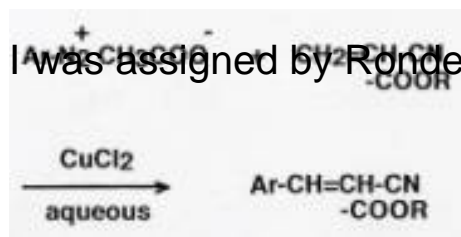


Figure 4: The Meerwein Reaction (Arylation)

The Meerwein reaction consists of reacting a diazonium salt in aqueous solution with acrylic acid derivatives such as acrylonitrile, ethyl acrylate and maleimide, in the presence of cupric chloride as the catalyst. Phenyl radicals were believed to have been formed during the decomposition of the diazonium salts and a radical arylation was believed to take place. We studied in great detail the arylation of maleimide by various substituted diazonium salts at  $\text{pH } 3$  in the presence of cupric chloride. We found that not only the substituted maleimides were formed but also 3-aryl-4-chlorosuccinimides. The relative yields depended on the type of the diazonium salt and the reaction conditions. The arylmaleimides were obtained in over 50% yield. Diarylated maleimides were also observed. Both electron attracting and electron releasing substituents in the phenyl. Ring of the diazonium salt increased the yield. We also

found that, especially with electron releasing groups, such as the anisyl group, diarylation was also observed (17, 19-21).

Coumarine was selected because it does not homopolymerize, and double bond vs. ring arylation could be studied. Arylation was observed in some cases, and mixtures of various 3 substituted coumarines were obtained. We focused on coumarine as the "acrylic" component for the Meerwein reaction, because coumarine could also be readily arylated by traditional free radicals such as benzoyl and other aromatic peroxides (18). Again, in this free radical arylation, it was very important to select the right solvent and we chose acetone, acetonitrile and ethyl acetate. Polar solvents were desirable solvents because we used not only peroxides but also N-nitroso-acetanilides and triazoles as radical generators for the arylations

It became clear that a simple free radical mechanism was could not fully explain the Meerwein reaction. On the other hand the carbenium ion mechanism was also found inconsistent with the direction of the addition and the reaction medium, water. We concluded that the homolytic character or radical nature was established but not that of a classical free radical reaction mechanism. We believed that an intermediate complex with an ultimate one-electron transfer could better accommodate the results of the Meerwein reaction. Additional careful studies of metal ions of the catalysts as well as the stereochemistry of the arylation of maleic and fumaric acid derivatives confirmed our earlier conclusions.

Although in the past, both carbenium ion and free radical mechanisms have been advanced for the mechanism of the Meerwein reactions, a third mechanism had to be considered. According to our experience, we proposed that an intermediate complex forms at pH =3 between diazonium salt, cupric chloride and unsaturated system. The stability and structure of the complex was influenced or even dominated by the solvent

acetone. The complex then decomposes by internal one electron shift to form products. The  $\text{pH}$  was found to be very important as well as were co-solvents such as acetone for the Meerwein reaction.

We ultimately concluded that the Meerwein reaction proceeded through an intermediate complex (at a  $\text{pH}$  3) which involved the solvent acetone the diazonium salt and aqueous cupric chloride. . The complex then decomposed by internal one-electron shifts to the final products.

Our results were in stark contrast to Kochi's work that concluded on the basis of studies in anhydrous systems that cuprous rather than cupric chloride was the actual catalyst for the Meerwein reaction. There was a largely ignored report by Betelman who had commented that cuprous copper was a relatively poor or a completely inactive catalyst for the Meerwein reaction. Unfortunately, Betelman did not give experimental details. Second, Betelman showed that acetonitrile - which Kochi claimed did not reduce cupric chloride - was about as good a solvent as acetone in the few cases examined. Furthermore, other authors observed numerous examples of the Meerwein reaction which give markedly inferior yields in the presence of acetone (and therefore cuprous chloride). Finally, Kochi did not demonstrate that cupric chloride was not catalytically active, only that cuprous chloride could be active. Considering the evidence we concluded that cupric chloride was the catalytic agent although it could not be excluded that cuprous chloride may be active in some cases, perhaps via a different mechanism.

The postdoctoral work at the University of Michigan gave me an excellent insight in radical reactions. I came from an Institute, which was almost entirely oriented on natural products, their isolation, characterization and their synthesis. The introduction to radical chemistry gave me a very good background for my later activities in polymer

chemistry, where radical reactions and radical polymerizations are of vital importance and central to and most important for polymerization reactions.

It was not only chemistry that occupied me in Ann Arbor. I had been very fortunate that I had found a convenient place to live, on the third floor of the Atwoods. It was a wonderful family that took care of me during my first year in Ann Arbor. The mother of Mrs. Atwood, Frieda, was German born and liked to speak German with me when I came home from the lab in the evening.

One of my most important objectives during the two years in Ann Arbor was to learn English. Kathy Spackman, a student of Professor Wyman Vaughn, helped me a great deal immediately after my arrival in Ann Arbor. After I received my first salaries, I joined the American Chemical Society (ACS), and prepared to give a short talk, based on my work in Vienna, at the Annual AC Meeting in Kansas City, and Kathy and Wyman wrote the required Abstracts (9) for me. Because of my limited English my first talk at this ACS meeting was terrible. Furthermore Galinovsky thought it was unnecessary to give a talk in America. The second talk a year later at the ACS Meeting in New York at the Statler Hotel on the Meerwein arylation was much better.

At the end of my first year in Ann Arbor I learned how to drive, bought a car and took a trip to the West Coast with two friends, Reifschneider and his wife. This was an exciting undertaking. There was so much to be seen in the big US, so much to be learned and absorbed. This trip helped me enormously to understand and appreciate the people and life in the USA. I decided to stay in the United States, and try to make my career here.

While many foreign students tended try to speak their mother tongue, I avoided this situation thoroughly. I did however, become involved in the International Student Center and became a senator of the Center. My roommate Erhard Schenker, a Swiss, tried to get me involved in the foundation of a European Club. It was a failure. At the

University they had a Chinese, Turkish, Arab and Thai Club but nobody needed a European Club. Europeans, unlike other ethnic groups, wanted to be absorbed into the US community as soon as possible. For most this was the reason to come to study in the US.

After my first year in Michigan Chris Rondestvedt offered me the position for a second year, which I was happy to accept. I moved to a house on Geddes Street with Al Hampton, an Australian born but British educated and Erhard Schenker, the Swiss from Basel.

The University of Michigan in those years as they have today, had excellent football, ice hockey and track and field teams. As I indicated earlier I always had an interest in soccer and had played at the University of Vienna. At the University of Michigan there was a fledgling soccer club. Soccer was not a varsity sport at the University but had Club status and post docs were eligible to play. We had a good team. Half of the players were also playing semi-professional in Windsor Ontario, right across the Detroit River and we had some excellent South American players. In 1953/4. We had a winning season, but I had to stop playing because of an ankle injury that did not heal rapidly. When I stopped playing the organizers of our soccer league asked to referee a few games which I did in the fall of 54.'

In Ann Arbor I had a Rackham Fellowship. The Rackham Foundation supported some research activities at the University. A centrally located building at the University of Michigan Campus was called the Rackham building and was used for various functions. Social gatherings were regularly organized in the building on Friday afternoons; I frequented some of the including a tea dance. On one of such occasion I met Jane Cunningham a graduate student at the University. After a short courtship we decided to get married. In June of 1955 we were married at the St. Andrew's Church in Ann Arbor and she became Mrs. Vogl.

My wife has never completely forgiven me that after a short honeymoon we went to the Organic Symposium at Purdue University in La Fayette, IN. This was necessary because I needed to keep the "vacation time" for the second year of my fellowship. In August, before my two years were quite over in Ann Arbor, Jane and I boarded the USS United States for Le Havre and went to Vienna. On this trip we had our real honeymoon.

In Vienna I completed my responsibilities as an Instructor at the University and prepared for my final departure to the United States. I was then assigned to the organic teaching lab whose head was Matthias Pailer. He actually tried to convince me that I should work with him and for him. He was unsuccessful. I was sad that I could not reestablish my interaction with Galinovsky. After I left my position in Vienna and parted for America I should never see him again. He died in 1956, only 50 years old.

We left Vienna in the beginning of November 1955. There was still the time of ship travel. We decided on the Holland American Line and took the Maasdam from Rotterdam. This time, married, the departure to New York was much more fun and we thoroughly enjoyed our trip and Princeton was only an hour by train from New York.

I had agreed to work for Dr. Edward C. Taylor, an Assistant Professor who had just moved from the University of Illinois to Princeton University. Ted had arranged for me the proper visa formalities, a first preference quota visa, which gave you permanent status, as it would now be called a "green card." I have always been grateful for what Ted had done for me.

You will notice that when I selected to come to the US I chose two young Professors as my bosses. In both cases Chris Rondestvedt at the University at Michigan and Ted Taylor at Princeton University were two young Assistant Professors at the beginning of their career. This was in part deliberate (I also had chosen a youngish Docent as my thesis advisor and probably based on my experience in Vienna) and my desire to

demonstrate my independence by being associated with other young people. I felt I could contribute as an equal partner to the scientific work.

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## **B. At Princeton**

With the US visa in hand and a new wife and job in an exciting research group in Princeton, I was ready to conquer the world.

Jane and I settled in Lawrenceville, the town next to Princeton. Lawrenceville had only one traffic light, a gas station and a candy store, but was the home of the Lawrenceville Prep School. We found an affordable apartment for \$ 65 over the candy store. It needed some decorating which we enjoyed doing. The bus stop was across the street and the bus took us directly into Nassau Street in Princeton. We did not need immediately a car and Jane found a well-paid job at the Education Testing Service in Princeton. Princeton is a paradise of intellectual activities and everything could be done on foot. Across from the Frick chemistry building there was the Firestone library, which my wife Jane extensively frequented and there was the Institute for Advanced Studies.

Princeton was a quite different atmosphere from Michigan. I had had my two years at the Big Ten School and entered now the life of an Ivy League school. The Chemistry Department in Princeton was quite good. Charlie Smythe was the Chairman and the department had such important people as Turkevich, Everett Wallace, the inventor of the isosteroide rearrangement, Pacsu, of Hungarian descent who was the director of the Textile Research Institute, which was also at Princeton but not directly connected with the University. Pacsu was a specialist in cellulose chemistry. Of the younger people there were Arthur Tobolsky, Dick Hill, and a new arrival, Paul von Ragué Schleyer.

By chance my laboratory was in Room 215 at the end of the corridor where the offices of Tobolsky, Taylor and Hill were located. As a consequence, by accident I got acquainted with Arthur Tobolsky and with his work and found him a delightful person. I worked with his students Henry Hsieh, Ferguson, Bob Conley, and Ken O'Driscoll. In Taylor's research group were Tom Osdeen from England, a student of Adrian Albert, Harvey Loux and Bob Donaldson, Donaldson was a member of the Du Pont family and frequently visited his "Uncle Pierre" in Wilmington.

I became very friendly with Tom Osdeen (née Oesterreicher) who was also of Austrian birth. Work on purines and pyrimidines were very fashionable in 1955 because purines and pyrimidines had been recognized as important components of nucleic acids. They were also the basis for similar heterocycles, pyrimido-pyrazines, which were the basic structures of folic acid. Ted Taylor had as his research and life objective the synthesis of heterocyclic compounds, a task that he very ably carried out with great success. My work with E.C. Taylor was generally directed toward the synthesis of nitrogen heterocycles (23). Purine and pyridine antimetabolites had become increasingly more interesting for the understanding of biological processes.

Taylor's group had just discovered a new synthesis of purines from aminomalonamideamidine and aminomalondiamidine Cyclization with ortho esters led to the synthesis of adenine and hypoxanthine.

The parent compounds were obtained with trimethylortho formate in the presence of equal amounts of acetic anhydride. Using other orthoesters it was possible to obtain 2,8 symmetrically disubstituted purines.

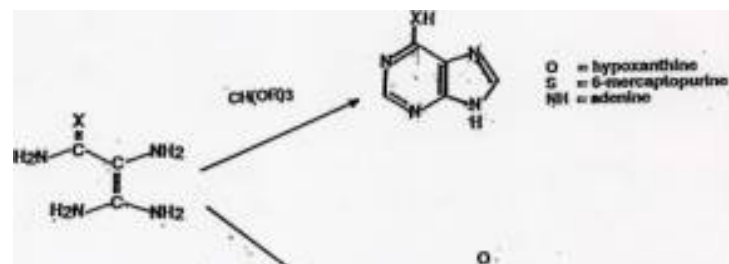
One of first accomplishments in Princeton led to a fast and efficient synthesis of 2-substituted adenines. Amidines salts of isonitrosomalnonitrile were quantitatively isomerized.

My first major contribution to Taylor's research group and to pyrimidine chemistry was that I could show a new facile synthesis of 2- substituted adenines (22). I was able to demonstrate that amidine salts of isonitromalononitrile could be prepared in almost quantitative yields by mixing the amidine hydrochloride with the silver salt of isonitrosomalonalonitrile, removing the silver chloride and concentrating the solution. They were thermally isomerized to 2-substituted 4,6-diamino-5-nitrosopyrimidines. In the presence of sodium hydrosulfite in dimethylformamide (DMF) with formic acid they gave directly 2-substituted adenines in high yields.

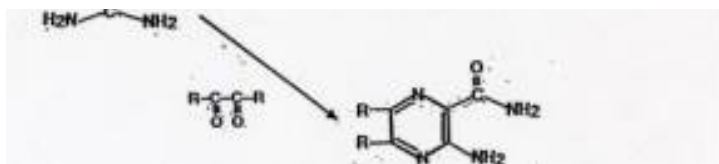
I discovered this cyclization method while Ted Taylor was away in Germany for three or four months in the summer of 1956 visiting Professor Brederick in Stuttgart. Heating the nitroso compounds with sodium bisulfite and urea gave the 2 substituted purines in very high yields. By this general method numerous purines were prepared, not only simple but also difunctional purines starting with diamidines such as adipamidine. The emphasis of all these approaches was on single step and on high yield reactions (Figure 5).

Ted Taylor was quite friendly with a group of Borrows-Welcome led by George Hutchings, his assistant. They were working on antimetabolites of nucleic acids, specifically of 6-mercaptapurine and good yields for a purine synthesis were highly desirable. As you may recall Hutchings and Gertrude Elion received the Nobel Prize in 1989 for their work on purines and pyrimidines that started in the late 1940's. Ted's group had another competitive research group with whom we were quite friendly during my time in Princeton. This was the group of Robin Roberts now at the University of Nevada.

Aminomalonamidine and aminomalonamide amidine were excellent starting



ses as I mentioned earlier. Orthoformates or liamidine by double ring closure to adenines rines. I have used this reaction later - with



meric polypurines.

Figure 5: Purine and Pyrazine Syntheses

Aminomalonamideamideamidine could also be cyclized with diketones to 2-aminopyrazine-3-carboxamides. Asymmetric diketones gave exclusively the 5-substituted product, with methylglyoxal, 2-amino-5-methyl pyrazine-3-carboxamide.

We were also interested in the preparation of N-oxy and N-amino-N-heterocycles. First the synthesis of N-amino compounds. The hydrazide of 2-aminopyrazine-3-carboxylic acid was protected by preparing the propylidene and benzylidene derivative and then cyclized with acetic anhydrides and trimethylorthoformate to 3-amino-4(3H)pteridinone (26). Surprisingly this unprotected compound was not very stable in aqueous solutions; hydrolyses in acid and alkali yielded 2-aminopyrazine-3-carboxyhydrazide (25).

Our next objective was to see whether we could also make N-oxides purines and pyrimidines. N-Oxides were believed to be metabolites of nucleic acids and had never been synthesized directly Ted Taylor thought we might be able to prepare hypoxanthine-1-N-oxide directly from 4-amino-imidazolo-5-hydroxamic acid which could be cyclized to hypoxanthine-1-N-oxide (27) with ethyl orthoformate. In fact some of the purine N-oxides had been known but they were obtained by hydrogen peroxide oxidation of the purines. The structure of the N-oxides obtained this way could not be proven unequivocally because there are four nitrogen atoms in the molecule of hypoxanthine, which could be attacked during the hydrogen peroxide oxidation to hypoxanthine-1-N-oxide. Once formed, the N-oxide could be hydrogenated to hypoxanthine with palladium oxide as the catalyst.

Purine\_N-oxides had been of interest because of their potential as possible purine

metabolites, but also because of the possibility that they may function as intermediates in biological interconversions of purines. We reduced 4-nitroimidazole-hydroxamic acid to 4-aminoimidazole-hydroxamic acid which, on ring closure, gave hypoxanthine N-oxide. It could be hydrogenated with platinum oxide to hypoxanthine.

We also carried out work in the pteridine family. First, I developed a direct synthesis of 2-amino pyrazine-3-carboxamides by condensation of aminomalonamideamidine instead of with orthoesters, which leads to purines, with dicarbonyl compounds such as glyoxal or diacetyl, which gave in excellent yield the pyrazine carboxamides. I synthesized a number of these compounds.

The reaction of aminomalonamidamide (used as the dihydrochloride) with ortho-dicarbonyl compounds gave not only 2-amino pyrazine-3-carboxamides but also as a side product the 4,5-dimethylimidazolyl-2-amino carboxamide. This direct synthesis of 2-amino pyrazine-3-carboxamides by condensation of glyoxal, the  $\alpha, \beta$ -dicarbonyl compound, with aminomalonamide amidine dihydrochloride became the reaction of the choice for the preparation of the family of 2-aminopyrazine-3-carboxamides. The synthesis was used to prepare unsubstituted, symmetrically substituted 5,6 disubstituted pyrazine derivatives and particularly the synthesis of 5 substituted 2-aminopyrazine-3-carboxamides.

Ted Taylor saw the possibility that this reaction could be used for the synthesis of naturally occurring pteridines for example the folic acid derivative biopterin. It was part in our continued focus to synthesize purine or pteridine anti-metabolites and purine glycosides. He thought that purine glycosides in which the sugar group was attached through a substituent amino group rather than directly to the ring might be of interest as potential antifolic acid agent. For this purpose we set out to synthesize a simple pteridine "glycone" of the type, 3-amino-4(3H)pteridinone.

For this synthesis 2-aminopyrazine-3-carboxyhydrazide was prepared by treatment of 2-aminopyrazine-3-carboxamide or methyl 2-aminopyrazine-3-carboxylate with hydrazine. It became apparent that the primary amino group of the hydrazide had to be blocked before the cyclization reaction was carried out. 2-Aminopyrazine-3-carboxyhydrazide was treated with acetone or with benzaldehyde to give isopropylidene or benzylidene derivatives of 2-aminopyrazine-3-carboxyhydrazide. Subsequent reaction with ethyl orthoformate and acetic anhydride/ ethyl ortho formate mixtures gave the cyclized product.

Subsequent reaction with ethyl orthoformate in acetic anhydride brought about smooth cyclization to the isopropylidene and benzylidene derivative of 3-amino 4(3-H) pteridinone respectively. Removal of the blocking group revealed that the N-amino substituted pyrimidine ring of the pteridine system was extremely labile to hydrolysis. The structure is forced to exist in the 'keto' form and could not form the aromatic hydroxypyrimidine structure. Successful removal of the benzylidene or isopropylidene blocking group was achieved however by treatment with cold 0.1- N hydrochloric acid. The durability of 3-amino-4(3H-pteridinone) to alkali of pteridines lacking electric donating substituents and an enolic hydrogen atom on the basis of these results (which was the first time 1-aminopteridines had been prepared) indicates that the instability of 3-amino-4(3-H) pteridinone would preclude consideration of this type of intermediate for (pseudo)pteridine glycosides.

Three years of post doctoral experience besides the three years experience as an Instructor the University of Vienna gave me a tremendous amount of experience in steroids, alkaloids, free radical reactions and other natural products, in the chemistry of folic acid and nucleic acids. I was still only 28 years old, but felt I was not competent enough for an academic career in the U.S.; consequently I decided to go into Industry.

The year 1956 was very excellent for job hunting. With my experience in the field of chemistry I had 13 interview trips and I obtained 12 job offers. Only the Dow Chemical.

Co chose not to offer me a job, although 20 years later I consulted for Dow for several years.

With my background and the jobs available, it became clear that I would have to decide between two types of industrial work. One option was to work for a pharmaceutical company or two to work for a large chemical company, which would probably lead to work in the relatively new area of polymer chemistry. The pharmaceutical companies that I interviewed at that time offered 10% to 15% less salary than the offers, which I received from chemical companies. From my interviews with three Departments, the Polychemicals Department, the Chemical Department and the Central Research Department of the DuPont Company I received two offers. Only the Central Research Department did not make an offer. I decided to accept the offer of \$725/month from the Polychemicals Department of E.I. Du Pont de Nemours & Co. in Wilmington, Delaware at the Experimental Station. It was a splendid decision as I found out later. At the end of November 1956, Jane and I moved to Wilmington.

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## III. The Industry Years at Du Pont

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[C. Central Research Department](#)

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### A. The Polychemicals Department

#### a. The Beginning

Three years as a postdoctoral fellow in addition to three years as an Instructor at the University of Vienna provided me with a solid background in research. I had acquired knowledge in steroids, alkaloids, free radical reactions and heterocyclic chemistry related to folic acid and nucleic acids. In 1956 I was 28 years old and it was clear to me that I was not ready to pursue a successful academic career in the US at that time, I decided to spend some time in Industry and thought I might even follow an Industrial career.

The year 1956 was excellent for job hunting. With my experience in the field of chemistry I had 13 interview trips and I obtained 12 employment offers. Only the Dow Chemical. Co chose not to offer me a job, although 20 years later I consulted for Dow for several years.

With my experience and the jobs available, it became clear that I would have to decide, between two types of industrial work. One possibility was to work for a pharmaceutical company; another was to work for a large chemical company, like Du Pont or Procter & Gamble, which might lead to a career in application or production. Another aspect of working for a company was the possibility of working in the relatively new field of polymer chemistry. When I was still in Vienna I had spent one month in a summer course at the BASF in Ludwigshafen and was intrigued by the polymer work that was being done in polystyrene and PVC.

The pharmaceutical companies that I interviewed at this time were involved in work that was similar to my work on natural products. They also had access to graduates from the best schools in the US where natural product chemistry was conducted. Pharmaceutical companies also offered salaries 10% to 15% less than offers from chemical companies. The decision-making became narrowed to two companies:

Aerojet Corporation in Southern California and DuPont in Wilmington. Aerojet was interested in the production and utilization of rocket fuels of optimal efficiency and had as Research Director a certain Karl Klager, also a native of Vienna. Klager interviewed me (and my wife) in New York and made me immediately the offer, which was much higher than the other offers I had received.

The interview at DuPont in Wilmington were scheduled for openings in three Departments: Polychemicals, Chemical and Central Research. The Chemical Department was located across the Delaware River in New Jersey; the other two Departments had their laboratories at the Experimental Station in Wilmington on the Brandywine River, near the Hagley Museum. The old powder mills on the Hagley museum grounds were the basis of the business where the fortune of the DuPont family was made. Many members and descendants of the DuPont family live in this section of the countryside.

Like many other circumstances in life, fate took care of my decision. The prospect working and commuting "across the river" every day to the Chemical Department had no appeal to me -- and Central Research Department did not make me an offer. I decided to accept the offer of \$ 725/month from the Polychemicals Department of E.I. DuPont de Nemours & Co. in Wilmington, DE. In November 1956, Jane and I moved from Princeton to Wilmington.

On the afternoon of November 29, I believe it was a Friday, I arrived at the

Experimental Station to take care of the necessary formalities. I intended to begin officially on Monday morning, but was told to sign the papers of employment immediately in order to become an official employee and to receive my salary right away. Jane and I needed the 3 days of paycheck (the week-end) for two hours of work (signing papers) signing papers and with the first salary I bought a dark business suit for \$ 69.

We went through the usual readjustment periods which we had to do several times in our live: finding an apartment, getting used to life in Wilmington and making friends. Wilmington was a sprawling City of about 150,000 inhabitants dominated by the old traditional chemical companies: DuPont, Hercules and Atlas where many young professional, technical people were employed. We found a convenient 2-bedroom apartment in Monroe Park for \$ 98.50, almost within walking distance to the Experimental Station. I did not feel like commuting for long distances, but preferred to get to work quickly.

On Monday I arrived at the Experimental Station and was assigned to the Exploratory Research Section in Building 267. This building was located on the Brandywine River. Formerly, 2 centuries ago, it was a mill river, later the river used to produce black gun power for DuPont's powder mills. Frank Gresham was the manager of the section assisted by 2 Supervisors, Arthur Anderson and Max Robinson. The group consisted of 22 scientists and was supposed to provide inventions for the further technical development and business opportunities of the Polychemicals Department and DuPont.

We had two man labs supported by one technician, in other words, we were assigned one half a technician per scientist. It was an exciting period with many discoveries, inventions and innovations underway, just completed or in planning stages.

Gresham, who was spearheading this group, had about 140 patents to his credit, and an idea notebook full of ideas. Some of these ideas were extraordinary, some trivial, or

even ridiculous. Later on, I checked out 3 of his notebooks from the early 1940's from the storeroom of the library. The 200 page notebooks had 3 ideas per page written and co-signed for possible use in case of a patent application. We were all required to keep a. idea note book in addition to the lab note book, which was copied for record keeping from time to time. This is how we learned to be alert for possible ideas, especially of interest to the company and to document conception.

As I mentioned Gresham's group was exploring new areas; some of them became commercial products. I should mention that this would not be possible without the guiding and protecting hand of Frank McGrew, then the director of research of the Polychemicals Department. The work of the discovery of polypropylene and coordination polymerization had by now become "mature" projects for the Exploratory Section. More and more monomers were explored as potential candidates for polymerizations. Prominent among them was norbornene and its cousin, dihydrocyclopentadiene. Copolymerization of ethylene with dihydrocyclopentadiene was underway, and so was the polymerization of norbornene, discovered by William Truett. Even though this polymerization gave a polymer with cis-linkages and a trans double bond using "only" titanium tetrachloride/aluminum alkyl coordination catalysts, it was without question the first example (and now rarely cited) of a metathesis polymerization.

Eleuterio was in the process of preparing hexafluoropropylene oxide and its polymers. Hexafluoropropylene oxide became the starting compound for an entire new family of fluorocarbon compounds and polymers, elastomers and ultimately Nafion<sup>R</sup> the fluorocarbon Ionomers and polymeric super acid. Lansbury worked on the preparation and purification of intermediates for the newly discovered aromatic polyimides. Other projects included the polymerization of methacrolein through the double bond, polyphenylene ethers, especially flame retardant polymers and a project on Nylon intermediates. Since the commercial success of Nylon, some inventive research on polyamides was always kept active.

I was assigned to a laboratory in the middle of the corridor with Charlie Smoot as my lab partner and my job was to find a new synthesis of methyl methacrylate. For the last 40 years, a new and catalytic synthesis of methyl methacrylate that was technically achievable was the goal of many attempts, especially at DuPont. The company had a good business position in acrylics in the form of sheets, paints and casting resins. From time to time a new employee was asked to try some of the more exotic approaches.. At that time methyl methacrylate was synthesized from acetone and hydrogen cyanide. The cyanohydrin was dehydrated and etherified with methanol with sulfuric acid. Methyl methacrylate produced by this route also produces one mole of ammonium sulfate, tainted with some cyanide. As the business of poly(methyl methacrylate) increased, so did the need for methyl methacrylate. It meant that the production of ammonium sulfate also increased and started to create a disposal problem.

My assignment was to find a new technically feasible synthesis of methyl methacrylate or methacrylic acid. I was restricted in my approach. It was to be done from isobutylene, sodium or potassium hydroxide with air or oxygen using some sort of catalyst. This was a relatively difficult assignment, since the procedure had to be catalytic and oxidation with oxygen required my learning how to handle explosive mixtures under pressure. Fortunately the reactions were carried out in the high pressure lab in shaker tubes. Highly skilled technicians handled the reactions and safety was of the highest priority. We never did obtain any methacrylate. The only product obtained was  $\alpha$ -hydroxybutyric acid. (It should be remembered that these investigations were done before gas chromatography and NMR were available). The best catalyst was obtained in the presence of lead dioxide but in molar amounts of sodium plumbate. It was clear the an epoxidation of the double bond of isobutylene was the first step in this reaction and  $\alpha$ -hydroxybutyric acid did not give methacrylates. For the final step of dehydration to proceed the hydroxyl group had to be introduced into the methyl group,. the  $\beta$ -hydroxy moiety to produce methacrylic acid derivatives.

by dehydration. The hydroxy group in a-position gave other reaction products (1).

## **a. Polymerization of Higher Aldehydes**

### *i. Elastomeric Polyacetaldehyde*

After the first six months in Gresham's Exploratory Section I was transferred to the Delrin section. This was the shortest time anybody stayed at Gresham's group and I was judged ready for the "firing line." My assignment came directly from the Director of Research, Frank McGrew. He called me one day and said "Otto, we have been making a tremendous effort to get polyformaldehyde commercialized. We have now succeeded in the commercial synthesis, the process and product development. We have not looked at the polymerization of acetaldehyde and higher aliphatic aldehydes. We need to check to see if they can be made and if they can be made we need to look at a broad patent protection. In the Delrin group, Dennis Funk had been assigned on a temporary basis to check the literature but this project would become my responsibility.

In 1929, Bridgeman and Conant started investigations on the effect of high pressure on small organic molecules. Bridgeman had constructed a high pressure apparatus that could create pressures up to about 8,000 at. The studies included the behavior of aldehydes at high pressures. Conant reported that higher aldehydes gave highly viscous liquids when subjected to high pressure but they did not last long; waxy solids were obtained from the bulkier isobutyraldehyde.

In 1934, two papers appeared almost simultaneously, one authored by Travers and the other by Letort. Both reported the transformation of acetaldehyde to a rubbery material when acetaldehyde was cooled below its melting point and then the crystalline acetaldehyde ("crystallization polymerization") was allowed to melt. Shortly thereafter, Staudinger investigated the polymer by IR and suggested that the polymer was a polyacetal. The discovery of the polymerization of acetaldehyde was an accident and

could not be explained. Attempts to understand why the polymerization occurred was extensively investigated by Letort and his group for the next 20 years. Several factors were believed responsible for the polymerization: the crystal structure of acetaldehyde, the rate of cooling, and even the influence of ultraviolet light.

We know today that any monomer including acetaldehyde can only polymerize below the ceiling temperature of polymerization ( $T_C$ ). What was important in Letort's experiments was that temperatures below  $-40^\circ\text{C}$  were needed. Impurities on the glass surface with acid functions probably acted as initiators. The crystalline structure of the acetaldehyde was irrelevant for the "crystallization polymerization" of acetaldehyde. The  $T_C$  of polymerization increases with pressure. Consequently in the Bridgeman experiments the ceiling temperature was above room temperature and polymerization was observed. However, when the pressure was released depolymerization set in unless the polymer had terminated.

Dennis Funck had already repeated the work when I arrived and found it was correct. We utilized the Letort technique of freezing and thawing acetaldehyde (at  $-125^\circ\text{C}$ ) in order to synthesize a sizable amount of this elastomeric PAA. One problem became almost immediately apparent, Dennis had found that the polymer yields varied from run to run, and on some occasion no polymer was produced. Letort had described yields as high as 50% polymer; those yields were reported on relatively small-scale runs. When we used a larger amount of monomer for polymerization, the yields usually decreased. We suspected that the "surface to volume" effect played an essential role in the "crystallization polymerization." The polymer was quite stable at room temperature although we routinely kept it at low temperature

Our first objective was to stabilize the PAA. The polymer was end-capped by the well-established acetate or alkyl end capping techniques. Acetate capping in solution of acetic anhydride with a small amount of pyridine gave acetate-capped PAA. The addition of soluble copolymer of Nylon 6,6-6,10 in 1% quantities and aromatic amine

antioxidants at 0.1% substantially improved the thermal and oxidative stability of capped PAA (2,3).

This work was accomplished in about 3 months, and I could pursue my ultimate goal: the polymerizations of acetaldehyde and higher aldehydes using well-defined initiators for the polymerization. In the mid 50's, the general knowledge of ionic polymerization was very limited, but an accidental discovery opened the door for the polymerization of acetaldehyde on a large scale. To purify acetaldehyde, it had to be distilled in a low temperature distillation apparatus. We had used such an apparatus, which had a condenser, which was filled with dry ice/acetone. One day my technician, Jake Mansure, broke the low temperature distillation apparatus. We borrowed a similar distillation apparatus from a friend who worked in the fluorocarbon group. Jake decided that prior to its use it should be cleaned. He used to clean the inside, especially the condenser with fuming nitric acid, let it sit over night rinsed and dried carefully.

When the cleaned apparatus was used for the distillation of acetaldehyde the entire condenser part of the apparatus was filled with a rubbery opaque substance, which was soluble in the acetaldehyde that was being distilled. When the condenser was brought to room temperature, the material had disappeared -only acetaldehyde was left in the receiver and the distillation pot. In other distillation experiments we found small amounts of rubbery material in the distillation flask when the acetaldehyde was rapidly evaporated. This rubbery material was identical with the elastomeric PAA that had been obtained by "crystallization polymerization." With this observation, we had demonstrated that acetaldehyde could be polymerized **above** its melting point but well below room temperature (Figure 6) and that "crystallization" was not essential it was then October 1957.

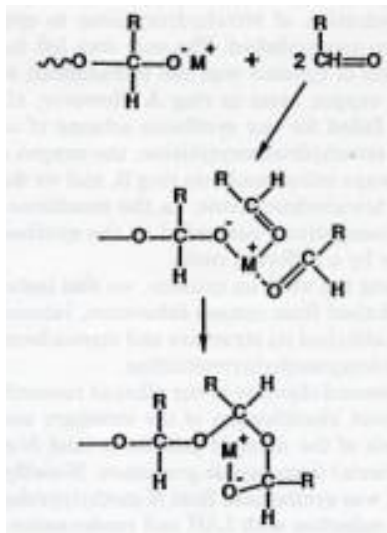


Figure 6: Polymerization of Higher Aliphatic Aldehydes

From this essential observation it was now easy to progress further to the development of the cationic polymerization of acetaldehyde. The basic principle was very simple: the polymerization had to be carried out at temperatures below  $-40^{\circ}\text{C}$  to avoid the competitive reaction of trimerization. Acetaldehyde trimerizes to paraldehyde, the cyclic trimer, or to metaldehyde, the cyclic tetramer. The polymerization has a low  $T_C$ ; the  $T_C$  of the cyclotrimerization is well above room temperature. The concept of the  $T_C$ , published in the famous paper of Dainton and Ivin did not become available, until the inventive phase of our acetaldehyde polymerization was completed.

Since acetaldehyde polymerization did not require crystallization it was easy to screen reaction conditions, such as type and concentration of catalyst, solvent and polymerization temperature. The polymerization experiments were carried out in simple test tubes capped with rubber septum. The key hurdle turned out to be the isolation of the polymer. In the beginning of our polymerization attempts, we had seen many times a highly viscous solution of the polymer, or even a plug of polyacetaldehyde had formed when acetaldehyde was cooled in a solvent and treated with an acid initiator. When the sample was then allowed to come to room temperature, the tube contents lost their viscosity and no polymer was isolated. It became imperative that the acid

initiator residues were neutralized *at the reaction temperature* (i.e., the dry ice temperature). Once neutralized, the temperature could be raised to room temperature without depolymerization. High molecular weight PAA was isolated in nearly quantitative yield.

One additional problem for the efficient preparation of elastomeric PAA had to be solved. Acetaldehyde is a very fast polymerization, almost explosive and required temperature control. When the polymerization was carried out in a dry ice/acetone bath, sometimes a portion of the acetaldehyde was transformed to the trimer paraldehyde and not to the desired polyacetaldehyde. When "good solvents" for the polymer were selected as polymerization solvent [58], a sharp increase of the local temperature was noticed. The heat of polymerization could not be dissipated fast enough. The  $T_c$  was exceeded and prevented high polymer formation and resulted in cyclotrimerization.

We found a simple solution: Polymerization of acetaldehyde in liquid ethylene as the solvent. Acetaldehyde is miscible/soluble in liquid ethylene. Acetaldehyde is not soluble in lower boiling hydrocarbons at very low temperatures but is soluble in olefins. Polymerizations in low boiling saturated hydrocarbons are two-phase systems, similar to the polymerization in neat acetaldehyde. The low boiling temperature of ethylene ( $-104^\circ\text{C}$ ) is capable of keeping the temperature under control. Even in propylene, which has a boiling point of  $-68^\circ\text{C}$ , where acetaldehyde is less soluble, some paraldehyde was formed. The cyclotrimer, paraldehyde and the cyclotetramer, metaldehyde incidentally have a stereospecific *all-meso* configuration []. The other cyclotrimer has been described but has to be prepared in a different way. It is noteworthy that should the polymerization of acetaldehyde continue beyond the cyclotrimer state isotactic PAA would be obtained.

On the basis of our discovery of the cationic polymerization of acetaldehyde and the stabilization of elastomeric PAA a patent was filed with Dennis Funck as the co-author. (2) It was submitted as a US application, August 18, 1958, and was called: "Thermally

stabilized PAA, the elastomers and the process for the preparation and mixtures "of same" with polycarbonamides." It was issued as a US patent with a Canadian equivalent patent

This particular invention related to the process for polymerizing acetaldehyde in solution and stabilizing the resultant elastomeric polymer of acetaldehyde and to the novel thermally stable elastomers. The patent described the thermal stability of less than 3% per minute at 111°C and described the number average molecular weight of 100,000 to 3 million. The polymer was capped with acetic anhydride, polyamides were added as thermal stabilizers and aromatic amines particularly AgeRite White as antioxidant.

The patent described that the polymerization was started preferably at -120 in liquid ethylene, and borontrifluoride etherate was used as the initiator. It was described that after a short induction period the reaction vessel filled very rapidly with rubbery PAA. The polymerization was terminated by addition of triethylamine, the temperature was allowed to reach the boiling point of ethylene and ethylene was evaporated. Stabilization was accomplished by end capping with acetic anhydride with some pyridine added. A copolymer of Nylon 6,6-6,10 or a number of other nylon type copolymers, which were soluble in methanol an AgeRite White were added. Elastomeric PAA stabilized that way had a thermal stability of 0.2% a minute at 111°C. The thermal stability at 138°C was 0.35% per minute. A number of variations of the types of Nylon, capping conditions and different additives were also mentioned in patent.

Our acetaldehyde polymerization was much better described in a paper in 1964 (3). Essentially every cationic initiator that has at least a limited solubility in the solution could be used as long as the reaction temperature was kept low. Useful solvents for the polymerizations were ethylene and propylene because of their convenient and low boiling points. Other active initiators included sulfuric acid, acidic sulfate, such as

aluminum sulfate, regular metal chlorides, and transition metal chlorides, although the type of the transition metal was not significant. Protic and Lewis acids were found to be very convenient initiators. The polymerizations when carried out in diethyl ether but also hydrocarbon and chlorocarbon solvents were effective as long as the temperature could be and was very carefully controlled. Otherwise the polymer produced was of low molecular weight and its formation was accompanied by the formation of paraldehyde and to some extent metaldehyde. Typical reaction temperatures described were  $-50^{\circ}\text{C}$  to  $-65^{\circ}\text{C}$  with initiator concentrations of 0.5%.

Some of the differences in stability of PAA samples could be related to the presence of residual initiator fragments in the solution-polymerized PAA. The Letort polymer was usually cleaner as the initiator apparently was left on the surface of the glass. The mechanical properties of these polymers were also described. It was found that the glass transition temperature of the elastomeric PAA was about  $-18^{\circ}\text{C}$ .

A mechanism for this polymerization was proposed in which the monomers were already associated in solution especially in hydrocarbon solvent, which consequently assisted very greatly the polymer formation. The cationic initiation was by addition of the carbenium ion (or the proton) of the initiator to the carbonyl oxygen of the carbonyl group, forming the carboxonium ion. Subsequent further addition of the carbonyl oxygen of the aldehydic carbonyl group to the growing cationic site gave the high molecular weight polymer (4,5)

In one case, out of a run of several hundred grams of acetaldehyde we obtained a small amount, about 0.5 g of insoluble PAA. After careful analysis, we concluded that this polymer sample was crystalline isotactic PAA (5).

*\* The NMR spectrum of polyacetaldehyde and long-range order*

The high resolution  $^1\text{H}$  NMR spectroscopy of elastomeric PAA was initially obtained on a 60 MHz instrument to determine the tacticity. Spectra on acetate capped samples

were obtained at elevated temperature in solution of carbon tetrachloride or tetrachloroethylene. High molecular weight and relatively low molecular weight material. Two triads were detected. The methyl group was located 1.3 ppm and the methine group at about 5 ppm. The triad peaks showed good separation and were compared with the spectrum of paraldehyde. Paraldehyde was known to be the all *cis* cyclic trimer of acetaldehyde. PAA was shown to consist of a 2 to 1 ratio of meso and racemo triads. As a consequence, the polymer was considered to be atactic but had with 60% isotactic dyads. The methine component of the structure of elastomeric PAA was also compared with the trimers of chloral, which can be more readily prepared in all *cis* or in a 2:1 *cis-trans* configuration (7-9).

In 1963 the first superconducting NMR spectrometer, which Varian had constructed for DuPont, became available. It was a 200 Mz instrument and had only a room temperature probe. As a consequence we had limited experimental conditions to obtain optimal results. Our work was done in 1964. I persuaded Ed Brame to overlook our NMR activities. Once completed, I asked him to report our braking results at one of the famous Saturday morning seminars at the Polytechnic Institute of Brooklyn in January 1965.

We had indeed discovered new insights into the PAA problem when elastomeric PAA was subjected to high resolution NMR spectroscopy using the 200 Mz instrument. Ray Ferguson had to be convinced by Ed and me that it was worth looking into PAA problem in new ways and in great details. Do I remember the evenings until midnight that Ray and I spent on the project? Liquid helium had to be refilled every 4 hours and the liquid nitrogen, which kept the helium from explosively evaporating, had to be filled every 8 hours. When we worked on this project, several times I went to the Experimental Station at 2 a.m. "to refill".

May I remind you the NMR study of elastomeric PAA was a bootleg project and have no direct interest to the company. To our surprise, the spectrum of PAA, measured

with the 200 Mz NMR instrument looked significantly different from the spectrum obtained at 60 MHz at higher temperature. The main methyl peak was broad and - with some imagination showed some structure. Ray told me what you are seeing is the effect of the viscosity of the medium. Since we had no way of measuring the PAA probe at higher temperatures, Ray said to just leave it that way. However I insisted that this observation had nothing to do with viscosity effects and we were seeing higher order in the spectrum of the polymer structure. In other words, instead of triads we are probably see pentads (Figure 7).

I would like to point out that we were in the pioneering phase, the "stone age" of NMR spectroscopy of polymers. The 200 MHz spectrum could not be decoupled and also showed the spinning side bands. Ray said that he had a so-called curve resolver and that we could possibly analyze the PAA spectrum with the aid of the then newly developed DuPont curve resolver. Indeed, the analysis showed that there are 7 pairs of lines that contributed to NMR spectrum and the spectrum could be reconstituted. Two pairs of

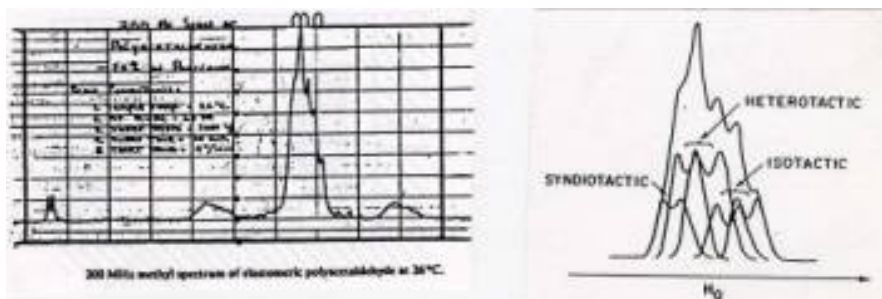


Figure 7: 200 MHz NMR Spectrum of Polyacetaldehyde

peaks could be assigned to isotactic methyl groups, two to heterotactic methyl groups and one to syndiotactic methyl groups. The two pairs related to the isotactic methyl groups were on the high part of the complex peak and one pair related to the syndiotactic methyl group peak at the low field side. The three remaining pairs due to heterotactic groups were in intermediate positions. The area measurements showed that 14 % of the complex patterns could be attributed to syndiotactic methyl groups, 62 % to heterotactic methyl groups and finally 24% to isotactic methyl groups. We stated

that the area measurements were attributed to three different kinds of triads in the polymers. The appearance of two sets of pairs of the isotactic and heterotactic methyl groups demanded that some secondary effects must be occurring as well. The indication was that methyl groups further removed than adjacent methyl groups were effecting the methyl groups under examination (pentads).

On the basis of on this NMR analysis, PAA was nearly a random polymer. Still, the polymerization favored the structure of isotactic grouping over that of syndiotactic. This result showed for the first time that longer range, pentads could be detected if the high-resolution instrument was available and the measurement conditions were done appropriately.

While we were working on the cationic polymerization of PAA and on the interpretation of the NMR spectrum, we also worked on the anionic polymerization, the stereospecific polymerization of acetaldehyde and the polymerization and stereospecific polymerization of higher aliphatic aldehyde.

Unfortunately after the patents were filed in the middle of 1959 it became clear that elastomeric PAA was not going to be the next product in the acetal line. As a consequence, in July 1959 I was assigned to develop first a printing ink and then to develop a painting technique for Delrin.

## **b. Isotactic Polyacetaldehyde**

For the polymerization of acetaldehyde to elastomeric PAA we had only used cationic initiators

We had been thinking that acetaldehyde with its methyl substitution on carbonyl carbon had similarities to propylene. Acetaldehyde has an oxygen atom in place of the methylene group in propylene and should be capable of producing a substituted POM

and should exist in a stereospecific form, isotactic PAA, if the right polymerization conditions could be found. We knew that the polymerization had to be carried out at low temperatures. Today it looks obvious but then isotactic polymers were in their infancy, isotactic polypropylene had just been discovered and Isotactic poly(propylene oxide) had been described in a patent. A few months before we started to think about stereospecificity in aldehyde polymerization. In both cases the propylene and the propylene oxide polymerization the stereospecific polymerization to isotactic polymers were conducted with coordination initiators of the transition metal type

By December 1957 I was ready to look into anionic initiation for the polymerization of acetaldehyde. From my student days I had an attachment to LAH and I selected LAH as the first initiator. Since there was no danger for cyclotrimerization with anionic initiators, I conducted the polymerization in diethyl ether at -65C on January 6, 1958. The LAH (3 mg) that I used was not completely ether soluble, but I obtained about 0.5 g of a product, presumably a polymer of acetaldehyde. It was different from anything I had seen previously when I used cationic initiators. It was a solid, *and* was stable at room temperature [61-64]. I set it aside and did not immediately investigate it further. I thought it was a mixture of some aluminum compounds. Still, the product was 100 times as much as the LAH I but only about 10% of the acetaldehyde that I started with. I did not believe that I had the isotactic, insoluble PAA on hand and tried to "hide" my "failure." After a couple of weeks, when I realized that the polymer was quite stable, I felt that I should characterize the material (9,10).

By then I had also isolated from a large run of an acetaldehyde polymerization with borontrifluoride etherate, in about 0.3 % yield, an insoluble fraction, which I had, the feeling, was PAA (Figure 8).



## Figure 8: Calculated Structure of Isotactic Polyacetaldehyde

I had started my anionic acetaldehyde polymerizations with a common anionic initiator, not with coordination initiators. Everybody involved in polymerizations, believed that it was essential for the preparation of stereoregular polyolefins, particularly of isotactic polypropylene to use coordination initiators, of the transition metal type. This is true. The reaction temperature had to be low. However, it is not as significant as the reaction temperature at the cationic polymerization of acetaldehyde and other aldehydes because in this case the trimerization to paraldehyde cannot occur (under anionic conditions). The rate of polymerization was also studied at -75 and it was found that the reaction was substantially complete at 10 minutes and 2/3 complete in 5 minutes.

The question was how could we characterize these samples? I remembered from my student days, that one of the techniques used to characterize aldehydes and ketones was their transformation into 2,4-dinitrohydrazones. In 58,' there was some IR but no NMR was available. To obtain an x-ray scan was very complicated and time demanding. I remembered this 2,4-dinitrophenylhydrazone technique and decided to try it for the characterization of our acetaldehyde polymers. I first tried elastomeric PAA. As expected the strong acid medium 2,4-dinitrophenylhydrazine solution degraded the PAA. At the same time, the "freed" acetaldehyde reacted with the 2,4-dinitrophenylhydrazine reagent.

We carried out the 2,4-dinitrophenylhydrazone technique successfully on several samples of our elastomeric PAA. We also checked the insoluble sample from the borontrifluoride etherate polymerization and the sample from the LAH initiated polymerization. They all gave in nearly quantitative yield the acetaldehyde 2,4-dinitrophenylhydrazone. These experiments proved the basic structure of the polymers as polyacetals and our specific polymers as PAAs. They also demonstrated the 2,4-dinitrophenylhydrazone technique as a convenient method for analyzing polyaldehyde

structures as polyacetals. We also characterized polyformaldehyde by this technique, and later, polymers of higher aliphatic aldehydes.

A frantic period of work followed because we had discovered a general method of aldehyde polymerization and also a method to synthesize a new type of stereoregular polymer, i.e., stereoregular polyacetals. We were going in several directions at the same time: a.) Catalyst search, b.) Polymer stabilization and c.) Polymerization of higher aldehydes (11-16)

In the catalyst search, we focused on alkali alkyls and alkoxides. The argument was that, after the addition of the first monomer unit, the propagating species became an alkoxide. Bases that were too strong were subject to side reaction on the monomer. Important was the "solubility" of the initiator in the reaction medium, the solution of the aldehyde in the inert solvent, hydrocarbons, cyclohydrocarbons or olefins. Alkoxides with relatively "or-ganic" groups were often more effective. In the next few months we also explored a number of aldehydes for their polymerizability. Aromatic aldehyde such as benzaldehyde and olefinic aldehydes such as acrolein and methacrolein did not polymerize, but phenylacetaldehyde did.

Our initial thrust was the characterization of isotactic PAA. Isotactic PAA was acetate and alkyl end-capped (17-19). The solution viscosity, and the infrared spectrum was measured, and the m.p. was determined and found to be 165°C. A very useful technique to characterize the isotactic polyaldehydes was their gel point. I was determined as a function of concentration and the type of the solvent.

A flurry of activities commenced between January and May 1958. It culminated in a number of patent applications, the first one issued in July 9, 1959 and it was Belgium patent, which described crystalline polyaldehydes. It was followed by the French patent in August of 1959. The U.S. patent had to be refiled several times and the patent did not issue until 1965. The patent applications were fairly complicated because of the different patent laws in the different countries and involved also the separated patents

for polymerization and stabilization for example in Belgium and in Britain.

The fundamentals of the basic patent relates to novel polymers of aldehydes and more particularly it relates to crystalline polyaldehydes having an acetal chain structure and having 2 to 10 carbon atoms per monomer unit. The objective of this invention was to provide novel crystalline polymers of aldehydes having 2 to 10 carbon atoms in the molecule and the process of preparing these novel polyaldehydes. Basically the polymers were prepared by maintaining a reaction mixture of an inert liquid organic solvent. The aldehyde to be polymerized and the catalytic amount of an alkali metal alcoholate at a temperature of  $-30^{\circ}\text{C}$  to  $-110^{\circ}\text{C}$  until the aldehyde polymerizes. Described in the patents was the polymerization of acetaldehyde, the polymerization of propionaldehyde, n-butyraldehyde, isobutyraldehyde and their polymers of a molecular weight of at least 20,000. The patent also described the end capping of the polymers obtained with acetic anhydride for acetate capping and with trimethylorthoformate and other orthoformates for alkyl capping. It describes stabilized products with a degradation temperature of about 0.01% per minute at  $138^{\circ}\text{C}$  and about a 0.1% per minute at  $222^{\circ}\text{C}$ .

Very soon it became clear that this polymer would not lead to a commercial product. Stability isotactic polyacetaldehyde was not sufficient to compete with polypropylene, the obvious competitor and that the stabilization would be extremely difficult, and very likely, the window of fabrication as compared to stabilization was believed to be out of the question. As a consequence, shortly after the first patent had issued we decided to publish in the open literature

Our publication on the polymerization of isotactic polyacetaldehyde was delayed and in fact it was rejected by JACS because some Manager of the Textile Fibers Department of the Du Pont Company had decided we could not disclose the melting points of the polymers at this time. We were able to publish a short note in August of 1960 in the now classic paper in the Journal of Polymer Science. At about the same time two notes

appeared in *Die Makromolekulare Chemie*, describing isotactic PAA, one from the Natta and one from the Furukawa group. Their work was done one and a half years later than ours. By the time I was allowed to publish the polymerization of higher aldehydes in 1964, DuPont had decided not to pursue the work on the polymerization of higher aliphatic aldehydes any longer but tried to commercialize polychloral. Natta had received the Nobel Prize for polypropylene,

I could now disclose the melting points of the isotactic polyaldehydes and compare them with those of the corresponding polyolefins. The polymers of higher aldehydes, the crystalline isotactic polymers were of no commercial interest any longer.

### **c. Polymerization of Higher Aliphatic Aldehydes**

As was mentioned in the last section, polymerization of aliphatic aldehydes with more than 2 C-atoms was also studied and the results were included in the comprehensive patent of the polymerization of higher aliphatic aldehydes. The most common aldehyde is n-butyraldehyde. Consequently, it was first studied with cationic initiators. With stannic chloride as the initiator completely amorphous PBA was obtained with a  $T_g$  at room temperature. Other cationic initiators gave PBA with sometimes significant isotactic fractions.

The polymerization of a number of "aliphatic" aldehydes to isotactic polymers was undertaken. Many of the lower aldehydes were studied at DuPont, the higher ones at the University of Massachusetts: they included: polypropionaldehyde, poly(n-butyraldehyde), poly(isobutyraldehyde), poly(n-valeraldehyde), poly(n-hexaldehyde), poly(n-heptaldehyde), poly(n-octaldehyde), poly(n-nonaldehyde), poly(n-decaldehyde), poly(n-undecaldehyde) poly(n-dodecanal), poly(phenylacetaldehyde) and poly(3-ethoxypropionaldehyde), but later on also poly(methylglycidate).

The polymerization behavior of aldehydes can be categorized into 3 groups.

Aldehydes, when exposed to water a.) Form oligomers (formaldehyde, methyl glycidate) b.) Form hydrates (haloaldehydes, i.e. chloral) c.) Do not significantly interact with water. In this section we are only involved with category c.).

The polymerization of higher aldehydes was accomplished with a number of alkoxides in aliphatic and aromatic solvents. The ultimate favored combination became lithium tert-butoxide (LTB) in methylcyclohexane. LTB can be purified by sublimations soluble in methylcyclohexane, which melts at  $-125^{\circ}\text{C}$ . Polymerizations resulted in the preparation of isotactic polymers. They were end-capped, the melting points, gel points, infrared spectra and solution viscosities were determined and the 2,4-dinitrophenylhydrazones were prepared.

The polymerization must be carried out at  $-60^{\circ}\text{C}$ . At lower temperatures, n-heptaldehyde crystallizes and the polymerization does not proceed. This phenomena became an increasingly more important problem as the length of the paraffinic side chain of the aliphatic polyaldehyde increased.

Polyaldehydes made with anionic initiators always have one end, the initiating end group from the alkoxy initiator. The other end group is a hydroxy group or a dormant alkoxy end group. Capping with acetic anhydride is difficult because such end groups are secondary hemiacetals. These ends are imbedded and covered with a hydrophobic matrix, which prevents the acetic anhydride from reaching the reaction site. Once fully stabilized, such polymers, as poly(n-heptaldehyde) are resistant to autoxidation because the oxygen cannot penetrate the paraffinic matrix.

Initially the following polyaldehydes were prepared and studied: Polypropionaldehyde ((iPPA), m.p.= $185^{\circ}\text{C}$ , poly(isobutyraldehydes) (iPIBA), m.p.> $260^{\circ}\text{C}$ , poly(n-valeraldehyde). The latter has two melting transitions, one at  $155^{\circ}\text{C}$  and the other at  $85^{\circ}\text{C}$ . Poly(n-hexaldehyde) (iPHxA) also had two transitions, the higher melting one at  $150^{\circ}\text{C}$  and the lower at  $75^{\circ}\text{C}$ . If measured by DSC at least two transitions were found between  $87$  and  $90^{\circ}\text{C}$  (24,25).

Poly(n-butyraldehyde) (PBA), m.p.=225°C was potentially the most important polyaldehyde. It is readily available, had the right price, a desirable boiling point for purification and the isotactic polymer had a melting point similar to Nylon 6. It also had as a disadvantage a rather unpleasant odor. PBA is readily prepared using LBA as the initiator. It precipitates during the polymerization as a gel, which has selectively imbibed much of the monomer.

Consequently we took this behavior into account for our polymerization mechanism. We proposed a mechanism of higher aldehyde polymerization, especially the polymerization that leads to isotactic polymers by anionic polymerization. The mechanism suggested that the stereoregulation during the polymer formation led the growing polymer chain directly and immediately into isotactic configuration and helical conformation. Stereoregularity in the polymer increased with increased bulkiness of the side chain. It also proposed that at least 2 monomer molecules were involved in the transition state (31,32).

As in POM and PAA, higher polyaldehydes also have to be thermally stabilized. Complete end capping is the first step for a stable polyaldehyde. It is also the basis of stabilization against autoxidation. Sensitivity against autoxidation is the Achilles heel of polyaldehydes including POM. I have always believed that autoxidation is aided by the presence of monomeric formaldehyde which remains absorbed on the polymer. This monomer is readily autoxidized and the peroxide assists in the further autoxidation of the polymer. This autoxidative instability becomes more of a problem when the monomeric aldehyde is not very volatile and it and the oxidation products remain on the polymer. POM has a carbon hydrogen bond, which is sensitive to hydrogen abstraction because it is flanked by two ether oxygen atoms. With higher polyaldehydes the aliphatic side groups enhance the abstractability of the tertiary hydrogen atom (Figure 9). Unrefined acetate capped PBA when left at room temperature depolymerized completely over night when left in a closed container in air.

Interestingly enough, the sensitivity of higher polyaldehyde such as iPHpA decreases. Most likely the oxygen cannot penetrate the crystalline paraffin matrix of the side chain crystallization. I kept a molded sample of iPHpA for 40 years in a closed container in my desk. There was a trace of odor noticeable and n-heptaldehyde was easily detected.

While n-butyraldehyde has an unpleasant odor, n-heptaldehyde has an odor of roses. It and phenylacetaldehyde are major ingredients in the perfume industry. n-Heptaldehyde is readily available and became the main focus of our polyaldehyde work at the University of Massachusetts. The polymerization laws follow those of the general polymerization of higher aldehydes.

IPHpA had one transition at 147°C, the melting of the main chain. A lower transition of "paraffin melting" consisting of three melting transitions between 78°C and 101°C was ascribed to the "paraffin melting" of the n-hexyl side groups. Their position is slightly changeable and depends of the thermal history of the sample and annealing (26,27).

The anionic polymer of n-heptaldehyde was studied by x-ray diffraction and by other techniques, such as DSC and TGA (Figure 10). The polymer degraded between 150°C and 170°C even though it was carefully acetate capped. The NMR spectrum was measured at a 300 MHz instrument and showed a single sharp peak in the acetal region indicative of the isotactic nature of the polymer. The crystal structure of isotactic iPHpA showed a c-axis of 4.52 Å. The tetragonal units contain 16 monomer units and the polymer has a calculated density of 0.95 g/cc. Crystalline copolymers of n-heptaldehyde and n-butyraldehyde are compatible over the entire composition range.

Monomer	Melting point, °C.	
	Polyaldehyde (X = O)	Polyolefin (X = CH <sub>2</sub> )
CH <sub>2</sub> CH=X	165 <sup>a</sup>	165
CH <sub>2</sub> CH <sub>2</sub> CH=X	185 <sup>b</sup>	125
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH=X	225 <sup>b</sup>	75
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=X	155 (85) <sup>c</sup>	None
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=X	150 (75) <sup>c</sup>	None
CH <sub>2</sub> (CH <sub>2</sub> ) <sub>5</sub> CH=X	35	None
(CH <sub>2</sub> ) <sub>6</sub> CHCH=X	>260 (dec.)	310
HCH=X <sup>a</sup>	178	137

Figure 9: Isotactic Polyaldehydes, Melting Points

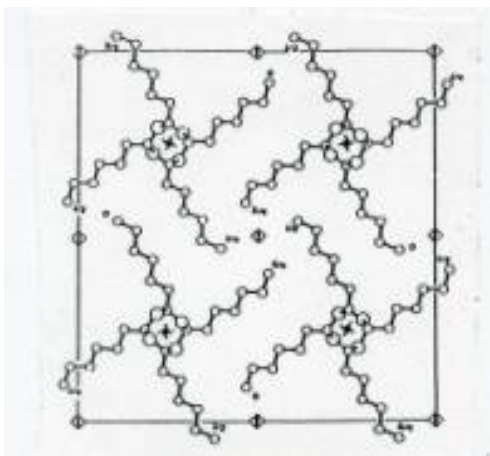


Figure 10: Structure of Isotactic Poly(n-heptaldehyde)

We have also studied other polyaldehydes: Poly(n-octaldehyde) had only the lower melting transition with 3 peaks between 49°C and 61°C. Poly(n-nonaldehyde) showed 3 transitions between 46 and 72°C (28). The m.p. of the trimer is 36°C. Poly(n-decaldehyde) also had three transitions between 58°C and 62°C, and the trimer a m.p. of 46°C (29). Poly(n-undecaldehyde) also shows three transitions between 57°C and 61°C (30), with the trimer melting at 55°C. Poly(n-dodecaldehyde) had several transitions between 55°C and 61°C.

I had recognized that when polyaldehydes had a carbon side chain of four carbon atoms, 3 methylene groups and a terminal methyl group, iPVA, the polymer had a double melting point. The double melting point was probably caused by the melting of the side chain, separate from the main chain. This phenomena was later found to be correct and I will devote a section on polymer "side chain crystallization". On the other hand, poly(n-octaldehyde) has only one melting point, the melting point of the crystalline paraffin side group. The helical backbone chain is not part of the crystal

lattice of the polymer any longer but is imbedded in the paraffin matrix of the polymer.

The crystallinity of the isotactic polymers with side chain crystallization depended very much on the history of the polymer. Mechanical treatment, extrusion above the first transition range effected the backbone orientation but also the crystallization of the side groups. Extrusion of the higher members of the aliphatic polyaldehydes was possible at modest temperature. It was conveniently done above the side chain melting point.

Side chain crystallinity had been demonstrated previously in isotactic or atactic poly (alpha)-olefins, substituted polybutadienes, polyacrylates and polymethacrylates, and polyvinyl esters) as well as poly(N-n-alkylacrylamides) with linear aliphatic side groups but a side chain length of 10 carbon atoms was necessary to notice side chain crystallization. Higher aliphatic polyaldehydes, isotactic polyaldehydes with their polyacetal structure was found to be a good subject for the studies of side chain crystallization isotactic aliphatic polyaldehydes. Isotactic aliphatic polyaldehydes with short chains are highly crystalline because of the helical structure of the backbone chain which is efficiently packed. In the case of crystalline isotactic polyaldehydes with moderate ( $C_4$  side chain) to longer aliphatic side chains high crystallinity may have a contribution from the crystallization of the POM backbone, the paraffinic side chain or both. It was found that in the medium range of isotactic polyaldehyde side chain crystallization occurs, but above ( $C_8$ ) isotactic poly(n-octaldehyde) only one melting point that of the side chain was observed. It was possible to calculate from the heat of crystallization that indeed 3 methylene groups are necessary for the side chain crystallization to occur.

Over the years we have published a number of articles on aldehyde polymerization and illuminated the subject from different angles (33-38)

## d. Cyclic Oligomers of Aldehydes

Formaldehyde forms a cyclic trimer, TO, and a cyclic tetramer when treated with specific acids under the proper reaction conditions. TO is used commercially on a large scale for the preparation of POM copolymers. The cyclic tetramer, is more difficult to prepare, but polymerizes more readily. TO when prepared is always accompanied by POM of low molecular weight. The  $\Delta H$  value for the ring opening polymerization of TO is  $-4 \text{ kcal/mole}$ , which means that it can be readily polymerized to POM.

When higher aliphatic aldehydes are treated with Lewis or protic acids at room temperature they form cyclic trimers. The cyclization of acetaldehyde to paraldehyde has been particularly well studied. The normally obtained paraldehyde is the all-*cis* isomer which exists in the equatorial conformation (eee). The *trans* isomer [eea] has also been synthesized, but by an indirect method. The cyclic tetramer of acetaldehyde, metaldehyde can exist in 4 distinct stereoisomers. The *cis* (eeee) isomer, m.p.= $246^\circ\text{C}$  is the most common form, another isomer of metaldehyde with a *cis, trans, cis, trans* linkages, m.p.= $46^\circ\text{C}$  has also been reported. The 2 isomers of chloral the all *cis* (eee) and the *trans* (eea) isomer are known and we have characterized them by NMR. They cannot be synthesized by acid catalyzed trimerization by an indirect way.

Paraldehyde is prepared above the  $T_c$  of acetaldehyde polymerization. The  $T_c$  of cyclotrimerization of AA is above  $100^\circ\text{C}$ . Unlike TO, the polymerization of paraldehyde or any other cyclic aldehyde trimer or tetramer, has never been achieved. The free energy of polymerization of cyclic trimers of higher aldehydes is believed to be positive.

As the chain length of the aldehyde increases, the trimerization becomes more difficult and, although some trimers of higher aliphatic aldehydes have been prepared, few specific data are available. As the aliphatic chain length increases, the predominance of the carbonyl group decreases.

During the course of our investigations on the preparation of crystalline polyaldehydes, we recognized that acetaldehyde polymerization can only be used as a typical example of an aldehyde polymerization for aldehydes with very short chains. These facts have been recognized also for the cyclotrimerization of the higher members of the aliphatic aldehydes (39).

The polyaldehyde with  $C_4$  to  $C_8$  carbon chains have a "double melting point " one that is associated with the polyoxymethylene backbone chain and one associated with the n-alkyl chains. As the length of the side groups increased, the polymer becomes more and more comb-like and "paraffinic."

In acetaldehyde polymerization initiated with cationic initiators, the cyclic trimer, paraldehyde, is always present. It has never been observed as an impurity in anionic aldehyde polymerization. Cyclic aldehyde trimers can always be present when the polymerizations of higher aliphatic aldehydes are conducted under cationic conditions or under conditions whose anionic mechanism is not beyond question, and which may possibly proceed by a cationic mechanism. Trimers formed along with polymer during polymerization could co-crystallize with the polymer but might be very difficult to detect if the polymer is of low molecular weight and, in fact, could be very difficult to differentiate from the polyaldehyde, particularly when the alkyl group increases in length. We have also prepared several cyclic trimers either in ether solution with antimony pentachloride as catalyst or in the bulk with sulfuric acid. The cyclic trimers of n-nonanaldehyde, m.p.=36°C, n-decaldehyde, m.p.=46°C, n-undecaldehyde, m.p.=55°C and n-dodecaldehyde, m.p.=61°C. were prepared and characterized as the all *cis* (eee) isomers. We also investigated the side-chain crystallization behavior of the cyclic trimers and compared them with the crystallization behavior of the corresponding isotactic polyaldehydes.

From the company's point of view, the pursuit of the project on the polymers of higher aliphatic aldehydes could no longer justified. The  $T_c$  of the polymers were too. As

secondary hemiacetals of the more desirable isotactic polymers, they could not be efficiently end capped. The polymers could not be stabilized against autoxidation, because the electron donating aliphatic side group rendered the acetalic hydrogen atom oxidatively much more sensitive than polyformaldehyde. Consequently I abandoned the polyaldehyde work when DuPont quit but completed some unfinished work in academia.

### c. Delrin Projects

It was in the summer of 1959 when the project of polymerization of higher aliphatic polyaldehydes was in the state of patent filing. We had done the basic work on the filing of the US patents and had to decide in what other countries we should file and which way. Some work needed to be done to support the filing procedure. Other pressures also mounted in the research arm of the Delrin group. The Delrin plant was being built in Parkersburg, WV, marketing and sales were evaluating the application possibilities and weaknesses in the product properties had to be eliminated.

***Silk screening ink:*** In July I was asked to evaluate the possibility of silk screening for Delrin. Sales found a potential application for Delrin. The Avon Company was considering the introduction of a new style bottle for one of their products, a lotion or a spray. Avon considered using a plastics bottle. When we saw the design of the bottle we were told and soon recognized the problems that we had to face. We were not given much time and I was depressed because I never had to face a time-limited problem where I could foresee failure. I had Jake Mansure, working for me as technician. When I told him my concern, he said: "Do not worry, we will solve the problem in some way."

Within a week we learned what printing and silk screening inks were and what silk screening was. We obtained a few used silk screens and began to practice applying silk screening ink via a silk screen on a Delrin surface. We learned how important

adhesion was and how to test the adhesion of the silk screening ink. Normally silk screening had to be baked to be fixed on the surface.

Delrin has a smooth surface and few materials adhere to it. In our assignment no pretreatment was allowed. We ordered over a dozen commercially available silkscreen inks and applied them. They were all ineffective on Delrin, the scotch test which was the test procedure, failed in all cases.

We decided to start "synthesizing" our own silk screening ink from scratch. The silk screening ink consists of a "vehicle", pigments and other additives. We ordered a number of such vehicles and a few of them adhered quite well to a Delrin surface. On addition of the pigment that was needed for the right color, the adhesion was lost. I kept ordering more and more of the additives, changed the combinations and Jake applied the new combinations and tested the adhesion with the "scotch tape" test.

I was concerned that I had to face the inevitable failure. However, after the end of the 6th week, we had produced a composition that was an attractive and satisfactory silk screening ink. It was black as they had required and Jake and I were proud of our achievement, which was done, in record time.

We presented our results to the management and found out that a glossy black ink was required. Within the next week we found out that the silk screening ink of black color, which we had successfully synthesized, should have been glossy not satin. Furthermore it was not needed any longer because Avon had already decided to "hot stamp" the lavender colored bottle in gold color. Silk screening was only a back up if an effective silk screening ink could be found immediately and if hot stamping was a failure.

***Antioxidants and thermal stabilizers:*** As the commercial production of Delrin approached, the efforts to bring the best possible product on the market were

intensified. Everybody in the Delrin group was invited to try out his own ideas to improve the product, acetate capped POM. Stabilizers were believed to function in two ways: During the melt fabrication (Extrusion and injection molding) and during use (long term aging). Stabilizers for Delrin consisted of an antioxidant, Santa White Powder from Monsanto, a phenol, di-tert-butylated in the two ortho-positions and a thermal stabilizer, Nylon 6,10. I decided to try to improve the system. Many compounds had been tried,

Delrin was POM with hydroxy end groups (with some formate ends), acetate end capped by vapor capping, which gave a product that had 98 plus percent of acetate end groups with small amounts of monomer formaldehyde absorbed on the polymer. The antioxidant was needed to prevent autoxidation of the polymer chain and/or of the absorbed monomer. The thermal stabilizer was believed to be needed to scavenge the monomer liberated during the melt fabrication.

We tackled the problem of incorporating stabilizers into Delrin. I say we because Jake Mansure who was still my technician was an expert in injection molding, extrusion, handling the rubber mill, and handling the people that were associated with injection molding and extrusion equipment. Jake always handled the rubber mill himself. Jake would prepare the compositions at the 6 inch rubber mill which was steam heated to make sure that there was no over heating. We also had electrically heated rubber mills in the extrusion area. Their temperature could not be too accurately controlled and had the tendency to overheat in spots. Heat fluctuations, which could have caused degradation of the sensitive POM.

It was traditional to prepare the composition from virgin fluff of Delrin obtained from the plant specially packaged for our investigations. We must have made hundreds of compositions. None of them were particularly good over the ones that were already known. Some of the compositions were marginally better but they had some flaws such as the development of color.

We had made two Delrin compositions, which had outstanding thermal behavior: an antioxidant composition and a general new composition. First a little bit of background. When I had been teaching in the quantitative lab at the University of Vienna, we were teaching titrations as part of the laboratory course. At that time a booklet authored by Kasimir Fajans had been published, and we used it, that described titrations with "redox indicators". You might remember it was the same Fajans whom I know well, later at the University of Michigan. The most popular redox indicator was diphenylbenzidine, which could also be called 4,4'-bisdiaminobiphenyl. Aromatic amines, especially naphthylamines, were used effectively for rubber composition for tires. Compositions with such aromatic amines as stabilizers formed, on autoxidation, deep blue and purple colors, which does not matter in black tires.

In Delrin any color formation was unacceptable. We found that diphenylbenzidine even at 0.01% rather than the regularly used SantaWhite Powder at 0.2%, was superior. It did not even need a thermal stabilizer. During the incorporation on the rubber mill there was little color formation, using diphenylbenzidine from the bottle, not a specially purified product. Diphenylbenzidine had been described as readily prepared by oxidation of diphenylamine and was available at an acceptable price. The thermal stability of the Delrin composition was excellent. The composition and diphenylbenzidine had one flaw. The compound had a name derived from benzidine, which was at that time found to be a carcinogen. There was no report that diphenylbenzidine was a carcinogen, but the name alone eliminated the compound for further consideration. We did not even apply for a patent. Who knows what would have happened if we had described diphenylbenzidine as a derivative of biphenyl?

Nylon 6,10 was used as the thermal stabilizer for Delrin. It was believed that it perhaps scavenged free formaldehyde monomer. I reasoned that possibly some other reactive compounds, oligomers or polymers could also be effective. I decided on poly (butadiene epoxide) as a potential stabilizer for Delrin. We purchased and received poly

(butadiene epoxide) as a very viscous, slightly yellowish oil. When the compositions with Delrin were prepared on the rubber mill sheets were obtained that were ivory in color. Several compositions were made with various amounts of poly(butadiene epoxide), which were highly thermally stable and had a peculiar flow behavior. We speculated that poly(butadiene epoxide) probably capped in the unstable portion of POM probably also picked up the free formaldehyde and other impurities. We believed that poly(butadiene epoxide) may have produced a polymer with long POM branches.

Unfortunately, when the work was done it was not acceptable to add viscous additives to Delrin powder even though they had unusual properties. Only powders were allowed to be added for the purpose of subsequent extrusion or injection molding. As before the compositions were not further evaluated, nor were patents filed.

***Pigmented and metallized Delrin compositions:*** Later in the year a new opportunity opened for an application of Delrin. . The Chrysler Corporation was designing a new model for one of their 1961 cars and considered using Delrin as the material for the instrument panel. Three colors were considered: black, and a green or blue metallic composition. We considered two basic approaches: color matching with pigmented compositions and painting.

The black color could easily be color matched. The green and blue were more difficult but could be achieved. It consisted of combining the pigment Monastral green with aluminum flakes and Monastral blue with aluminum flakes. Even these two compositions caused some problems because the pigments and the aluminum flakes decreased the thermal stability of the polymer melt during injection molding. The color-matched injection molded Chrysler instrument panel looked initially very good but it became soon clear that exact matching especially in the blue and green metallic colors was impossible and not reproducible. Furthermore Delrin and only Delrin was on the surface. We had known that Delrin could not be considered under the windshield for long-term use. One of the requirements of a successful instrument panel was not only

the mechanical properties but also a desirable photo oxidative stability of the surface of the cluster for years without cracking or whitening.

The color matching of Delrin metallic blue and green compositions for the Chrysler panel was abandoned and we concentrated on the painting of the panel.

Before we were involved in this endeavor we decided to use our experience in selecting the proper aluminum flakes for the metallized green and blue compositions. We decided to develop a "silver" and "gold" pigmented composition for Delrin. It required to select the metal flakes with the right size and shape and surface properties. Aluminum and bronzes have metal oxide surfaces based on their way of fabrication or preparation for their intended end use. Knowing this we simply decided to try out a number of commercially available metal flakes from various manufacturers and hope for the best. We settled on an aluminum flake from the Reynolds Company. It provided the best thermal stability of the Delrin composition. We also selected a bronze composition. In both cases we decided that compositions of 5% of the metal powder gave the acceptable color at the retention of the mechanical properties.

I still remember when we prepared the compositions from the Delrin fluff, this time with the commercially used stabilizers added and the metal flakes. As the molten composition came out of the extruder, the molten strands were beautiful, silvery and gold, but as they solidified they became gray and yellowish dull looking. It was depressing to find that the beautiful nicely oriented metal flakes in the transparent Delrin melt turned into insignificant dull colors. What we did not recognize was, that Delrin crystallized and during this process the metal flakes twisted, wrinkled and turned giving the dull appearance -- but in 1960 the understanding of polymer crystallization was in its infancy.

When the metal flakes were incorporated into a colorless paint base and applied by brushing, where the flakes were oriented, - and the base coat was amorphous, the

expected brilliant metallic colors prevailed.

I should mention that by that time William Truett had become my lab partner and he worked on black Delrin compositions. My interaction with him and the discussion of our projects became invaluable for me.

Still, while we had made two metallic compositions that were used commercially, the beauty of the product was not what we expected. On a personal note: When the silk screen ink and the project of the design and preparation of the Delrin aluminum and bronze composition was finished, some "vehicle" and the aluminum and bronze powder was left. Rather than disposing of it I took some of it home and prepared a silver paint from the aluminum flakes and a gold paint from the bronze flakes and the vehicle. For Christmas I painted several dozen of walnuts, with a toothpick at the end. We have used these golden and silver walnuts for the last 40 years as Christmas tree decoration and a memory for the two Delrin projects.

***Painting of Delrin:*** We were struggling to color match the three Chrysler colors by creating pigmented Delrin compositions, an effort that was predictably doomed from the beginning, but it had to be done. Our management had already agreed with Chrysler that the instrument panel had to be painted and it was my place to find a way to make the Chrysler paints adhere to the Delrin panel. Chrysler had already specified exactly their color and paint composition and it was not sensible to even think of color matching a pigmented composition, rather than painting the Chrysler Instrument panel. We therefore reoriented our efforts and started to try to paint the Delrin panel with Chrysler paints.

Normal paints did not adhere to Delrin surfaces when subjected to the scotch tape test. The polymer POM did not allow good adhesion. In addition when the polymer is injection molded into the final object a mold release agent is used, which at that time was zinc stearate, which provided a surface coating for Delrin. During our development

of workable silk screening ink, a printing ink, we had noticed that an extra additive, namely aluminum stearate played an essential role for the adhesion of the printing ink to Delrin. But any addition to the Chrysler paint was not allowed.

It became very clear that the surface of Delrin had to be abraded or etched in some way for the paint to stick. Initially chemical etching of the Delrin surface was also not permitted

As a consequence, we looked for mechanical abrasion to prepare the Delrin surface for painting. Jake Mansure with his many connections throughout the technical staff of the Polychemicals Department found out that somewhere a water spray apparatus called "Liquamator" existed that sprayed a water suspension of an abrasive. This machine was used to clean equipments that was contaminated with strongly adhering materials. We thought that we might be able to use this abrasion mixture for the preparation of Delrin surfaces for painting. Our first tries showed that "liquamating" was indeed a possible way to prepare Delrin surfaces for painting.

However liquamating was not completely satisfactory because the abrasion of the Delrin surface was not uniform and could not be carried out in an efficient and time effective way on complicated and larger objects around all corners. As a consequence, we looked at some more time-effective ways of etching the surface of Delrin instrument panel for subsequent painting.

We had learned that a machine existed that was used for mechanical abrasion of surfaces of complicated and larger objects. It consisted of an apparatus that "fluidized" small metal particles and exposed an object randomly to this fluidized bed. The velocity of the particles could be controlled, and the etching could be done at room temperature. The type of etching could also be controlled by varying the particle size and the velocity of the particles.

The company, called Wheelabrator that produced this machine was located in South Bend, Indiana, actually in Mishawaka a twin city of South Bend. We made the proper contacts and it was decided we had to test the painting of 16 instrument clusters with all three standard Chrysler colors, black, blue and green because if successful the Polychemicals Department was prepared to buy the machine that at that time cost \$18,000. It was clear that I was not really capable of painting and testing the clusters, work that Jake had done for over a year for me and with me. The question was now how to get Jake to go with me to Indiana. Although the Experimental Station was not on the union rule, it was very tricky to get a non-salaried employee to travel on company business. I finally made a personal deal with the laboratory director and with Jake. Jake promised that he would not ask for overtime and that he would wear a suit because it was perhaps necessary to have lunch with the research director of the 'Wheelabrator' Company. In return we took a First Class Delta Air Line Champaign Flight from Philadelphia to Chicago.

Everything worked out beautifully. We arrived in South Bend Indiana, stayed at the Morris Inn on the Notre Dame campus. Jake was an enthusiastic football follower and was on cloud nine and I was happy that we would find a quick solution to the problem of abrading the Delrin surface for painting. The next day we used the Wheelabrator apparatus for the abrasion in a commercial run. Jake painted in white shirt and tie with an overall and we went for lunch with the research director. Everything looked like "go" but the metal beads of the Wheelabrator apparatus were too abrasive and did not give a even surface on the edges of the instrument panels. Consequently, the Wheelabrator approach for the abrasion of Delrin had to be abandoned, although the trip was highly successful, the paints stuck, to the polyoxymethylene beautifully but the surface, especially at the lip was undesirable.

Jake and I came home as heroes to other technicians because we had broken the company rule and we had also shown that nonexempt employees could be used as equal companions for travel with technical people. The close relationship with Jake

lasted for another year but we saw each other for many years and laughed at our strange situation sitting at the Morris Inn drinking beer and talking about the football strategy of the University of Notre Dame and the adhesion of paint to Delrin.

As I mentioned etching of Delrin surfaces was initially not allowed. I was transferred to the special research group and Walter Brunner took over the preparation of Delrin surfaces. He combined the liquamating and Wheelabrator system into an agitated bath with an abrasive and a controlled amount of acid and called it "satinizing" which was used subsequently for the painting of Delrin pieces.

### **c. Formaldehyde Polymers**

#### *i. Alkyl Capped Polyoxymethylene Based on Direct Formaldehyde Polymerization*

Polyformaldehyde or polyoxymethylene (POM) is commercially produced as homopolymer from formaldehyde and as copolymer from Trioxane and ethylene oxide.

To prepare polymer grade formaldehyde. It must first be transformed into the hemiformal of an alcohol with high boiling point, such as cyclohexanol and 2-ethylhexanol. The hemiacetal is purified and thermally cracked. This polymer grade formaldehyde is now passed into a hydrocarbon (cyclohexane) solution of the catalyst and polymerizes. Since POM is insoluble, it also precipitates. The type of "solvent" for the polymerization determines the "habit" of the crystalline POM. Typical initiators are dialkyldimethyl ammonium acetates. Although the polymerization is formerly initiated by the acetate anion much of the polymerization proceeds via chain transfer reactions. Chain transfer agents are trace amounts of water, alcohols, formic acid and formate esters. Protic chain transfer agents form POM with one hydroxyl end group, water produces two hydroxyl end groups. Formic acid derivatives give formate ends and the alkoxide portion alkyl ends. Unstable end groups must be end capped to increase the thermal stability of the POM to an acceptable and commercially useful level.

Stabilization is commercially carried out either by vapor capping with acetic anhydride at 159°C or by "solution capping" in acetic anhydride. POM is soluble in acetic anhydride near the boiling point. Solution capped POM gives a better product, but is an expensive procedure. Vapor capping leaves a small "unstable" fraction of about 1-2% in the polymer. It consists of formate ends and hydroxy end groups that are not accessible for the vapor capping reaction. One of the POM products marketed by Asahl Chemicals uses polyoxyethylene glycols (POE) as chain transfer agents to form block copolymers of POM and POE.

Acetate capped POM's have good thermal stability but are not very "base stable." This is fairly important, because it prevents the use of basic stabilizers and fillers. Efforts have been undertaken to produce base stable POM by vapor capping with trimethyl-*ortho*-formate or suspension capping with dimethylsulfate. This type of capping had only a limited success and was not commercially feasible. One major problem was that some of the hydroxyl groups were buried in the crystalline polymer structure and were not accessible for a successful capping reaction in the solid state.

During the development of the POM process the polymerization of formaldehyde was not only studied under anhydrous conditions, which was ultimately commercialized, but also in hydroxylic media. The hemiacetal of formaldehyde under supersaturated conditions is the actual monomer. This process guarantees one methyl end in the polymer and polymerization and crystal growth occur simultaneously. Even so, a considerable amount of hydroxy end groups of the POM made by this "methanolic process" were occluded and trimethyl-*ortho*-formate capping was not quantitative.

Burt Anderson and I believed we could solve the problem of preparing alkyl capped POM directly from formaldehyde using trimethyloxonium tetrafluorido borate as the cationic initiator and carrying out the formaldehyde polymerization by a cationic rather than the anionic mechanism normally used for the preparation of POM. We were

inspired to try this route, because Blaine McKusick, the laboratory Director of C R & D had asked us to "check" the preparation of trimethyloxonium tetrafluoroborate, a compound first synthesized by Meerwein and his groups. McKusick was the Editor of Organic Synthesis an ACS publication and he needed to have the "prep" checked before publication. This is how we learned to know the compound, its potential use and how to handle the compound.

Our idea was to carry out the cationic polymerization in inert hydrocarbon solvents and to cap the solid polymer in the suspension immediately with sodium methoxide (Formula 11). We used the laboratory apparatus that was used for formaldehyde polymerizations and improvement in the process that was invented by MacDonald. He was the inventor of the now commercially used process to form high molecular weight POM. Our polymerizations, and we carried out a number of them, proceeded smoothly. Still the POM that we obtained had in the average only a 60% base stable fraction.

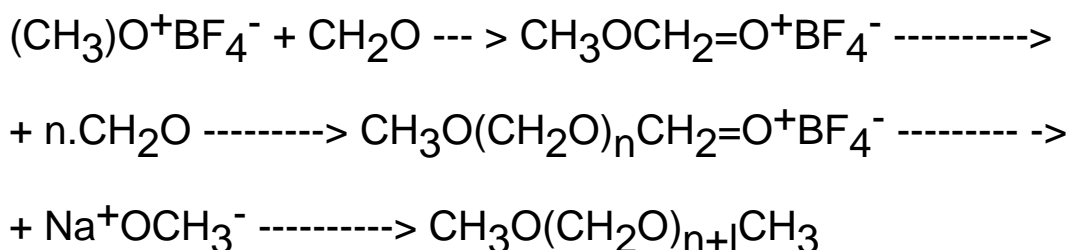


Figure 11: Alkyl Capped Polyoxymethylene

It was clear as anticipated that the polymerization was initiated with the methyl cation of the trimethyl oxonium cation. This provided the base stable end group from the initiation. Capping with sodium methoxide should have given us a polymer that has methyl groups on both ends.

The question was why did we not obtain a high molecular alkyl capped POM with high base stability? The answer seemed to be obvious. We had carried out the capping in suspension. We had no doubt that a quantitative capping reaction would have

happened, if the reaction had been carried out in solution, but POM precipitated from the solution. Even in the case of the commercial vapor phase acetate end capping of anionically prepared POM, was not quantitative. The end capping had to be carried out at 159°C to take advantage of a crystal-to-crystal transition at about 135°C which provides enough mobility in the crystalline POM for the acetic anhydride to penetrate and to actually perform the solid-state reaction.

A similar problem seems to exist in our cationic polymerization of formaldehyde. The polymerization produced a white fluffy solid with some ends of POM cation occluded within the crystal lattice. The polymeric oxonium ions are "ingrown" which means they were are no longer accessible for the reaction with an alkoxide anion to perform the alkyl termination.

In conclusion, the objective of this work was in principle successful, but it did not give commercially feasible alternative. Much more time had to be invested on a full time basis to produce a product. In addition it would have required a combination of knowledge in organic chemistry together with solid-state physics to possibly solve the problem. Even though this work was intriguing it was neither published nor patented.

### *ii. Trioxane and Solid State Polymerization*

Trioxane (TO), correctly called 1,3,5-trioxacyclohexane is the cyclic trimer of formaldehyde. It is a white crystalline compound melting at 60°C, sublimes readily and is soluble in many common solvents. TO is prepared by trimerization of formaldehyde using an acid catalyst. It can be considered a source of formaldehyde and a mean of purifying formaldehyde (similar to the hemiacetal purification mentioned earlier). Acid catalysts will polymerize TO POM by ring opening polymerization. Melt polymerization with Lewis acids especially with borontrifluoride to prepare POM copolymers commercially.

The first polymerization of TO was accomplished by Hammock and Boiree in 1923. They believed it was a radical polymerization. In the mid 30's Kohlschuetter studied the sublimation of TO and recognized that TO frequently left a residue of POM on sublimation. In the late 40's the now well-known Schneider patent described the polymerization of TO with many protic or Lewis acids.

By the late 50's POM based on copolymers of TO with EO were commercialized. They now constitute about 60% of the entire POM market, which is about 200.000 tons. DuPont had decided that POM's based on TO be not commercially feasible and discouraged any activity on TO polymerization in the company even on a "boot legging" basis.

Some indication existed that TO also polymerized in the solid state. Still, I was interested to have answers to two questions? Why and how does TO polymerize in the solid state? and why did Kohlschuetter observe polymerization during TO sublimation?

***Solid State polymerization of TO:*** Trioxane was known to polymerize in solution but it was observed that TO actually polymerizes rather slowly in solution or above the melting point. On the other hand, it was reported that TO polymerized readily below its melting point. No melting of the TO crystals was observed during the polymerization of TO because it is a ring opening polymerization which produces about 3 kcals/mol.

I was fascinated by TO and had grown crystals in a test tube, which were almost transparent. They had grown in a closed container, which was about 10% full, and these crystals had grown by themselves over a period of time. I had a number of such crystals 3-4 cm long and perhaps 1-2 mm in diameter, and decided to check their polymerization behavior.

I took one of these crystals, placed it in a small test tube and closed it with a rubber stopper. After a while (equilibration) I injected a small amount of gaseous boron

trifluoride into the tube. Within seconds, the surface became opaque and after a day or two the crystals had become completely opaque with some surface cracks. The crystal had become a crystal of POM. This experiment was very reproducible.

We clearly had on hand an example of "solid state" polymerization. About a year before at least two groups had started to investigate acryl amide, which also polymerized in the solid state. Since this was a new technique, this principle created a considerable amount of excitement. It was postulated that the crystal structure of the monomer and that of the polymer had to be very similar so that solid-state polymerization can occur. A relatively small positional change in the individual monomer molecules in the crystal was all that was necessary. It provided the proximity for the single bond for the polymer structure to form. The authors did not consider the obvious difference of the density between monomer and polymer.

After completing my work on the "solid state" polymerization of TO we worked on a monomer casting process for POM. We focused on copolymers of TO with oxiranes and selected the oligomers of butadiene oxide as the epoxy component. Although a copolymer product with 5-10 % oligo(butadiene oxide) was interesting, the POM casting was abandoned. In order for a monomer casting to be successful, the polymer had to be and must remain soluble during the polymerization.

I did not believe much of the solid-state polymerization and thought for a different and better way of explaining this polymerization. What had been proposed was a polymerization of:

**crystalline monomer --> crystalline polymer**

could be explained better in another pathway:

**crystalline monomer (mobile form) --> short gaseous monomer phase ----> solid crystalline polymer.**

I believed that the capability of "sublimation" of the volatile monomer, rather than the rigidity of the monomer crystal might be the cause of this facile polymerization. I further

believed that the reasons for the fast rate of polymerization below the melting point of TO might be caused by the movement of single individual monomer molecules. TO molecules as single molecules were approaching the propagating cation of POM. This process allowed a fast and non-competitive propagation of the polymer chain. The polymerization in the melt or in solution relies on solvated propagating species that are solvated with clusters of monomer molecules that compete with each other and wish to a partner of the propagation reaction.

I decided that two sets of experiments could decide what was the likely mechanism.

In the first experiment, one of our needle-like TO crystals was subjected to the same treatment as before, it was placed in a small test tube and after awhile was subjected to a small amount of borontrifluoride gas. However this time, as soon as the opaque film of POM had been formed on the surface the partially polymerized needle was taken out of the test tube and placed in a different test tube and again closed with a rubber stopper.

A totally different result was observed. After awhile the needle had superficially the same dimensions but now POM appeared porous. It had several almost colorless crystals of TO, cubes of about 1-2 mm base length in several places outside the POM sheath.

What was the difference between the two experiments? In the first experiment of our solid-state polymerization borontrifluoride gas had been added to the test tube containing the TO crystal. The test tube was also under an atmosphere of equilibrium vapor pressure of TO. It seems that boron trifluoride initiated the TO on the surface of the crystal and formed solid crystalline POM terminated with a dormant terminal cation. As the mobile TO approaches it can revive the polymerization and ultimately ends up in a needle of POM

In the second experiment the partially polymerized TO crystal was taken out of the equilibrium TO atmosphere and the POM cation is deprived of the vapor phase. Now only the sublimation of the TO occurred exclusively. The system is aiming to reach equilibrium of TO in the atmosphere. During this process, recrystallization of the TO crystals occurred as TO cubes outside of the original crystal with the POM sheath. These experiments were very reproducible.

This work was done in the early 60's and polymer crystallization had not reached the degree of sophistication that it has today. I am convinced that this type of polymerization had produced crystalline POM as extended chains. We ran on "sloppy" melting point determination in a melting point tube found melting at about 197°C and discarded the result. As we know today, Delrin, as extruded or injection molded has an m.p. of 178°C, is 60-80% crystalline and crystallizes as folded chain crystals.

Now a new set of experiment was set up. We studied the "solid state" polymerization of TO as a function of temperature with gaseous boron trifluoride as the catalyst. We prepared TO powder with a relatively uniform size particles size particle of about 1/2 to 1 mm placed 1 g samples in closed test tube in oil baths 5°C apart and injected the same amount of borontrifluoride and shook gently. After one hour the reaction was stopped, excess TO was dissolved and the residue weighed. The yields of POM were plotted as a function of temperature and it was found that it decreased linearly to 10°C below which no more polymerization occurred. We called it the temperature of the limit of the TO monomer mobility in the crystalline state.

I then decided see my friend Bill Statton. Statton was a manger at the Textile Fibers Department of DuPont. His interest and responsibility were to study and perfect solid-state behavior of textile fibers especially poly(ethylene terephthalate) (PET). He used broad line NMR spectroscopy with a typical line width of about 10 Gauss for the determination of the mobile phase in PET fibers. The mobile phase has a line width of a tenth of a Gauss or less.

I asked him how if he could measure the mobility of a TO crystal by broad line NMR. He said the mobility of monomer crystals in principle is not different from that in a polymer. I explained my idea and he thought that it should be possible to detect a mobile fraction in a TO crystal if it existed. What needed to be done was to take a broad line NMR spectrum at various temperatures and measure quantitatively the narrow peak of the mobile phase over the rigid phase of the matrix. He said we have done it frequently for PET.

The experiments were set up to determine the mobility of TO in the TO crystal as a function of temperature. The experiments were very exciting. Statton found that a substantial narrow peak attributable to the mobile fraction existed which decreased as the temperature of the measurement increased, and, at 12°C, the narrow peak of mobility disappeared. These sets of experiments convinced us that the mobility in the TO existed, down to 50°C below the melting point of the monomer and it is this phenomena that causes the "solid state" polymerization of TO

This principle and the broad line NMR substantiation of the so-called "solid state" polymerization was further solidified by a similar behavior of a totally different type of monomer and type of polymerization. Nylon 62 prepared in the sold state from c-62 below its melting point.

***Sublimation Polymerization of Kohlschuetter's:*** Kohlschuetter had observed POM formation during sublimation of TO in L-shaped glass tubes. I decided to check the Kohlschuetter experiments and try to find an explanation of this behavior.

I designed my experiments as follows. Purified TO was placed in an L-shaped glass tube, which had a side arm through which the reaction tube could be filled with TO crystals of a particle size of about 1-2 mm. After filling the tube to about 20-25%, the tube side with the TO was cooled in dry ice, evacuated and the side arm was sealed

off.

The experiment was continued as follows. The empty part of the L-tube was placed in a cooling bath of dry ice/acetone; the other side was left at room temperature. The TO started to sublime to the cold part of the L-tube. The sublimation was allowed to proceed over night. The entire content of TO crystals had sublimed into the cold part of the tube. When the sublimation was carried out using a dry ice/acetone bath, from the second sublimation on, some POM was observed as residue. For the next sublimation, the tube was reversed and the TO sublimed into the original end of the tube. After each sublimation, more POM was formed on both sides.

Since it was known that TO can only polymerize by a cationic polymerization, we tried to detect the source of the cationic site on the glass surface. When the glass tube was not treated at all, the back and forth sublimations produced increasing amounts of POM on both ends of the tube. After 10 sublimations about one half of the TO had polymerized.

Now the glass tubes were treated in various ways. The tubes were first washed with nitric acid, in part to clean the surface of the tube, in part to see the effect of the acid treated surface on the polymerization. After careful drying and "flaming out" under vacuum, the tube was filled sealed and the sublimation was allowed to proceed. Already after the first sublimation a substantial amount of POM was observed and after 10 sublimations the entire TO had polymerized. This result indicated that this "sublimation" polymerization of Kohlschuetter is, just like the regular TO polymerization, a cationic polymerization.

Another tube was washed with a sodium ethoxide rinsed once with ethanol, dried and used for the TO sublimation polymerization. During the first of several sublimations no polymer was detected but after 5-10 sublimations, POM was beginning to appear. After a little later the sublimation behaved as if it had been carried out in an untreated tube.

A number of sublimation polymerizations were performed with different types of surface treatments of the glass tubes. The result varied slightly but did not substantially differ from the general observations described above as long as the cooling bath was dry ice/acetone ( $-78^{\circ}\text{C}$ ). Similar results were obtained using a liquid nitrogen-cooling bath

When the sublimation was carried out in an ice water bath, the sublimation proceeded very slowly, but no polymer was observed in spite of several attempts

How can we explain the polymerization behavior during the sublimation of TO? We believe that the simplest explanation is as follows. When the glass tube was placed in a dry ice bath, tiny microscopic cracks occur on the glass surface, which have cationic character. When the TO sublimates into the cracks cationic initiation takes place. The polymerization probably does not terminate and POM cations remain in a dormant state. When the next sublimation is conducted, these POM cations become alive with the incoming TO monomer and restart the polymerization. We believe that the TO must deposit from the vapor state to penetrate first into the glass surface cracks and later to the sites of the POM cations. This explanation can also be used for the polymerization with a base treated surface. The base sodium methoxide is fixed on the glass surface but as the cracks are formed it cannot penetrate to the cationic sites, gaseous TO can.

How efficient the polymerization of TO "from the vapor phase" can be was demonstrated by Ube Industries in Japan. They patented a polymerization process by condensing TO vapors on a cold surface in the presence of a Lewis acid catalyst. Polymerization occurred and the POM was removed from the cold surface by a "windshield wiper" type action. The process was investigated on a semiworks scale, but no commercialization seem to have undertaken.

### *iii. Polyoxymethylene Ionomers*

I can trace my interest in ionomers to several events when I was still a chemist at the Polychemicals Department. The first one that I remember goes back to my work on stabilizers for Delrin.

I mentioned in the chapter on "Delrin projects" that my technician and I used a "rubber mill" in Building 323 at the Experimental Station for incorporating stabilizers into Delrin by melt blending. At the same time a very innovative scientist at Polychemicals was interested in influencing the crystallization of polyethylene and decreasing its crystallinity. He was Eric Baer, who later became the founder of the Polymer Science Department of Case Western University in Cleveland. Eric was adding all sort of potential nucleating agents to linear polyethylene melts, among them was sodium chloride. I remember this coincidence of our meeting in the processing area very well. I remember also that Eric found a decrease in crystallinity using this nucleating agent. I mentioned earlier that my technician normally carried out the blending on the rubber mill and I joined him and checked how our melts behaved. On rare occasions I myself did the work on the rubber mill. By being in the "processing area" I got to know other people that used the rubber mills and became acquainted with their research interests.

About the same time, Gresham, the head of the Exploratory Section of the Polychemicals Department, wrote a general memorandum to all research chemists of the Department: "We need a polymer that flows normally under injection molding or extrusion conditions, but, when solidified, has properties like a crosslinked resin without creep." I was intrigued by this subject and wrote a proposal: We should use a blend of equal amounts of a polyanion polymer (polyamine) and a polycation polymer (polycarboxylic acid). I was young and naive and did not know that for such a proposal to be successful and ultimately to be accepted required also some negotiating, finding supporters or modifiers of the idea and some campaigning to get the support.

The answer was, as I should have expected. Not Gresham but Art Anderson, the senior supervisor under Gresham sent me a devastating and humiliating answer. I still have the scribbled answer to my proposal: How stupid it was to suggest a polymer mixture whose "crosslinking" was based on ionic interactions in the solid state.

Of course my memo was a naive suggestion and as such, not workable. However, two years later the ionomers were discovered. Rees found that ionic "crosslinking" is indeed the key to provide such properties. For polyolefins, polyethylene, 10-mol % of ionic carboxylate groups in the polyethylene were sufficient, indeed, more are undesirable. Another polymer to provide the cationic portion was also undesirable. A regular "inorganic" counterion such as sodium or, for other purposes, magnesium or zinc was sufficient to produce polyethylene-based ionomers with reduced crystallinity and other novel properties.

With this much background information and my involvement with POM I was ready to extend the ionomer principle to POM. I was fortunate to have a friend whom I convinced of the potential usefulness for this project: Ken Martin. He was an Australian and an adventurer and ready to try anything that had reasonable promise for success. Ken was also willing to bypass the company policy that TO should not be touched as a "monomer" for formaldehyde polymers.

Polymers with pendant carboxylate groups, ionomers, by the time Ken and I became seriously interested in POM based ionomers (Figure 12) had been established as a commercial polymer product. Ionomers exhibit interesting and useful properties substantially different from the regular base polymers. The most thoroughly studied ionomers were based on olefin copolymers, i.e., those with only carbon-carbon bonds in the backbone chain. Interaction of pendant ionic groups with the hydrocarbon backbone is minimal, leading to "clustering" of the ions.

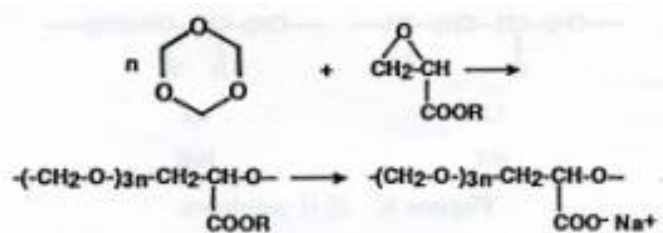


Figure 12: Polyoxymethylene Ionomers

The introduction of heteroatoms, specifically oxygen, into the chain backbone, was expected to change the nature of the backbone-ion interaction, and was expected to affect significantly the polymer properties.

Over the years, I have been started three areas of research on ionomers with oxygen in the backbone chain: a.) POM based ionomers. b.) Ionomers based on polymers from cyclic ethers. c.) Ionomers of polyolefins and poly(ethylene oxide) whose carboxylate groups is separated from the backbone chain by flexible spacer groups, such as methylene groups.

*Polyoxymethylene oxide Ionomers:* In the last Chapter I discussed my interests in POM's from TO. My interest was fanned by the "solid state polymerization" of TO and the "sublimation polymerization" of Kohlschuetter. In the early 1960's, as POM homopolymers were prepared for commercialization as Delrin resins by DuPont, a new type of polymer was developed for commercialization also by DuPont- ionomers. These were salts of copolymers of ethylene and methacrylic acid prepared by high-pressure polymerization with about 10-12% of methacrylic acid in the copolymer.

Initially we thought we should make the ionomer equivalent of POM with about 10-12% of carboxylic acid groups and make sure that they had base stable end groups and then hydrolyze them their salts. It was very clear that the polymer and copolymer had to be made by polymerization and copolymerization of TO with the appropriate carboxylate functional comonomer, methyl (MG) or ethyl glycidate (EG). We could see a serious problem, which had to be overcome. The reactivity, represented in the copolymerization ration of TO and the glycidates are vastly different and it was

expected that we might obtain copolymers whose glycidate incorporation was either at the end of the polymer chains and introduced at the end of the copolymerization. The result would be a low base stable fraction and/or low molecular weight of the base stable fraction of the polymer. Such problems could be overcome by a.) Addition of the comonomers in reverse order of their copolymerization ratio, b.) Using a monomer with a better copolymerization ratio such as 1,3-dioxolane (DO), or c.) Polymerizing under steady state conditions. We decided to pursue all three needs.

Ken Martin constructed a reactor for a gas phase polymerization. This reactor was a stainless steel device which had a main chamber capable of being heated to 200°C, three outlets and an exit that was linked to a round bottom flask. To carry out the polymerization, the main reactor was heated to 135°C 10°C higher than the ceiling temperature of formaldehyde polymerization, which is about 125°C. One of the outlets was connected to the TO source, one to the comonomer, EG or MG. The third outlet was connected to the catalyst boron trifluoride diluted with nitrogen gas.

Initially the homopolymerization of TO was carried out. TO is very volatile and was swept into the reactor with nitrogen. POM formed as TO and the catalyst boron trifluoride was quenched to ice temperature, it was a very high yield reaction and the POM was solution capped in propionic anhydride. POM is soluble in boiling propionic anhydride but not in boiling acetic anhydride and is more conveniently carried out in the laboratory.

We consider our vapor phase process for POM from TO as a forerunner of the vapor phase process, developed by Ube Industries many years later.

For copolymers with carboxylic acid esters, comonomer of choice in preparation for producing POM ionomers was MG or EG. EG or MG were not as reactive as TO, consequently, the flow rate of the comonomer had to be adjusted accordingly for

acceptable incorporation and copolymers with up to 5% were obtained. Lower percentage of comonomer incorporation gave polymers of lower molecular weight and with a low base stable fraction.

In order to overcome these complications and to produce POM of high molecular weight and good base stability with a low base unstable fraction, we decided to prepare terpolymers of TO, DO and EG. These oxymethylene terpolymers gave polymers with the desirable properties. The POM carboxylate esters, copolymers and terpolymers, were hydrolyzed with sodium hydroxide to POM. The ionomers and their properties were investigated.

Much of the work on POM ionomers was done at DuPont. (40) The work was later checked at the University of Massachusetts and quantitative measurements were undertaken. I cooperated with William MacKnight who had been instrumental in the development of the explanation of ionomer behavior based on polyolefin ionomers. ((41-45). Initially our POM co and terpolymers were identified by their molecular weight, base stability, infrared and  $^1\text{H}$  NMR spectrum. Calorimetric studies provided the data for melting point peaks, melting behavior, crystallinity and heats of crystallization. Dielectric and dynamic mechanical studies at three different frequencies determined various relaxations and motions in the POM's. We demonstrated that EG could be incorporated into POM's. Our patent on the vapor phase copolymerization of TO with EG, MG and glycidonitrile was also described as workable comonomers and compositions of about 1-2% comonomer in the POM were obtained.

We also found that bulk and solution polymerization could also be used for the preparation of co and terpolymers, but the resulting polymers had only few percent of carboxylate groups incorporated. The polymers melted about  $10^\circ\text{C}$  lower than Delrin and had base stabilities from about 40% to a high value of nearly 60% for some compositions. For ease of characterization, they were solution end capped with propionic acid anhydride. The polymers were hydrolyzed to the acid form with sodium

hydroxide.

Later we have studied the gas phase polymerization and the copolymers obtained in more detail. Some copolymers were also synthesized in solution. Copolymers of TO and EG (or MG), but also of TO and DO and the terpolymerization of TO, DO and EG were studied. The m.p. Of Celcon, a 1.5% copolymer of TO and ethylene oxide (EO) under our conditions was about 160°C with a crystallinity of about 60%. For convenience we used DO, rather than EO as the comonomer. It does not give exactly the same copolymer but at these comonomer compositions it did not matter. For comonomer composition of 4% DO (feed 30%) the melting point decreased to 143°C and the base stability of a TO/DO copolymer was 60%.

A terpolymers of TO/DO/EG with 1.2% of DO (feed 10%) and 0.9% EG (feed 5%) melted at 145°C (the sodium salt of the free acid at 156°C). A composition of 2.0% EG (feed 15%) at 148°C (the sodium salt of the free acid at 152°C). The POM ionomer sodium salts could be transformed into lithium or cesium salts.

At relatively low comonomer compositions, the melting points of the POM copolymers were not effected when going from to the esters to the salts. This behavior suggested that the ester or salt side groups are probably in the amorphous phase of the terpolymers while oxyethylene units are partially in the crystalline phase of the polymers. From dielectric relaxation the salt groups are not free to move because they are grouped to clusters, which retain their integrity to higher temperatures

## **e. Polyoxamides**

### *i. Solid State Polymerization and Polyamide Casting*

The DuPont Company's research effort in a "super Research group" for possible future developments came to an end. I returned to Polychem and my assignment was in a

holding pattern. DuPont's interest was always, since the commercialization of Nylon focused in the periphery of the nylon polyamides

In the early 40's DuPont commercialized poly(hexamethylene adipamide) as Nylon 66. Competitors invented and commercialized successfully Nylon 6 – poly(caprolactam). Nylon 66 is made from adipic acid and hexamethylenediamine by melt polymerization, Nylon 6 by ring opening polymerization of caprolactam. Both processes are carried out in the melt and the polymer melt is directly melt spun to the fibers. Nylon 66 has a slightly higher modulus, it melts at 265°C and a water absorption of 5-6% while Nylon 6 melts at 225°C and has an equilibrium water absorption of about 8% Other interesting aliphatic polyamide have properties in between but were never considered of interest except Nylon 6,10, the polyamide of hexamethylenediamine and sebacic acid.

Niche properties of polyamides have one significant exception, Nylon 62, poly(hexamethyleneoxamide). It has a melting point of 325°C but degrades significantly at 280°C and a moist interestingly low water absorption of 0.5%. The polymer cannot be melt spun because of the high melting temperature which brings Nylon 62 into the range of melt fabrication of close to its thermal degradation. Furthermore, the polymer cannot be made by melt polymerization because of the low thermal stability of oxalic acid. Polymerizations using oxalyl chloride are equally unsuitable for preparing high molecular weight Nylon 62.

My next assignment was to prepare high molecular weight Nylon 62 by a different method, by ring opening polymerization of the appropriate cyclic monomer, which was called c-62 and attempt the ring opening polymerization of the cyclic monomer. In other words a polymer casting technique similar to the ring opening polymerization of caprolactam but with t monomer, c-62 of much higher ring strain was tried.

C-62 was recognized as a highly strained compound - which in turn was expected to be easily polymerized by ring opening polymerization. The synthesis required the well-

known technique of high dilution. The initial attempts of the cyclization of hexamethylenediamine gave, in addition to poor quality of the 62 polymer, that melted at 232°C. It was believed that this compound was the right compound. The molecular weight determination showed the compound to be c-6262 m.p.=303°C, the cyclic dimer, the cyclic trimer (c-626262) melted at 345°C. The three cyclic oligomers have distinct differences from each other and from the 62 polymer in the infrared region. Other cyclic diamides were also prepared, c-82, m.p. 260°C, c-42, m.p.=405°C, c-22 and 3-CH<sub>3</sub>O-c-62, m.p.=250°C. Even the cyclic co-diamide, c-6266, m.p.=238°C was prepared. During this work a diamine diamide was prepared which was later found to be a key intermediate in our work on regular copolyamides: H<sub>2</sub>N(CH<sub>2</sub>)<sub>6</sub>NHCOCONH(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>. It gave with oxalyl chloride c-6262 and with adipoyl chloride, c-6266.

The objective still was the synthesis of c-62. A large run of the ingredients in 85 gallons of benzene in a 16 hour of addition gave product that had 100 g of the real c-62.

The ring opening polymerization was successfully carried out with basic initiators, sodium ethoxide to a 62 polymer of respectable molecular weight. c-62, m.p. 232°C and c-6262, m.p. 303°C polymerized readily to Nylon 62, m.p. 320°C. The polymerization was typically carried out at 260°C. Polymerization was already beginning at 150°C, which was confirmed by broad line NMR, where mobility in the crystal of c-62 was first noticed at that temperature. c-62 was also able to copolymerize with other cyclic amides. With c-82 in equal amounts it gave a copolymer melting at ~260°C and with caprolactam at ~265°C. c-6266 was also prepared and it polymerized to "regular" Nylon 6266. The polymerization seemed to occur through the oxamide bond because c-66 did not polymerize under the same condition.

There is a curious sideline. Bill Simmons, the director of organic research (there were 5 directors) used my apparatus to prepare cyclic amides and co-polyamides. He studied the "in" and "out" structure of the amino groups by NMR but never used cyclic amines

as complexing agents. Jean Marie Lehn did it following DuPont's Charlie Pederson invention of crown ethers. He and Pederson shared the Nobel Prize and Simmons became Vice President at DuPont.

This polymerization turned out to be of great interest, because it was found that the polymerization of this highly reactive monomer could also be accomplished in the solid state. The recognition of the polymerization in the solid state showed an amazing similarity to the polymerization of TO in the solid state (45-49).

When the polymerization of c-62 in the solid state was carried out at temperatures from just below the melting point to temperatures much below, polymerizations became sluggish, and when one polymerization was used as a criteria, a point of temperature could be reached, below no more polymerization was achieved. This phenomena was studied in more detail in the polymerization of TO.

c-62 was the only cyclic monomer that was an objective of the program, but it was obvious that other cyclic monomers could also be subjected to ring opening polymerization.

We synthesized cyclic monomers such as c-62, c-66, c-42, c-68 and polymerized them (Figure 13). Still inspired from the Nylon 62 project, it became clear that other cyclic monomers could be synthesized and used as monomers for polymerization. Diamines amide intermediates were synthesized, such as 626. This compound could be cyclized with the appropriate diacid chloride to cyclic compounds, with oxalyl chloride to c-6262, with adipoyl chloride to c-6266, and with sebacoyl chloride to 6268. Polymerization of these cyclic monomers gave "alternating" copolyamides.

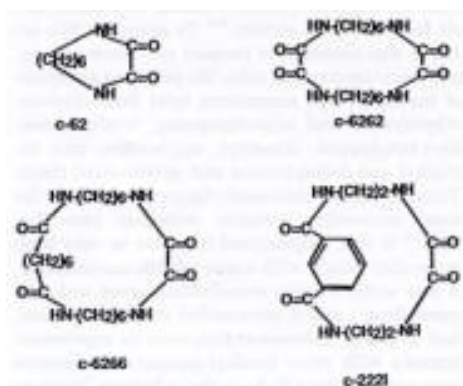


Figure 13: Cyclic Oxamides

Polymerization of c-62 was carried out with anionic initiators, hydroxides, hydrides, alkoxides and even acetates. Cationic initiators like sulfuric acid and some Lewis acids were also useful initiators. The effectiveness of the initiators depended on the basicity of the anion but also on the "solubility of the initiator. Best conditions for the polymerizations were at about 260°C. Higher temperatures reached into the degradation range

c-62 polymerized readily with other cyclic oxamides and with lactams. c-62 have a copolymer with c-82 melting at 258-68°C, with caprolactam of a melting range 260-270°C and with 3-CH<sub>3</sub>O-c-62 of 268°C.

At a rate similar to the polymerization of c-6262, c-6266 polymerized to a polymer at a melting temperature of 259°C. It is believed that c-6266 polymerized exclusively through the oxamide link because under the same conditions c-66 does not polymerize.

**Solid State Polymerization and Polyamide Casting:** Polymerization of c-62 was also observed in the solid state. The onset of polymerization can be traced to 150°C. with increasing polymerization observed as the polymerization temperature approached the melting temperature of c-62. This phenomena is similar to that of the polymerization of TO in the solid state and is clearly related to the mobility of the c-62 molecules in its crystalline lattice. Broad line NMR studied have confirmed, that the "peak of mobility"

diminishes at lower temperatures and disappeared around 150°C.

This work was terminated because it was only used as a research project for me as a "holding pattern. It gave sufficient and interesting results and it became for me a research objective several years later. We started to investigate "regular copolyamides" and ultimately, we selected the most promising candidate for desalination membranes.

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## **B. Exploratory Research Group**

From time to time in the past corporations have created special exploratory groups to boost innovation in the hope of having entirely new products in the future. The DuPont Company was no exception, in fact, it has spearheaded such efforts. The best and most successful example was started in the early 1930's when they hired a young Assistant Professor from the University of Illinois named Caruthers and charged him to play around. He chose to look at polycondensation reaction. In a couple of years the rules were established. By carefully redirecting the efforts from aliphatic polyesters to polyamides by the management, the Nylon business was established. The initial understanding of the preparation of aliphatic polyesters was extended by ICI (Atlas in Wilmington) to aromatic aliphatic polyesters.

The accidental discovery of Teflon created the new group of fluoropolymers. Another thrust effort started during the war and was involved directly toward investigating reactions of formaldehyde; in several ways it could be considered a "polar" ethylene. In the 1940's Robert McDonald prepared high molecular weight polyformaldehyde that had good mechanical properties and could be fabricated. This discovery was the basis of the commercialization of POM as Delrin acetal resin. Frank McGrew, was the Director of Research of the Polychemicals Department and was responsible for the

decision to go commercial with Delrin.

A few years later in the late 1950s, McGrew also allowed a sizable and most imaginative polymer physics group in the Polychemicals Department to coagulate. It was initially seen as support of the novel polymer Delrin, but was also important for growth of polyethylene and other new resins, candidates for commercial products. It included scientists such as, William Bryant, Fred Billmeyer, Phil Geil, Ed Clark, Jerry MacCrum and Ken Sinnott. As in many similar endeavors, the objectives were reached and the group became too large for its justification of support for the commercial products. It was ultimately dispersed and some of the scientists went to academia.

In about 1960, McGrew persuaded Sam Lenher, then Executive Vice President of Research at DuPont to create a special research group to try out exotic and "far-out" ideas of polymer research. The idea was to convince each of the operating departments with interest in polymers and C R & D to contribute one scientist, preferably their most inventive and innovative scientist to this group. The group would be placed in some building and the individual scientists were allowed to work on their ideas and create ideas and concepts.

Six people were assigned to this group, Burton C. Anderson from the Central Research Department, Charlie Berr (Film Department); Donald Simons from the Elastomers Department, now at the Medicinal Products Department, Bob Braun from F & F (Fabrics and Finishes Department), and Jim Coker (Electrochemical Department). I represented the Polychemicals Department. This idea of the Exploratory Research Group was a splendid one. It had, however, one inherent fault from the beginning. The Textile Fibers Department, which represented about 40 % of the DuPont business and controlled the Nylon and polyester business, did not join. The group was supposed to work without management and supervision, was to create their own environment and was located at a group of laboratories in building 336 of the Electrochemicals Department with Norman Hause, the Laboratory Director of the Research Division as

the "landlord". Bill Sharkey, a supervisor from the Central Research Department appointed himself as the Secretary of this group. This group worked extremely well independently and very efficiently for one year.

Very soon individual characteristics developed. Jim Coker and Charlie Berr continued along the lines of their own department while Bob Braun worked on reactions of the newly discovered hexafluoroacetone, grafting it and attaching it to monomers, polymers or just chemical compounds of interest to him. I believe during the year he had 10 or 12 patent applications on the subject.

Burt Anderson, Don Simons and I were more interested in novel concepts. Some of them we explored together. Individually Don Simons was interested in what we would call today now phase transfer catalysis. He was especially interested in making highly hindered amines, in other words non-basic but highly nucleophilic amines.

Burton Anderson and I worked closely together with some help from Donald Simons. I began seriously to work on the development of poly(trichloroacetaldehyde) - polychloral

Suffice it to say, as soon as the group started to function, problems that did not exist internally became apparent. In a company, it was not possible to allow a group to work without supervision although none was needed. However, after almost a year the group was abandoned. Maybe Lenher lost interest, McGrew lost power and influence. Our host Norm Hause had an idea to have an addition built to his building to accommodate the exploratory group more appropriately. Other priorities had come up in the individual departments, which required experienced manpower. An attempt was made to transfer the entire group to the Central Research Department where it would have actually fitted best. Since there were some experienced people involved, none of the departments allowed their scientists to transfer with the exception of the Polychemicals Department and I moved into the Central Research Department at the

end of this period.

I will discuss here the three projects, which were developed during the period of cooperation between Anderson, Simons and myself. It must be remembered that the basic principle of this group was to do some exceptional and some unusual and odd chemistry. The first problem that we were interested in was trying to conceive very stiff molecules that were not aromatic. (Figure 14) In the middle and late 1950's a tremendous effort was made to prepare fully aromatic and ladder polymers. The basic entrance in this field was DuPont's Kapton, the film based on the aromatic polyimide from pyromellitic dianhydride and 4,4'-diaminodiphenylether, but we wanted to have something colorless. Our concept was to carve out

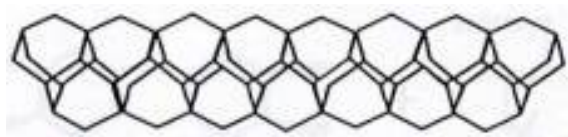


Figure 14: The Adamantalogous Series

of the diamond lattice or a boron nitride lattice, a cylindrical structure, which was easily considered as an accumulation of adamantane rings in "chain form".

The second project was an outgrowth of the diamantane work and consisted of our increased interest to force reaction by using excessive pressures.

The third was the control of stereochemistry of polymerization, but not with coordination catalysts but by selecting the side group size to force stereoselection, as it is sometimes seen in natural polymers, polypeptides.

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## C. Central Research Department

### a. Polychloral

#### *i. Beginning*

The project to pursue further the polymers of higher aliphatic aldehyde could from the company's point of view not longer be justified. The Tc was too low. The polymers as secondary hemiacetals were more and more difficult to end cap as the length of the aliphatic chain increased and the system became more hydrophobic. The could not be stabilized against autoxidation, because the electron donating aliphatic side chain rendered the acetalic hydrogen atoms oxidatively more sensitive then POM.

Consequently I abandoned the polyaldehyde work when DuPont quit but completed some unfinished work in academia.

I thought that polychloral, the trichloroacetaldehyde would be oxidatively much more stable, having a helical structure with the hydrogen atom pointing toward the inside of the helix and the electron withdrawing trichloromethyl group attaches to the acetalic carbon atom would have excellent stability against autoxidation. As a polymer with 72% chlorine in the molecule might have some promise as a flame-retarding polymer.

Polychloral had been known since 1832 when Liebig, in an attempt to prepare chloral by chlorination of ethyl alcohol, also isolated a "horn-like" substance. It was later extensively investigated around 1900 and called metachloral. When I became interested in polychloral it was clear to me that metachloral was a misnomer; it was not the cyclic tetramer of chloral but a high polymer

At the time that I started Nowak and Whalley published a paper and suggested, based of infrared data that metachloral was a polymer and more importantly a n isotactic

polymer. This conclusion turned out to be correct.

I started to work on polychloral in 1958. I used polychloral as a model for a vapor capping reaction on higher aliphatic aldehydes. At that time it was well known that polychloral is probably more stable than polymers of higher aliphatic aldehydes. In fact the first vapor capping reaction was carried out in Keith Brinker's (my former laboratory mate) small vapor capper. It could take 5 to 10 grams of polymer and gave encouraging result. Keith had been involved in vapor capping of POM using various kinds of capping reagents; among them was ethylene oxide.

The vapor capping with the polychloral as it was made according to the procedure of Boeseken was carried out at the boiling point of acetic anhydride. 30% to 40% of the polymer remained and was thermally stable. That did not mean that the polymer was actually vapor capped, it could also have meant that the unstable fraction was partially capped and thermally degraded. What remained was thermally stable polychloral. I made few attempts and always obtained undesirable and incoherent samples of polychloral. For about three years we did not do any work actively on chloral polymerization.

In 1962 I was transferred from Polychemicals to C R & D I convinced the management, Vaughn Engelhardt, one of the directors of C R & D that polychloral was a promising subject. I had worked on the polymerization of chloral in the Experimental Research Section the year before.

I was happy to be assigned to "my own" project. However, I experienced many months of frustration in at the beginning. The polymerization was faster than the injection of the initiator into the monomer solution.

## *ii. Cryotachensic Polymerization*

It was an interesting period, when I began my work at C R & D: I had selected the subject, the polymers of chloral and the project was moving forward but no real breakthrough was in sight. The time of reckoning was rapidly approaching. On April 8, 1963, I was scheduled to present the results of my work since my arrival in the department to the Steering Committee, but I had nothing truly positive to report. One more idea had occurred to me in the evening and I was determined to try it out. In desperation, I went to the laboratory at 5 o'clock in the morning to make a final attempt to polymerize chloral to a homogeneous piece of polychloral. Within an hour, I had found the solution. In a test tube, closed with a rubber septum, the monomer solution in toluene had to be *heated* above the  $T_c$ , and the catalyst solution could be added. The mixture was a colorless clear solution. Cooling in an ice bath formed homogeneous pieces of polychloral (Figure 15). By the time of the Steering Committee meeting, I not only had a story but I could also show a most convincing demonstration with three catalysts, lithium cholesteroxide, LTB, and triphenylphosphine (TPP). (48,49)

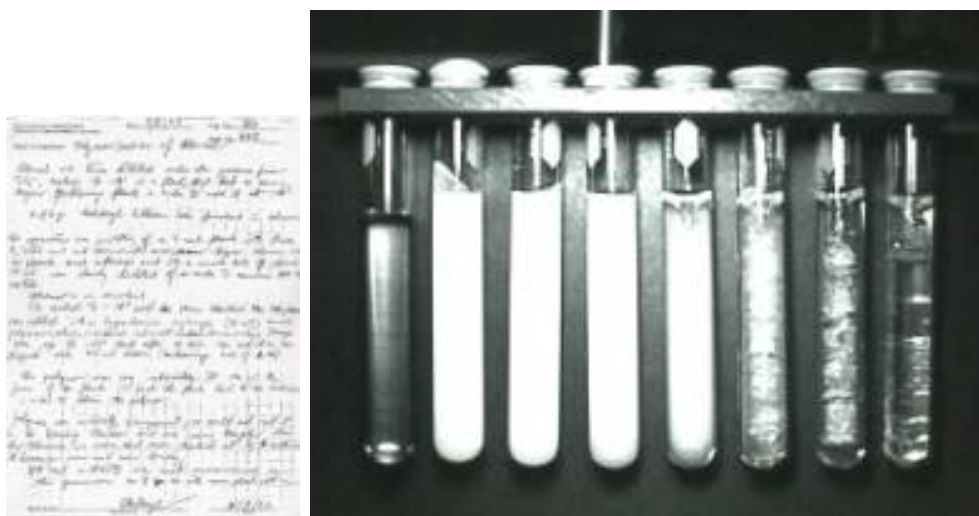


Figure 15: Cryotachensic Polymerization of Chloral in Test Tubes

Initiated chloral is a clear colorless liquid and could be handled above the polymerization temperature, which is for 1 molar solutions, the  $T_c$ . The mixture was then cooled in ice/water and polymerization started. At a conversion of 2-3% a homogeneous gel starts forming which is self-supporting. The gel was filled with

monomer, also with solvent if a solvent was used. If the gel was broken, the gel could not reseal except at very low conversions. As polymerization continued and monomer was consumed, the gel became opaque and remained opaque from 20% conversion to about 65% conversion. Then the polymer became transparent again and the polymerizations stopped near a 85-90% conversion.

Polychloral obtained by bulk polymerization contained about 15% of monomer. 8% to 10% could be removed by heating the sample for one hour at 100°C. Heating over extended periods of time removed only very little additional monomer, however extraction with a solvent such as with methanol or with acetone removed an additional 5% to 7%, indicating that some of the monomers is very tightly bound to the polymer matrix. This portion of the monomer can be extracted with acetone.

When the polymerization of chloral was carried out in an inert solvent, such as in pentane or in hexane, polymerization proceeded to 95% to 97% conversion. This suggested that the mobility of the monomer in the polymer matrix is restricted in bulk polymerization. If a significant amount of solvent, even a poor solvent for the monomer was present, the solvent displaced the monomer from the polymer matrix or made the monomer available for polymerization up to near quantitative conversion.

When the polymerization neat monomers conducted in a test tube shaped container. The polymer cracks because of the difference between the density of the monomer and polymer. Between 3 and about 10 minutes 50-75% of the polymer conversion was reached. The rate of polymerization depends on the efficiency of the removal of the heat of polymerization.

The extensive patent, which was ultimately granted, described an improved orientable high molecular weight polychloral. From this polymer articles were formed, which are tough nonforaminous, cohesive and infrangible. These materials could be made by a process involving the steps of a.) Preparing a homogeneous mixture of chloral, b.)

Anionic polymerization initiator for chloral c.) From 0 to 40% of the weight of the chloral or an aprotic for facilitating the uniform dispersion of the initiator either as a solid or as a solute throughout the chloral at the temperature above the polymerization threshold temperature of the chloral cooling the polymerization mixture below the polymerization threshold temperature to induce polymerization without agitation and finally separating the aprotic liquid from the polymer.

A flurry of activities followed to demonstrate the limits of my invention. Just like with the acetaldehyde polymerization: Catalyst studies, stabilization, copolymers, blends and also possibilities for practical uses.

In our first test of applications, chloral was polymerized in round bottom flasks. The homogeneous polychloral samples were stabilized by treating them with phenylisocyanate. After washing, the flask was broken, the polymer dried and pieces were machined from the solid polymer pieces (Figure 16). We produced plates, screws, and bolts to obtain some feeling of the properties of polychloral. This technique of fabricating a polymer



Figure 16: Machined Pieces of Polychloral

by monomer casting directly into a final shape required having a special name. Fortunately I had a friend of Greek origin, Andy Logathetis, who came up with a name. It uses an expression from classical Greek to describe the polymerization "driven by cooling" as cryotachensic polymerization.

The discovery of the cryotachensic polymerization led to a patent of the process of polymerizing chloral. The basic patent (50) was filed in 1965 and issued in 1969. It described an improved orientable high molecular weight polychloral as formed articles, which are tough nonforaminous, cohesive and infrangible. These materials could be made by a process involving the steps of a.) Preparing a homogeneous mixture of chloral, b.) Anionic polymerization initiator for chloral c.) From 0 to 40% of the weight of the chloral. Also described is also the possible use of an aprotic for facilitating the uniform dispersion of the initiator either as a solid or as a solute throughout the chloral. The mixing of the components must be done above the polymerization threshold temperature of the chloral. The polymerization mixture is filled into the hot mold and the assembly cooled below the polymerization threshold temperature to induce polymerization under quiescent conditions, without agitation and finally the polymer is taken from the mold (51).

I was very fortunate that Koichi Hatada, an expert in NMR spectroscopy joined our group in 1972. With other colleagues he studied the profile of the chloral polymerization in more detail in chloral/p-chlorophenylisocyanate copolymerization (52). The disappearance and mobility change of all components of the cryotachensic polymerization, chloral, comonomer and solvents were followed by  $^{13}\text{C}$  NMR spectroscopy (53). This part will be described in the Section on "Copolymers."

### *iii. Chloral Polymerization Initiators*

After the discovery of the cryotachensic polymerization, a vigorous period of work followed. First we had to find out what type of initiators were effective for chloral polymerization. You will probably notice that I am using the expression initiators rather than catalysts. Initiators, strictly speaking, become incorporated in the polymer chain, usually as the initiating end group. Catalysts assist in a chemical reaction without becoming part of the reaction products. Some argue that in coordination polymerization initiation of olefins, initiator and catalysis are necessary for the polymerization.

The most effective initiators of chloral polymerizations are anionic initiators. Chloral can also polymerize with cationic initiators (54). Only certain Lewis acids, not all of them, are effective. The bulk polymerization of chloral proceeded very rapidly with aluminum chloride or aluminum bromide. The rate was comparable with that of anionic initiators. Good results were also obtained with sulfuric and trifluoromethanesulfonic acid. In the presence of titanium tetrachloride and ferric chloride the polymerization was very sluggish and other potential cationic initiators were ineffective. The former two Lewis acids are relative complex structures and could (together with monomer) provide chloride ions for anionic polymerization.

We generally preferred anionic initiators, soluble in the chloral solutions or in the monomer chloral itself. The initiators can be categorized into: a.) Strong initiators and b.) Weak initiators (55).

**Strong Initiators:** This group, designated as  $R^-$  when added to one mole of chloral monomer formed  $R-CH(CCl_3)-O^-$ . The basicity of the catalyst  $R^-$  is orders of magnitudes stronger than the resulting chloral terminated alkoxide. This addition can proceed at any temperature above the  $T_c$  of chloral polymerization and is essentially quantitative. Propagation can only proceed below  $T_c$  and is the basis of the cryotachensic polymerization. Fine points of the polymerization depend to some extent on the type of anion,  $Li^+$ ,  $Na^+$  etc.

**Weak initiators:** We consider anions that do not have a great tendency to add to the carbonyl carbon of chloral as weak initiators. They are anions such as acetate, cyanide and most importantly chloride ions. The initiation is an equilibrium such as  $Cl^- + CCl_3CHO \rightleftharpoons ClCCl_3CHO^-$ . The result is an initiating Cl-end.

What are the results of weak and strong initiation. The strong initiators produce nearly living systems which seems to indicate, brittle polychloral samples. Weak initiating systems seem to produce polymers with a more "most probable" molecular weight distribution and polymers that are tougher.

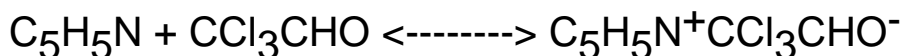
As pointed out in our patent (50), some of the initiators that were used include lithium aluminum hydride (LAH), hydroxides, acylates, cyanides, all sorts of alkoxides, amines, phosphines, stibines, aluminum isopropoxide and other compounds. Particularly important were the LTB and TPP. In our patent case was also described the preparation of sheets and films by casting between glass plates and various ways of manipulating these glass plates. Included in the polymerization techniques was the use of a stovepipe type of arrangements to compensate for the shrinkage that occurred during the chloral polymerization. It became very clear that the most favored initiating system was based upon triphenylphosphine. In later DuPont work it was actually found that aminoacetals such as the acetals of dimethyl formamide were also excellent initiating systems. A patent was applied for in 1965 and issued in 1969.

Ultimately we concentrated on 3 systems: LTB, TPP and triethylamine or pyridine. The initiation with LTB is straight forward, tert amine and TPP is more complicated.

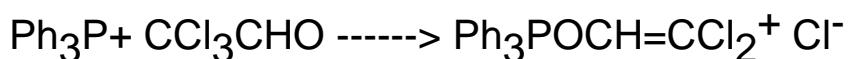
First tert amine initiation. This initiation and the subsequent polymerization is effective and gives good polychloral samples (56,57). When sheets were attempted, the glass plates adhered tightly to the polymer and had to be broken in order to retrieve the polymer and more often than not the glass splintered. The peculiar behavior of pyridine was observed by Donaruma et al. In their attempts to produce polychloral samples with controlled "instability" they used pyridine initiation. The idea was to use polychloral as a release for chloral. As the hydrate it is still one of the best candidates as an effective sleeping pill.

Many years later we found the solution for the mechanism of tert amine initiation of

chloral for example pyridine. It initiates by the addition of the tert nitrogen to the carbonyl carbon atom of chloral forming a zwitterion alkoxide, which on cooling forms the polymer:



Substantially different is the initiation with tert phosphines. Both aliphatic and aromatic phosphines react first with one mole of chloral to produce in quantitative yield the actual initiator. I will illustrate this reaction with TPP:



The structure of this phosphonium salt was determined by Guggenberger by single crystal x-ray analysis (58). The actual initiator of TPP initiation is  $\text{Cl}^-$ .

*<sup>31</sup>P NMR Analysis:* Phosphorous NMR spectroscopy was not common, when our work was done. We had at DuPont a NMR spectrometer, which could be transformed from the  $^1\text{H}$  to the  $^{31}\text{P}$  mode. This was very complicated, because it required that a whole section of spectrometer characteristic for  $^1\text{H}$  spectroscopy had to be disconnected and replaced by a similar section for  $^{31}\text{P}$ . The spectrometer also had to be connected to a simple strip chart recorder to record the spectrum. The chemical shift values had to be read from the instrument and drawn on the strip chart.

I still remember how we anxiously waited for our day of measurements. It took one day to set up and standardize the measurements, one day to measure and a third day to return to  $^1\text{H}$  NMR mode. The samples had to be ready for the one day. All the phosphines had undergone the reactions with one mole of chloral and were characterized by  $^{31}\text{P}$  NMR spectroscopy. Most impressive was the salt of tri tert butylphosphine with many lines.

### *Attempted estimation of the molecular weight of polychloral*

Since polychloral is not soluble we tried to estimate the molecular weight by end group analysis. We used 2 different dyes as initiators carried out the polymerization, carefully washing out the excess of dye initiator and measuring the color concentration of the polychloral film. We estimated a molecular weight of a 500-mer.

As we were getting closer to identifying TPP as the initiator for the chloral polymer another man was assigned to the project. His responsibility was to determine the molecular weight and other characteristics by using radioactive chlorine. It was very complicated. Today it would be impossible to do this work "en passant" in an industrial or even an academic lab. The half time of chlorine is thousands of years and the precautions to carry out this work would be prohibitive. To conclude, he also found a molecular weight of our TPP initiated chloral copolymer to be approximately a 500-mer.

### *iv. Chloral Copolymers*

Copolymers of aldehyde polymers are quite limited. Since the propagating species of anionic polymerization is a polymeric alkoxide, only comonomers of involving heteroatoms in the polymerizing groups are capable of copolymerizing. Few copolymers of formaldehyde polymers are known. They include isocyanates, preferably aromatic isocyanates and ketenes. A copolymer of chloral and FA has also been described.

Isocyanates and ketenes copolymerize well with chloral, using the cryotachensic polymerization technique. A number of anionic initiators were investigated but LTB and TPP were our favored candidates. Aromatic isocyanates have the right reactivity for copolymerization. p-Chlorophenylisocyanate provides the aromatic isocyanate with minimum color formation. The incorporation of aliphatic isocyanates is less effective and hindered aliphatic isocyanates terminate the chloral polymerization. We have also

used isocyanates to terminate chloral polymerization.

Because of the limited stability of chloral homopolymers, copolymerization had the most promise in the polychloral work. Indeed the copolymer case was first filed in June 1966 and was ultimately issued in June 1972 (59). It described chloral copolymers whereby chloral was copolymerized with one or more isocyanates, isothiocyanates, diisocyanates, diisothiocyanate or ketenes to produce copolymers (60-62), which were nonflammable and could be made into a variety of useful, shaped objects. The process was described again as making the copolymers which involves the preparing of homogeneous mixtures of monomers and polymerization initiators above the threshold polymerization temperature, the homogeneous mixture was cooled below the threshold polymerization temperature and was maintained quiescent during the polymerization. Not only were isothiocyanates and ketenes used in addition to the more favored isocyanates but also diisocyanates or diisothiocyanates were used and formed cross-linked materials (Figure 17).

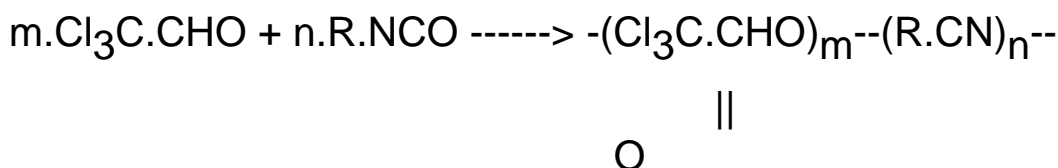


Figure 17: Chloral-Isocyanate Copolymers

Again the patent was very broad in terms of the amount of comonomers used. However, it became very clear that the copolymers with about 5 to 10 comonomers were the most attractive because they produced polymers, which were transparent. The homopolymer of chloral always was opaque and relatively unattractive. The copolymers, however, were transparent, but were still insoluble. Above 20% comonomers soluble polymers could be obtained. They were however never really investigated. In this case, in analogy to the basic chloral polymerization case, the copolymers were described to have been prepared in the presence of solvents or

diluents. The copolymerization proceeded by going from the transparent liquid phase to an opaque phase to transparency again in the later part of the polymerization. The polymerization initiators were quite similar to those that were used for the homopolymerization of chloral. However, the unstable fractions were very low, in fact polymers with high conversions to the polymer were obtained.

The preferred comonomers came from the categories of aromatic isocyanates, the most desirable one was p-chlorophenylisocyanate because it does not form colored by products on oxidation of the trace amounts of isocyanates that were left over at the end of the copolymerization and the isocyanates could hydrolyze to the corresponding anilines. The hydrolysis and oxidation products of p-chloroaniline did not form highly colored products.

Aliphatic isocyanates such as n-butyl isocyanate were also suitable comonomers for the copolymerization. However the aliphatic isocyanates were not to be as reactive and their cooperation was only a fraction of that of the aromatic isocyanates, which apparently copolymerized with equal reactivity ratios (63). Terpolymers of isocyanates (aliphatic and aliphatic isocyanates) with chloral were also prepared.

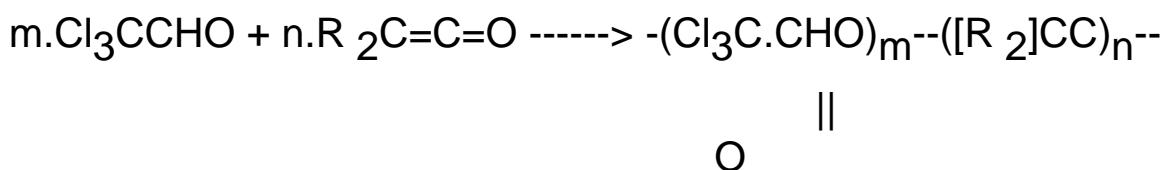


Figure 18: Chloral-Ketene Copolymers

An interesting category of copolymers of chloral were the copolymers with ketenes (64) (Figure 18). Ketene especially substituted ketenes such as dimethyl ketene, butylethylketene were studied. Most important were the copolymers of chloral and diphenyl ketene. As in the case of the isocyanates, diphenylketene has a copolymerization ratio very similar to that of chloral and could be very readily

incorporated into the copolymer. Ketenes form ester groups in the copolymers while isocyanates form urethane links in the copolymer. In principle, the ester groups were more desirable and potentially more stable. The isothiocyanates were relatively unreactive and could only be incorporated in small amounts into the copolymer.

We were interested in finding out how the copolymerization proceeded, what exact reactivity the isocyanates had with respect to the anionic chloral polymerization. The copolymerization rate could not be determined in the normally accepted isothermal way because the polymerization had to be carried out below the  $T_c$  and the polymerization temperature was actually the bath temperature of the cooling bath.

The copolymerization of chloral with LTB and TPP at 0°C was followed by  $^1\text{H}$  NMR spectroscopy (65). Information and the mobility of the comonomers and solvent molecules and the polymerization mixture was obtained by measuring the line width of the signals. The comonomers were not uniform in structure and the content of isocyanate units increased significantly in the final stages of copolymerization. The copolymerizations were carried out in a mol ratio of 10 to 1 of chloral to isocyanate with 0.2 mol % of the initiator.

The NMR signals of chloral showed only a slight broadening during the early part of the polymerization. In the last stage when the conversion of chloral was near 80%, line broadening occurred, suggesting the decrease of the mobility of the reagents (52). Although the methylcyclohexane signal of the diluent of the polymerization mixture was remarkably increased with increasing amount of polymer in the mixture even after 50% conversion. The broadening was increased much more than for the homopolymerization of chloral in the presence of methylcyclohexane. For the aromatic isocyanates, regardless of the substituents in the phenyl ring, the mol % of isocyanate incorporated into the copolymers was about the same. Once the isocyanate became less reactive, as in aliphatic or even more in hindered aliphatic isocyanates, they were not as readily incorporated as comonomers in chloral copolymers.

Initially smaller amounts of isocyanate are incorporated into the copolymer, at conversions of 50 to about 75%, whereas the conversion of isocyanate increased and the copolymer was enriched with isocyanate units.

Finally, in the last stage of the copolymerization, the polymer was an almost alternating copolymer. These conclusions suggest that we have a copolymer of "tapered" structure.

#### *v. Thermal Stability of Chloral Polymers*

The objective for commercialization of polychloral was the direct synthesis of the polymer with maximal thermal stability.

Polychloral, like all other polymers, but more important for polyacetals, have end groups that have significant implications. In POM the thermal stability of the end groups was essential for Delrin, as a commercial product.

Polychloral has as the initiating end group a tert butoxy end group, when initiated with LTB. It has a chlorine end group, when initiated with TPP. As anionic polymerization proceeds to high polymer, the end group of the final polymer is an alkoxy end group. The thermal stability of this polymer is rather low. Proton reagents, like water or alcohols will transform these end groups into OH groups.

Chloral polymers with either of the two end groups have insufficient thermal stability and are not very good for practical use. While the initiating end, either a tert butoxy  $(\text{CH}_3)_3\text{COCCl}_3\text{CHO-}$  or a chlorine end  $\text{ClCCl}_3\text{CHO-}$  are stable to nearly 300°C, it is the thermal stability of the terminal end group that determines the stability of the entire polymer chain.

The chloral polymers with  $-O^-Li^+$  end have a maximum rate of degradation (MDR) at 170°C, those with OH end at 210°C, at 300°C with acetate or alkoxy ends. Chloride terminated polymers (obtained by treating the polymer with phosphorous pentachloride) have a MDR of 340°C (66,67).

The stability of 5% isocyanate copolymers, or of chloral homopolymers terminated with isocyanates also have a MDR of 300°C (68).

The terminal group at the end of the chloral polymer chain always seems to be an alkoxy end group. Efforts have been undertaken to end cap this group into a more stable group. Some of the attempts have produced highly thermally stable polychloral samples. Treatment with phosphorous pentachloride produced the most stable chlorine terminated chloral polymer.

Polymerizations were also carried out with chain transfer agents such as benzoyl chloride for TPP initiated polymerization. It gives a benzoate end and a new chloride initiation. Acetic anhydride, acetyl chloride or especially tropylium chloride were also used as chain transfer agents, but produced polychloral samples of lower molecular weight (69).

Polymerizations were also carried out with decomposable cations, such as trimethylsulfonium or dimethylbenzyl sulfonium chloride (70). The idea here was to carry out the anionic polymerization of the chloral and to maintain a counter cation that is directly related with the polymeric anion. On heating, the counter cation would thermally decompose and allow the methyl carbenium ion to react directly with the polymer.

All these treatments gave improved thermal stability but the reactions were not quantitative. There was always an unstable fraction present that could not be eliminated completely. It should be remembered, that polychloral is insoluble in all

solvents, which means that the polymer ends are not available for reagents to interact. It was mentioned earlier that polymer ends of polymers that grow in the solid state (as in POM) have ends that become unavailable for post reaction including end capping.

Hindered aliphatic isocyanates, such as isopropylisocyanate, when added to the chloral polymerization mixture are incorporated only as end groups. They do not seem to be able to propagate with chloral monomer. (71).

We have found that the best way of end capping chloral polymers is by treatment of the polymer with isocyanate or by copolymerization. As it will be mentioned in the next section, isocyanates together with the "left over" strongly attached chloral monomer, terminates the polymer. It form [polymer ends of nearly alternating structure (65).

The other solution of forming stable polychloral is by copolymerization with 5% p-phenylisocyanate.

It was suggested that the melting point of polychloral could be above 350°C and could be as high as 450°C although degradation occurred below that temperature.

*Thermal Degradation Spectrum:* We have found that the most convenient and efficient way to characterize and judge polychloral samples is by thermal degradation. The instruments that were available determined weight loss and also the temperature of 5% weight loss. We felt that this characterization was not sufficient. One of my colleagues in the analytical lab believed it would be possible to determine the rate of weight loss as a function of temperature. With some outside help he set up an attachment to the DTG instrument that could determine directly the derivative of the thermal degradation of the sample. Instead of reading the degradation we could read the rate of degradation (72). We could determine the maximum rate of degradation as peaks in the spectrum. This new technique published in 1967 allowed us to characterize our polychloral samples. It also allowed us to determine unstable fractions and, from the line width, gave indications of the progress of degradation.

With this attachment we studied a number of polymers, most prominently the various kinds of poly(methyl methacrylate). These studies provided the seed for our investigations in academia on head to head polymers of commodity polymers

### *Vi Structure and Properties*

Polychloral is insoluble in all solvents, does not melt or fuse. The polymer is stable to acids, even oxidizing acids but degrades in hot amines. The density in water is 1.65 g/cm and in n-decane 1.9 g/cm. The theoretical, calculated density is 2.05 g/cm.

We have already mentioned earlier the results of our DSC studies regarding the thermal properties of chloral polymers. None of the polychloral samples showed any transition in the temperature region where a  $T_g$  was normally observed in addition polymers. At 210°C, a polymer sample was drawn for the x-ray fiber investigation which seems to indicate that there is some movement of the polymer chains. Thermal mechanical analysis of chloral homopolymer also showed no changes until nearly 300°C.

The tensile strength of polychloral is several hundred thousand psi, a tensile modulus of 2.5-3.5, a toughness (Izod impact) of about one-foot pounds (per inch), and an elongation at break 5% to 15%. When a good sample of polychloral was aged for 1500 hrs at 100°C in boiling water, the tensile strength was essentially the same although some weight loss had occurred. The hydrolytic stability of a 3 mm thick bar was also tested. The sample had a final weight loss of 0.1% per week in boiling water in a test that was exceeding one year. Other mechanical properties such as dynamic mechanical properties, dielectric intensities were also measured as well as wide-angle x-ray, microscopy, and light scattering.

A polychloral filmstrip that was drawn over a hot pin showed a c-axis of 5.1 Å and a  $4_1$  helical repeat unit. Computer simulation established the exact structure of isotactic polychloral as an  $11_3$  helix with a repeat of 5.23 Å. Chloral homopolymers and copolymers of chloral and p-chlorophenylisocyanate were studied by magic angle  $^{13}\text{C}$  NMR spectroscopy (73). The acetal carbon had a chemical shift value of 101.4 ppm down field from tetramethylsilane. The symmetrical sharp resonance of 3 ppm indicated that polychloral was stereoregular and isotactic. Spectra of chloral / p-chlorophenylisocyanate showed additional small peaks between 130 and 150 ppm coming from p-chlorophenylisocyanate carbons.

The  $^{35}\text{Cl}$  NQR spectrum (74) showed a broad asymmetric line that could be separated into two peaks. The ratio of the integrated intensities of these lines was 123.5 with the centers at the peak of 39.585 MHz and 39,785 MHz. The line width of the deconvoluted peaks were 300 KHz and 270 KHz. The ratio of the integrated intensity is 1 to 3.5. The two chlorine peaks indicate a difference in the population of the position the chlorine atoms of the trichloromethyl groups corresponding to two different environments of nearest neighbors. The results are consistent with polychloral having a helical polymer with 3.5 monomer units per helix repeat, very similar to the 3.67 found from computer calculations (75) (Figure 19). When

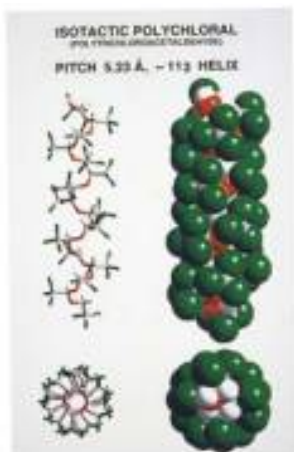


Figure 19: Computer Calculated Structure of Polychloral

polychloral was fully established as a good prospect for commercialization, Other objectives had to be met as the project shifted into the status of potential commercialization: Monomer purification and purity; knowledge of the initial steps of the polymerization; the ultimate thermal, oxidative, and hydrolytic stability of polychloral samples; the most effective and instant stabilization; the fabrication of samples for ultimate use.

To have a steady supply of chloral monomer with less than 100 ppm impurities, a 5 L distillation was continuously under reflux.

Hank Miller joined me on the polychloral project. Hank brought much experience in applications to our polychloral effort. He quickly confirmed my results and expanded on the application side. He worked out details with imagination and innovation.

Because of the shrinkage during the monomer chloral casting, sheets and films were made between glass plates separated with flexible spacers, gum rubber for sheets or Lycra yarn for films (76,77). Much of the work was done with triphenylphosphine initiated 5% p-chlorophenylisocyanate copolymers. By the end of our joint work we made 1/8" sheets (Figure 20) filled with 5% ferrous oxide to simulate Spanish style tiles for roofs. His most spectacular contribution was

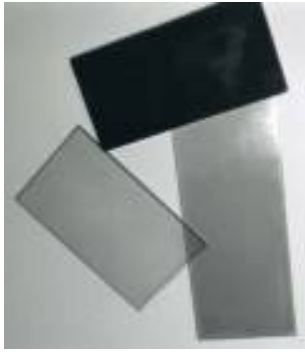


Figure 20: 1/8" Sheets of Polychloral

the solution to our shrinkage problem - the stovepipe principle. This was not my idea but that of my lab partner Hank Miller. The initiated monomer was poured into the mold and cooled "from the bottom". The assembly was lowered in a continuous way into the ice water bath, and solid piece without voids was obtained. This way he made pipes with a wall thickness of 1/2," he also imbedded an entire small radio.

Hank did much of the work on fillers and additives and prepared chloral polymers and copolymers of various filled compositions. The fillers were mixed into chloral and comonomers prior to the cryotachensic polymerization. After complete mixing the desired quantity of initiator was added and the mixture polymerized. Shaped objects were prepared such as flat, curved, corrugated or otherwise shaped sheets. The mechanical properties of the reinforced copolymers compared with those of the homopolymers. Mechanical properties of the reinforced copolymer panels compared favorably with the mechanical properties of fiberglass reinforced polymer compositions.

Copolymers of chloral and phenylisocyanates were prepared by Hank Miller with glass wool, with fibers of pivalolactone, polyethylene terephthalate, polypropylene and fiberglass. Copolymer was also prepared in the form of a fabric reinforced and non-reinforced pipes. Chloral copolymers were also filled

with carbon black, with a blue pigment, with Teflon flock composites and with various other pigmentations including titanium dioxide. All these examples became part of a large patent case. Examples in the patent, also described foamed polymer compositions with various Freons as foaming agents and various intricate modifications to make copolymer sheets.

This was a large patent case and included my, as well as Hank Miller's work, although he was not the co-inventor as determined by the company. DuPont applied for patent protection in a number of countries with a different strategy from country to country. It is also interesting to point out that during this period the patent law in this country and the implications had changed. Certain aspects of the inventions had to be patented from different points of view in the various countries. I spent months supporting the needs of our patent lawyers and became almost an expert in patent law and international patent law.

Hank was also responsible for the design of a test to detect the formation of phosgene during burning. He standardized the GC detection against survival of rats and found that about 5 ppm was tolerated by the rats.

Shortly after I left for the University of Massachusetts, DuPont abandoned the polychloral project. When the project of commercialization of polychloral had been conceived polychloral had many of its properties that were highly desirable, the polymer was nonflammable, did not melt and drip and had no liquid phase on heating. It did not decompose until nearly 300°C and the projected price of the monomer was very desirable. At the end of our investigations, disadvantages became predominant. In a fire polychloral produces phosgene and casting process under anhydrous conditions on a commercial scale was not acceptable. In addition, the monomer chloral had become a controlled substance

The failure of commercialization of polychloral was unfortunate and the company had spent about \$ 800,000 on this effort. From the scientific point of view the

polymerization of chloral and polychloral with all its ramifications became a huge success and a gold mine for me. In the following 10 years we clarified many points that had been left undone at DuPont. Chloral polymers, being isotactic, became the basis of our concept of Macromolecular Asymmetry, the genesis of stereospecific polymerization and the rigid single helix.

### *vii. Polychloral Blends and IPN's*

In the previous sections we have described our work that was done on chloral homopolymerization, chloral copolymerization, chloral stabilization and properties of polychloral. Polychloral and its copolymers with more than 80% chloral units in the copolymers were insoluble and infusible it meant it was not possible to prepare blends involving polychloral by the usual technique of melt or solution blending. However, we found it to be possible to prepare single-phase composites of chloral polymers and copolymers with addition polymers by a technique, which we called sequential polymerization.

According to the patent (78), the sequential polymerization consisted of a single-phase composite polymer comprised of a chloral copolymer and of an addition polymer, which were separately formed, but inseparable polymers. According to the patent they were chemically linked to each other to the extent of less than 10 % by weight of composite copolymer wherein the chloral copolymer was a chloral homopolymer or a copolymer of chloral and at least one comonomer selected from the group of isocyanates and ketenes.

These copolymers and interpenetrating networks were made also by a process of forming a single phase composite polymer comprising dissolving at the temperature above the threshold polymerization temperature of the chloral component a preformed addition polymer prepared from at least one monomer which included polyolefins, acrylates and epoxides. The mixture was then initiated above the ceiling temperature

and cooled to prepare the copolymers. The addition polymer was now intimately mixed into the copolymer unit. By this technique it was possible not only to make the normal polymers, but it was also possible to form the interpenetrating networks as a transparent to translucent material indicating the high degree of interpenetration. It was also possible to make these interpenetrating networks with additional fillers, inorganic fillers such as with pigments or carbon black. The interpenetrating networks could be prepared in the presence of fibers causing reinforcements, in the form of films and sheets and in the form of stabilizers. The polymers used for this technique of first dissolving the polymer followed by chloral polymerization were poly(N-vinylcarbazole), poly(methyl methacrylate), poly(ethyl acrylate), polychloroprene and terpolymers of ethyl-propylene-1,4-hexadiene.

Another technique of preparing these single phase composites was by adding the chloral and the addition polymerizable monomer, a radical initiator for the polymerization of the addition polymerizable component and the initiator for the chloral polymerization and/or copolymerization for example isocyanates (79,80). This polymerization was carried out under quiescent conditions and had the following two steps: First, the uniform solution was cooled below the threshold polymerization temperature of chloral, or chloral comonomer mixture, polymerize it (using the addition monomer as a solvent - which, incidentally gives higher chloral polymer conversions as it is known for any chloral polymerization in an inert solvent) and then, secondly, cause the addition polymerizable component to polymerize, for example, by raising the temperature above the temperature at which the radical initiator would decompose to cause the radical polymerization of the addition monomer.

As addition monomers styrene and methyl methacrylate were studied. When the polymerization was carried out a semi-interpenetrating network was formed in that the addition polymer was linear and still soluble and could be extracted with the appropriate solvent, though not completely from the blend of polymers. Specific examples were the copolymerization of chloral and phenylisocyanates in the presence

of ethylene-propylene terpolymer, the homopolymerization of chloral in the presence of polystyrene, of polyacrylate, of a blend of polyvinyl(acetates) in the presence of poly(N-vinylcarbazole) and various other addition polymers.

If the addition polymer had a crosslinking agent such as divinylbenzene or ethylene-di-acrylate then the interpenetrating network was formed.

One variation was devised as follows: A relatively porous film of polychloral was allowed to have its voids filled with the addition monomer (with an azo-type radical initiator dissolved in the monomer). Once penetration of the monomer into the voids of the polychloral film was complete, the addition monomer was initiated by heating the film to the decomposition temperature of the radical generator, which caused the polymerization of the addition monomer in the channels of the polychloral film. Again, when this was done with the proper crosslinking agents, insoluble polymer were formed within the polymer chloral film.

Blends and interpenetrating networks of polychloral with polystyrene and poly(methyl methacrylate) or poly(methyl acrylate) as addition polymers have been successfully prepared in the form of plugs and as films by "sequential polymerization". The addition polymers were completely extractable. In the presence of crosslinking agents, divinylbenzene for styrene and ethylene dimethacrylate for methyl methacrylate, interpenetrating networks with polychloral could be obtained.

Polymer blends and interpenetrating networks of chloral and homopolymers of various vinyl addition polymers were prepared by the sequence of two polymerizations. Initially the mixture of chloral, its comonomer, the olefin addition monomer and its initiator was heated above the threshold temperature of chloral polymerization. The initiator for chloral polymerization was then added and chloral was polymerized by cryotachensic polymerization. After the polymerization was complete, the mixture was warmed to the decomposition temperature of the radical initiator for the polymerization of the olefin

addition monomer. The polymerization of the vinyl monomer was then carried out within the polychloral matrix. It is very important to use relatively unreactive radical initiators for the polymerization of the olefin monomer, such as AIBN. The total conversion of all the monomers to polymers was 95%; it was very easy to prepare films by this technique.

The chloral interpenetrating addition polymer blends were studied for their properties and morphology. The blends of chloral/p-chlorophenylisocyanate and polystyrene were investigated for their thermal physical and mechanical behavior. The thermal degradation of the two individual polymers were independent of each other. The mechanical properties of the polymer blends were like those of two brittle polymers. In the swollen state the selective swelling of polystyrene gave high elongation, lower stiffness and improved tensile strength.

No  $T_g$ , not even that of polystyrene was observed, indicating a high interpenetration of the two polymer components. X-Ray and electron microscopy studies indicated that the domain size of polystyrene in the polymer matrix was about 200 Å to 500 Å. The DSC analysis showed at temperatures between 250°C and 350°C two strong endothermic peaks with bimodal characteristics. It appeared that the polychloral/polystyrene blends were substantially phase separated. They have a channel type foam structure in which polystyrene is imbedded.

The work on polychloral and its potential as a commercial product was rich in novelty and experience, which was invaluable for the rest of my career.

## **b. The Adamantalogous Series**

Completely strain free cage systems have fascinated organic chemists since adamantane was first found in crude oil in the early 1930's.

One concept that developed in the special research group with Burt Anderson was the idea of an adamantalogous series, which begins with adamantane. The structural framework of each member being composed of cyclohexane rings locked in rigid chair position. The "homologous" series consisting of short and long sequences of methylene units had been the basis of paraffin chemistry and ultimately polyethylene. If one could to carve out of the diamond lattice a structure, which was an accumulation of adamantane, rings in "chair form", this polymer would have a tubular structure looked feasible. Today one could consider this concept a forerunner of the now famous family of carbon nanotubes (81).

The name diamantane was selected to be the second member of an adamantalogous series whose three dimensional ultimate is diamond. Triamantane and tetramantane would then be the logical name for the next "linear" member of the adamantalogous series.

The question was, how to synthesize diamantane and the next member, triamantane ? What could one do to design reaction conditions that would lead to a polymerization and which monomer could be used for this polymerization ?

The original idea was to connect our ideas of polymerization at extremely high pressures with the proposal of an adamantalogous series. Could we, under extreme pressure induce benzene to be a hexaradical that could transform into a strain-free "polyadamantane"?

But first the actual practical approach to the problem: Diamantane was not considered easy to synthesize in a conventional way. Consequently we first concentrated on the synthesis of a derivative of diamantane - hexaoxadiamantane (82).

Shortly before we became interested in the possible synthesis of a tubular strain-free polymer of carbon, Staab reported the synthesis of hexaoxaadamantane in nearly

quantitative yield from all *trans* phloroglucitol, 1,3,5-trihydroxycyclohexane with trimethyl-*ortho*-formate. We immediately thought that all *trans*-1,2,3,4,5,6-hexahydroxycyclohexane, scillitol with trimethyl-*ortho*-formate should easily be transformed into hexaoxadamantane. We had forgotten the stereochemistry and an axial conformation was needed. *Trans*-1,3,5-phloroglucitol initially in equatorial conformation has flexibility that was needed to transform it to the axial conformation as the reaction proceeded. Scillitol had a much greater structural rigidity to take the equatorial to the axial position, which had to be overcome by more forcing reaction conditions to achieve double ring closure.

First we started with the synthesis scillitol. A 1,2,3,4,5,6-hexahydroxycyclohexane, inositol was commercially available, scillitol was not, Inositol has one hydroxy group in the *cis*, all other 5 in *trans* configuration. It was also known that the *cis* hydroxy group could selectively be oxidized biochemically to inosose. Again Burt had a friend who was able to carry out this tricky biological oxidation, which was to produce inosose in sufficient amounts. Inosose was reduced with LAH to what we wanted - scillitol.

As mentioned scillitol is the all *trans*-hexahydroxycyclohexane and has the hydroxy groups in equatorial configuration which makes it insoluble in non-hydroxylic solvents. We had only one hope for our proposed double ring closure scheme with trimethyl-*ortho*-formate (or later trimethyl phosphite) to succeed. We hoped that the trimethyl-*ortho*-formate would initially react with one or more of the hydroxy groups of scillitol and form soluble mixed *ortho*-esters. We expected that this scheme would "solubilize" scillitol and allow the ring closure to proceed, which actually happened. However it was not enough to have the scillitol derivatives in solution. The cyclohexane substituents still remained in equatorial conformation (Figure 21). We do not know the conformational positions in the solvent of choice, DMSO. Ring closure to hexaoxadamantane with trimethyl-*ortho*-formate does not occur at room temperature. We found that this desired ring closure required higher temperatures and could be carried out in boiling DMSO. These conditions must have forced the equatorial hydroxy

groups now substituted with the solubilizing *ortho*-formate fragments into axial positions which spontaneously cyclized to hexaoxadiamantane (Figure 22).

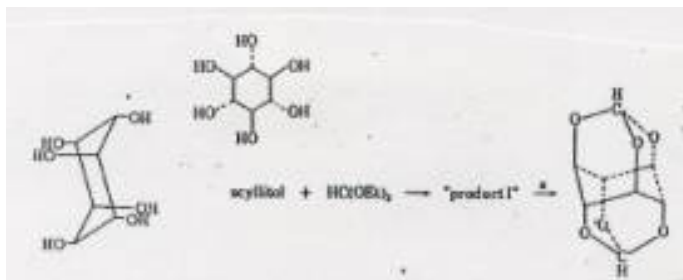


Figure 21: Reaction of scyllitol with trimethyl-*ortho*-formate



Figure 22: Structure of hexaoxadiamantane

Under similar conditions scyllitol with trimethyl phosphite gave diphospha-hexaoxadiamantane. This compound, like hexaoxadiamantane, was soluble and could be readily purified. Diphospha-hexaoxadiamantane was readily oxidized with hydrogen peroxide to the diphosphate. This compound was insoluble and behaved like a polymer apparently because of its strong dipolar structure that was capable of aligning to a "polar" polymer.

I would like to mention a curious and strange coincidence which occurred when we submitted the paper describing and claiming the adamantalogous series which was ultimately published in Tetrahedron Letters in 1966. The manuscript was originally submitted in early 1965 to the Journal of the American Chemical Society. The referee report received in early July pointed out that the compound that we now called

diamantane had been synthesized by a rearrangement of the proper carbon skeleton by carbenium ion rearrangements. It was pointed out that we did not refer properly to the paper that was to be published in the issue that was to appear in late August of the same year (in six weeks time) in the JACS. This strange refereeing behavior was never explained to us.

### **c. Polymerizations under Extreme Pressures**

Some polymerizations such as the polymerization of ethylene are carried out at pressures from 1000 to about 3000 atmospheres.

In the mid 30's the metal alloys were developed that allowed reactors for high-pressure reactions to be constructed. One of the reactions that were successfully carried out was at about 1,500 at was the polymerization of ethylene High-pressure reactions that sometimes lead to polymerizations were reported by Bridgeman and Conant. In the so-called Bridgeman apparatus pressures in the range up to about 8000 atmospheres could be achieved.

After the war a high-pressure apparatus became available at the National Bureau of Standards, which allowed the creation of pressures up to 20,000. Leo Wall established a group of scientists to work on polymerizations at high pressures, particularly the polymerizations of fluorocarbon olefins. Wall published his book on high-pressure reactions, he concluded that above about 20,000 no new polymerizations were expected to occur.

For polymerization reactions under pressure, steric factors have been cited to explain the precedence of termination and alternate reactions over the propagation to linear polymers especially in internal olefins and in cyclic olefins like cyclopentene. Consideration of the effect of pressure on rates suggest that propagation is favored more than other reactions by pressures above a few kilobars. High pressure has been

used to carry out reactions not possible atmospheric pressure and to accelerate the rate over other reactions. In the 1950's pressure apparatus were developed based on Bridgeman's principle of massive support and solid pressure transmitters, possessing useful working volume. This made research at pressures of more than 5 GPa and temperatures up to 1500°C practical. A most convenient device for this work is the tetrahedral anvil apparatus (Figure 23).

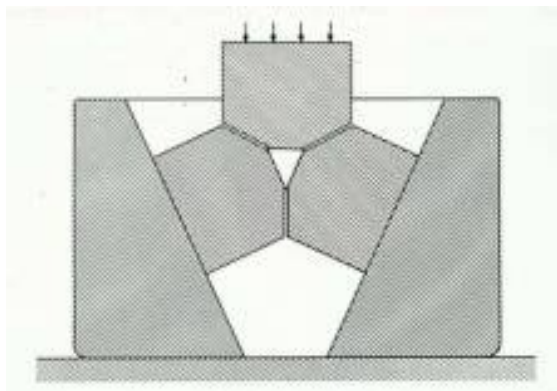


Figure 23: Tetrahedral Anvil Apparatus (schematic drawing)

At DuPont this apparatus was available. It could in principle up to 100,000 atmospheres pressure. Indeed, a number of reactions were carried out that created new primarily of inorganic materials. The tetrahedral anvil apparatus played also a role in the discovery of chromium dioxide. which was later essential for the development of high quality magnetic tape. This apparatus was not much used at that time and what is more important, its ingenious operator, Connie Hoover was available and willing to cooperate with us.

Monomer for polymerizations are usually liquids or even gases and condense just below room temperature. Connie, Burt's and I sat down and tried to design a small reaction vessel that would contain liquids with boiling points down to about -20°C. A set up that could then be operated at the pressures of the tetrahedral anvil to 65,000 at without leakage. Burt designed a platinum tube that could be sealed (platinum sealed) and placed in the solid flow material of the tetrahedral anvil apparatus. The seize of the reaction tube,(actually barrel shaped) was such that it could contain 0.2 ml of liquid .

Gases boiling at  $-15^{\circ}\text{C}$  could also be sealed (Figure 24), the small barrel had to be filled correctly (under dry ice cooling) but it could under no circumstances be overfilled. Thanks to a skilled technician the sealing turned out very well with a high yield of successful sealing. The little reactor was placed into the flow material,

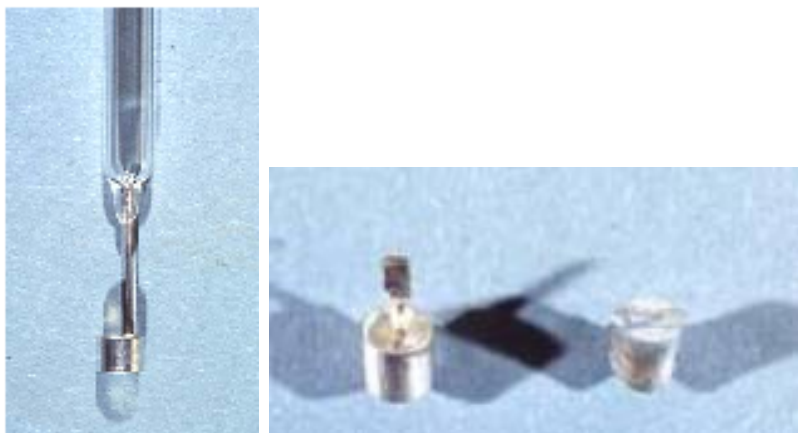


Figure 24: High Pressure Reactions, Platinum Reaction Tube

the anvil sealed and pressure applied. It was necessary to carry out the reactions at  $300^{\circ}\text{C}$ . It was known that pressures of about 100 at increased the m.p or solidification temperature by one degree. It was experimentally (by trial and error) found that only at  $300^{\circ}\text{C}$  was mobility in the monomer achieved that allowed a reaction to occur. The barrel was kept for 3 hr at  $300^{\circ}\text{C}$ , cooled and taken out. The little barrel had superficially the outline of the tetrahedral shape of the pressure that was exerted. One run (with preparation and clean-up) required a whole 8 hr shift

The platinum barrel was carefully cut opened with a sharp knife and the reaction contents examined. At this time NMR was not available, and all the characterizations were carried out by elemental analysis and IR. spectroscopy.

It is very unfortunate that NMR analysis that could handle very small samples was not available at that time; now it is easy to obtain NMR spectra routinely from samples in milligram quantities. It would have been very nice to analyze the stereochemistry of

these compounds but it should be pointed out that for each run only 0.2 g of samples were available.

The apparatus was basically a barrel shaped platinum tube that could be filled by condensation with the liquid material, pinched, crimped and platinum sealed. The small little barrel of about 5 mm tall and about 3 mm in diameter contained about 0.3 g of liquid.

Not only did Burt and I have Connie Hoover as the expert in running the high-pressure apparatus with all its ramification (it took 8 hours or one shift for one run). Burt and I had just hired a new technician of unusual quality, Lem Hammond. He recognized and appreciated the problems (and if my recollection is right) about 80% of the sealings were successful, that is the filling of the apparatus and platinum sealing without a leakage. Because of technicalities it was very easy to overfill the container, which caused a rupture and failure during the run. Burt and I had ran over 100 of those runs in a period of two years.

Earlier studies were limited to solids because no container was known which could contain liquids in the tetrahedral anvil apparatus. The net effect of pressure on polymerization of a compound clearly depends on the influence of pressure on the individual rate constants of the initiation, propagation, and termination. The acceleration of the polymerization by pressure is caused by the increase of the rate of chain propagation and the decrease in the rate of termination of the polymer chain.

Nearly 50 monomers (83,84), olefins, dienes and miscellaneous monomers many of which have not been polymerized before were subjected to up to 6.5 GPa of pressure in the tetrahedral anvil apparatus and temperatures up to 300°C. Most monomers produce polymers under those reaction conditions. The polymers were viscous oils to waxy greases and in some cases hard solids. No initiators were used for the high-pressure polymerization and it is assumed that those polymerizations were induced

by radical produced under these heroic conditions. It was found that cyclic olefins including cyclohexane, internal olefins including tetramethylethylene 2-butene and others gave polymers by 1,2 addition polymerization under those conditions. No polymerizations were observed much below 200°C. In spite of these heroic polymerization conditions the reaction products are colorless and oligomers to low molecular weight polymers. Spectroscopic analysis indicated they had indeed been produced by 1,2 addition reactions without rearrangements and without side reactions produced in the reactions of monomers. This is particularly important because the polymerization of internal olefins particularly of 2-butene have been published in the early 60s and its polymerization created quite a sensation, only later was it found that the reaction caused by acid clays caused initially a rearrangement of the internal olefin to the terminal olefin which then polymerized. All polymerizations of 2-butene by transition metal initiators or by solid support such as clay were finally traced to rearrangement and the 1-butene polymerized and the polymers consisted only of poly (1-butene) structures.

More recently, in the last few years the polymerization of some internal olefins, most prominently of esters of maleic acid and fumaric acid but also maleic anhydride under very specific conditions produced high polymers with interesting properties by radical means.

No catalysts or initiators were added. The reaction was either initiated by high temperature, trace amounts of impurities, or by the platinum surface of the reaction vessel. Trioxane was one of the monomer studied by this technique and was and still is known that it only polymerized by a cationic mechanism.. Consequently cationic initiation had occurred.

The polymerization experiments were carried out for various reasons. For TO because the polymerization was well known, and the polymer was well characterized. For internal olefins because they could not be homopolymerized at that time (Figure 15).

For example, 2-butene was known under certain conditions to polymerize but was subject to rearrangements and poly(1-butene) was obtained. Cyclic olefins such as cyclopentene polymerized.

Another objective was to see if it was possible to contain lower boiling (below room temperature) monomers such as vinyl chloride, butadiene and isoprene. Indeed with great care these monomers could be filled and sealed in the little platinum container (by our technician Lem Hammond).

The following unsubstituted cyclic olefins were polymerized in 55 to 75% yield. cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclododecene,

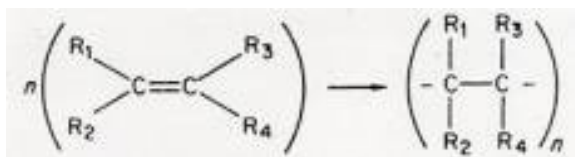


Figure 25: Polymerization of Olefins

The following internal olefins were polymerized in 70 to over 90% yield. 1-methylcyclopentene, 1-cyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, 1-phenyl cyclohexene, methylene cyclohexane, 1-methylheptene, 3-methylcyclooctene, norbornene

Cyclic Dienes in 90-100% Yield: 1,4-cyclohexadiene, 1,3-cyclohexadiene, norbornadiene, 1,5-cyclooctadiene, *trans, trans, cis*-cyclododecatriene, 1-methyl-1,4-cyclohexadiene.

$\alpha$ -Olefins, mostly 90% yield: butene-1, pentene-1, isobutylene, hexene-1, 3-methylpentene-1, 4-methylpentene, styrene,  $\alpha$ -methylstyrene, methyl methacrylate.

Internal olefins in yields of 50-80%: 2-*cis*-butene, 2-*trans*-butene. 2-*cis*-pentene, 2-

*trans*-pentene, 2-hexene, 2-methyl-butene-2, 2,3-dimethylbutene-2, 1-cyanobicyclo [3.1.0]hexane indicating a radical mechanism for the polymerization. Dienes in 60-80% yield. butadiene-1,3, 2-methylbutadiene-1,3, 2,3-dimethylbutadiene-1,3, 1-methylbutadiene-1,3, 2-chlorobutadiene-1,3, 2,3-dichlorobutadiene-1,3, 2-cyanobutadiene-1,3 mostly black powders at 300°C,

TO which is known to polymerize only by a cationic mechanism gave POM in quantitative yield.

Burt Anderson and Connie Hoover continued the work on the polymerization under extreme pressures and focused on the polymerization of 1,4-benzoquinone. This compound gave a polymer that was extremely hard similar to diamond.

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## IV. At the University of Massachusetts

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### The Beginning

I had been an Instructor at the University of Vienna from 1948 to 1955 and I had dreamed of becoming a University Professor. My education at the University had prepared me for a position on the teaching staff of the University, but the question was would circumstances develop that would favor my becoming a Professor in Vienna ? Because I had no family connections nor did I wish to become involved in party politics, obtaining a professorship in a reasonable time in Vienna would be very difficult if not impossible. As a consequence, I came to the US, became a post doc fellow for 3 years and ultimately spent several years in industry. I worked for 13 years at in research at DuPont, the "industrial Harvard". When I left Princeton I was not sufficiently prepared for a professorial career in a "good" academic institution. I had not perfected my English and I was not yet familiar with the "American" way of succeeding. These necessary fine points I acquired through my experience in industry.

I had carried out research in industry on inventive and quasi-academic subjects. I still expected to eventually obtain an appointment as a Professor at a prominent University. In 1969, I was approached by representatives of the Polymer Program of the University of Massachusetts and was asked if I would consider joining them as a Professor on their faculty. I accepted the appointment at the University of Massachusetts for June 1970 in the Polymer Program at the University which was not a department but a "Program" reporting to the Dean of Natural Science and Mathematics. I was one of four Professors and my responsibility was organic chemistry of polymers.

When I arrived in Amherst with my family I was faced with a multitude of challenges. I expected them and was looking forward to my new position with great anticipation. The University life in Amherst, as in all Universities with emphasis on research, was based on the three traditional pillars: teaching, research and funding. The Polymer Program at the University had just been created. As soon as I arrived I was told that in two weeks the summer program in which I was expected to teach a 20-hour summer course on polymer synthesis was scheduled to begin. Having had little experience in classroom teaching in the US the preparation of the course was a challenge and a new experience. I was familiar with Polymer Chemistry and with many of its practical aspects from industry. This summer course became, with many improvements, additions and deletions, the basis of the course that I was to teach for many years to come.

Once I had the summer course organized, I had to develop my research program. In the beginning I had no students in the Polymer Program, but I found a chemistry student, H. J. Chang, a delightful person who was interested in joining my program and I started my first research project. I also needed funding to provide for Chang and other students and future coworkers. This meant obtaining grants from government and other agencies, and later, from industry.

In this section we are only concerned with the research aspects of my activities. How were the research projects conceived, what inspired them and how were they influenced by past experiences ? You must remember that few new ideas and inventions are not based on previous experience and knowledge.

As I indicated my research was influenced by my past. From the time of my thesis and my days as an Instructor I was an organic chemist. I was accustomed to thinking that natural products were of the greatest and perhaps only importance. These compounds had biological activities, were optically active and chiral. In the meantime I had spent time in industry and had significantly contributed to polymer science -- aldehyde polymerization, well recognized at that time as a new and exciting field that could possibly become important - it did not.

I had developed some interest in what I later called "Functional Polymers." It started with reaction on polymers with a potential of introducing biologically active groups into polymer structures. I also had developed some interest in structure/property relationship in polymers of unusual structures. Structures that were similar to the structures of polymers that we know as commodity polymers: These have head to tail attachments, we decided on the complementary head to head structural attachments of the monomers.

Polyamides had been of interest since my involvement in the Nylon 62 project. This project was finished but it had spawned another: Regular Polyamides.

With these initial projects and the remnants of the abandonment of the aldehyde polymer projects from the DuPont days I started my new research career at the University of Massachusetts.

I will first discuss the exciting developments and discoveries on the polymers of chloral, the polymer of optically active polychloral, the trihaloacetaldehyde polymers, and the genesis of chloral polymerization.

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## **A. Macromolecular Asymmetry and the Single Helix**

### **a. More Isotactic Polyaldehydes**

Aldehyde polymers are similar to the polymers of olefins but they have some fundamental differences. A methylene group is substituted by an acetalic (ether) oxygen and the C-C linkage of 1.54 Å is replaced by the C-O linkage of 1.41 Å. This means that the zig-zag of the bonds that result in an all trans conformation in polyethylene results in a helical conformation in POM of a helix approximately  $2_1$ . As the key hydrogen atom in polyethylene is substituted by a methyl group, polypropylene, the isotactic structure

changes from an all trans conformation to a  $3_1$  helix with a  $120^\circ$  torsion angle. The same change in POM changes the structure of the polymer from a  $2_1$  helix to a  $4_1$  helix for polyacetaldehyde (1-3). These structures still randomize in solution and retain the isotactic structure. As Pino suggested in a talk at a Gordon Conference in the early 60's, helical structures of several turns of the helices are probably retained in solution.

As the side group size and the bulkiness increases the polymer chain becomes stiffer and stiffer. This effect was carefully explored in acetal polymers with increasingly larger side chains (Figure 26). It became obvious when it was recognized that polychloral with a trichloromethyl

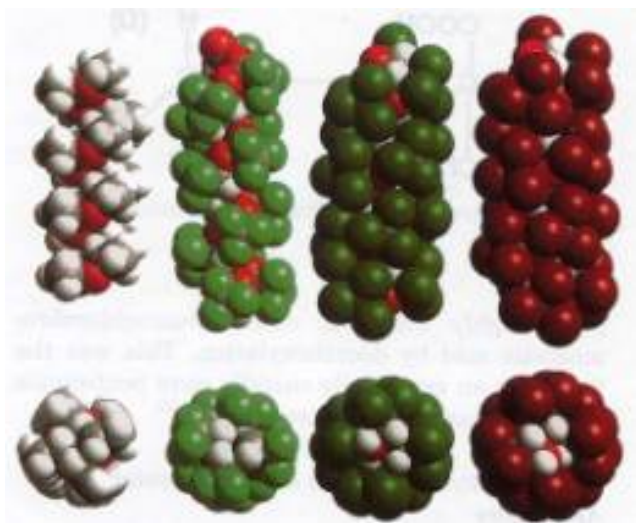


Figure 26: Computer Calculated Polyaldehyde Structures; Polyacetaldehyde, Polyfluoral, Polychloral, Polybromal

group attached to the aldehydic, polymerizable group, existed only in an isotactic form.

It was known from the work of Corradini on the structure of polypropylene, that for statistical reasons, helical polymers existed as 50:50 mixtures of left and right-handed helices. In fact it was later shown, that the arrangements of the left and right-handed helices are the results of different phases of helical polymers. This is well documented for polypropylene.

Having on hand the rigid helix structure of polychloral (26), it was obvious to propose to prepare the polymer of polymer structures on only one "one-handedness", It was this consideration that led to the concept of optical activity based on macromolecular asymmetry.

We have learned the rules for the development of stereospecific and conformational specific polymers, the rigid helix and optical activity based on macromolecular asymmetry (27-38). We have found under which conditions helical one-handedness can be achieved and that chiral nucleation might give entirely new structures of helical polymers. Since most polymers that crystallize in helical structures, give, for statistical reasons, mixtures of 50:50 left and right handed helices, such as PP. It should be possible to crystallize polymers to polymer single helix structures by chiral nucleation.. This principle should not be limited to chiral isotactic structures but to other helical structures such as POM, POE, polytetrafluoroethylene, and poly(1,1,2,2-tetramethyl ethylene oxide. A good example has been shown in the chiral nucleation of the crystallization of the inorganic salts, sodium chlorate and sodium bromate.

Reasons for the one handedness of the Polymer Helix: 1. Chiral center is in the main chain. Examples: Poly( $\alpha$ -amino acids), polylactides. 2. Chiral center is in the  $\alpha$ -position to polymerizable group. Examples: Nucleic acids, poly-3-methylpentene, poly(citronellal). 3. No true chiral center in the monomer unit, but one-handedness in a polymer helix is introduced by chiral additives. Example: Polyisocyanates. 4. Rigid helix. configurationally and conformationally specific. Examples: Polychloral, some poly(triaryl methacrylates). Chiral initiators: Chiral anions and chiral cations. 5. Chiral separation of rigid helix polymers; e.g., on chiral columns. Examples: Polyisocyanides. 6. Chiral nucleation of crystallization of helical polymers with flexible polymer chains.

Asymmetry in chemical structures may result in optical activity. The most common example for chemists is the asymmetric carbon atom. Other atoms surrounded by at least 4 different groups may be capable of existing in asymmetric, chiral, form (11-13). Many parts of our body are asymmetric, hands, feet, and others. Asymmetry may also result

from lack of rotation, as we may see in biphenyl, for example o,o'-dinirodiphenic acid. Crystals might be chiral such as quartz, where optical activity was first noticed and demonstrated by Biota in 1812. Importantly, some inorganic crystals may be obtained by accidental chiral nucleation.

One type of asymmetry was not fully recognized: Macromolecular Asymmetry based on helicity. We have recognized this phenomena early in our work on polychloral. It is the simplest and most convincing example. We had made it our goal, early in our work on polychloral, to prepare the chloral polymer as the single chiral helix. At the same time we felt it was important to establish the rules of how to conduct the polymerization to prepare the polymer with single one handedness of the structure.

## **b. Polychloral**

In 1963 during my initial study of the polymerization of chloral, I recognized that polychloral only existed in isotactic form and by implication would exist also only in a conformational specific form and in a rigid helix. It was considered possible (if the right chiral initiator could be found) to synthesize a rigid polychloral helix with optical activity based on macromolecular asymmetry. The initiator that was then used was cholesteroxide. Although the polymer was prepared, characterized and found to have unusually good mechanical properties, it took 15 years until it could actually be proven that the polymer that had then been prepared had optical activity. It was not quite correct to say it took 15 years because after 10 years, our group started a substantial thrust to prepare solid pieces of polychloral of complete transparency, have them polished properly and measure their optical activity. These measurements were a failure. Even with our present suspension measurements of powder samples, optically active polychloral samples could not be measured because of their birefringence.

On chromatographic columns of lithium alkoxide of cholesterol initiated polychloral was used as the column packing for the separation of racemic mixture of the isotactic polymers of R-(+) or S-(-)- $\alpha$ -methylbenzyl methacrylate. Partial resolution of the polymers

was achieved. (This result strongly implied that polychloral prepared with these optically active initiators had a helical conformation preferential in one screw sense). Polymer fraction eluted at the early stages showed positive optical rotation, those of later stages showed a negative optical rotation. This means that the polymer from the R polymers eluted preferentially from the column. This partial resolution of the racemic mixture is due to the optical activity at the adsorbent. Optically inactive polychloral was prepared with the LTB as the initiator. No separation of the corresponding R(+) or S(-)- $\alpha$ -methylbenzyl methacrylate polymer was achieved (14).

With regular polychloral as column packing, high performance liquid chromatography could also separate aromatic compounds. Three isomers of xylene were separated and several other aromatic hydrocarbons were studied including benzene, toluene, naphthalene, biphenyl, anthracene and pyrene. Interesting separations were also obtained with benzenes, substituted with chlorine, fluorine and methoxy groups (15).

In the late 70s a technique was developed by Steve Corley to prepare polychloral films in a thin form to swell them properly with an isorefractive solvent such as diphenylether, preparing those thin films in an optically transparent way. By rotating the films at random and stacking several very thin films, it was possible to make measurements of optical rotation of such films that had deviations not greater than 3% to 5%. As a consequence the solid-state measurements in films in transparent and isorefractive films are valid. They provided not only information about the optical activity of the individual polymer chains, but also provide optical activity measurements that are meaningful and probably provide the measurement of the optical activity of polymeric helices of polychloral in a super molecular structure. These super molecular structures were found in many cases to be not only reproducible but apparently converging to a value of  $4000^\circ$  in some with cases negative rotation and in some cases with a positive sign of the optical rotation.

Optical rotation of polychloral films that were very carefully prepared could be measured in sandwiches of laminated films. In all cases the transparency of the films was good. The polarimeter measurements in a cell containing the laminated films were performed at

three orientations  $0^\circ$ ,  $120^\circ$ , and  $240^\circ$ . The average rotations for the films and the average absolute rotations were determined, together with average specific rotations, and expressed as rotations per millimeters. The rotation used for polychloral samples prepared with achiral initiators were essentially  $0^\circ$ , however, the rotation of polychloral samples prepared by chiral initiators such as phosphonium salts of (+)-ketopinates showed large rotations in the neighborhood of about  $50^\circ$  per millimeters, indicating that high optical rotation could be obtained from polymers that had been initiated by a initiating anion that was chiral, as in the case of (+)-ketopinate and an achiral counterion. Chiral polychloral was also obtained with a chiral phosphonium salt, which has an achiral initiating anion but had a chiral counterion.

The optical activity of polychloral films was firmly established. Corley had demonstrated (4) that (+) and (-) polychloral could be obtained. Chiral anions could produce polychloral of helical asymmetry. Chiral counter-ions in anionic polymerizations could also produce chiral polychloral. How much chirality was accomplished remained a question that ultimately required a careful and involved investigation (5-10).

By sheer accident, first recognized by Corley, but more intensely investigated by Harris, was that the ultimate optical activity of the polymer depended on the history between addition of the initiator and the polymerization by cryotachensic technique. Some times it became practical and convenient to "incubate" the initiated monomer. Subsequent polymerization produced polychloral films with varying degrees of optical activity. Some measurements gave high values of optical rotation after "standing" of initiated chloral monomer, initiated with chiral anionic initiators and kept for various amount of time above the polymerization temperature prior to polymerization. Data were obtained that had optical rotations of  $1000^\circ$  or even  $4000^\circ$ . It should be remembered that the measurements were carefully checked for the quality of the samples measured: Transparency, birefringence and randomness of the sample's position for measurement.

Anionic polymerization of chloral can be initiated by "strong" or "weak" initiators. Strong initiators are aliphatic alkoxides and weak initiators carboxylates or chloride. Harris found

that polychloral samples were made with the following strong initiators, lithium methyl-(+)-hydroxide mandelate gave values of optical rotation as high as  $[\alpha]_D = +3,600^\circ$ , and lithium methyl-(-)-hydroxide mandelate initiated samples as high as  $[\alpha]_D = -4670^\circ$  (16,17). Weak initiators such as tetramethylammonium D(+) or L(-) acetylmandelate gave optically active polychloral with a specific rotation as high as  $-320^\circ$  per ml/dm.g or even  $(+670^\circ$  ml/dm.g (18). It was interesting that the (+)initiator yielded (-)polychloral and the (-)initiator yielded (+)polychloral, which has to do with the absolute configuration of the molecule and is well known. It should be emphasized that the initiator end group contributed at most  $2^\circ$  to the optical rotation of the polychloral samples.

Scattering of the values of optical rotation had been observed and it became apparent that the time and the temperature during the incubation period played an important role in the final specific rotation.

We finally decided that Gary Jaycox should study the initiation of chloral polymerization, the "incubation period" in more detail. We selected first initiators from the series of sterin alkoxides. Two issues came up. Polymerization of chloral with sterin initiators that had the hydroxyl groups in 3 $\beta$ -position, such as cholesterol, cholestanol and allocholesterol, gave, after routine treatment of the initiated chloral monomer, polychloral of rotations of about  $2000^\circ$ ., the 3 $\alpha$ -koprostane, which has a much more restricted stereochemical structure, gave a polychloral with a rotation of about  $3000^\circ$  (19,20).

Jaycox found a sensible solution when he investigated the chloral polymerization as a function of temperature and "incubation time" with lithium (+) and (-) n-octanoxide as the initiator. Polychloral samples, both with (+) and (-) rotation decreased in the value of the optical rotation as a function of time. The decrease was faster at higher temperature and, as the incubation time was increased. The initial values of about  $3000^\circ$ - $4000^\circ$  decreased to about  $1000^\circ$  in about 30 minutes of incubation time.

The values of the optical rotation depend on the wavelength of the light used for the

measurement. Lithium (-)-methyl hydroxide mandelate initiated polychloral gave rotation measurements at the sodium line at 589 nm of  $-4700^\circ$  while at 435 nm it was  $-9500^\circ$ . The data were assembled on Young-Doty plots used for ORD data.

These observations resulted in two major observations. The type of initiators undoubtedly result in immediate and nearly quantitative initiation. The size of the initiating anion and its stereochemistry determines the addition of the first monomer addition and results in a chiral chloral terminated anion.. Incubation could possibly influence the first initiation process. Since these reactions are equilibrium reactions, racemization of the initial chiral addition could occur. However, the basicity of the original "aliphatic" alkoxide" is probably orders of magnitude higher than the chloral terminated addition, they are probably stable and not under the influence of an equilibrium.

Even above the polymerization temperature, the chloral-terminated initiator is in equilibrium with the dimer and trimer. It is there that "racemization" occurs. After 4 monomer units are added, the polychloral oligomer has attained the structure of a rigid helix and the conformational structure that has been developed will remain in the final polymer.

In my opinion, it is the second and third addition of the chloral monomer that is involved in the racemization in the "incubation period". If an equilibration occurs at this period the optical rotation of the final polymer is reduced. The percentage of polychloral chains with single helix sense has been reduced and more "racemates" (mixtures of right and left handed helices) are present.

To summarize our observations: High optical rotation of polychloral samples were observed when the polymerization was carried out rapidly after the mixing of the chiral initiator and chloral monomer. However, when the initiated monomer was allowed to stand an elevated temperature above the polymerization temperature was sometimes the polychloral formed was inactive. The new type of racemization' is related to the stereochemistry of the equilibrium of the initiation step, specifically the degree of

stereospecificity of the addition of the first chloral to the anionic chiral initiator (22-25).

Subsequent addition of monomer units are also subject to the stereochemistry of addition. When the first turn of the polychloral helix is formed, monomer adds then strictly meso- to form isotactic polychloral. This work was later completed in detail using the study of oligomers as the initial and embryonic step for trihaloacetaldehyde polymerization.

If complete control of the stereochemistry of the addition of the first monomer unit to the chiral initiator could be achieved, synthesis of the perfect helix would be accomplished. Conformational energy calculations are being carried out for polychloral and its oligomeric model compounds by using the MM2 program. Among the dimer models ( $X=2$ ), (S,R)-g<sup>-</sup>g<sup>-</sup>, (S,S)-tg<sup>-</sup> and (S,S)-g<sup>-</sup>g<sup>-</sup> were found to be low energy conformation. The meso and racemo fraction in the equilibrium mixture was estimated to be nearly the equivalent. These were also compatible with gas chromatographic data, which clearly indicated that both m, and r isomers were both produced during the early part of the polymerization process. Calculations further suggest that the mm isomer may be the only growing species at the trimer level for the polymer. The isotactic sequence leads to the most preferred conformation. Experimental values of the dihedral angles for the acetal linkage obtained from X-ray diffraction data could be reasonably reproduced by the calculation. The geometries in conformational energies deduced for polychloral with related compounds by the MM2 programs were thus found to be consistent with various experimental observations (39).

To summarize we have shown that isotactic and helical polychloral of high optical rotation can be made from a chiral anion and an achiral cation, but also from an achiral anion and a chiral cation. It would be desirable to explore the polyaddition of trihaloacetaldehydes with salts that have an achiral anion, the chiral cation and ultimately with the right chiral anion and the right chiral cation. Ultimately, I would like to see whether it would be possible to prepare chiral compounds, chiral polymers from bulky achiral anions and chloral in the presence of polarized light.

With our experience with the polymerization of chloral and the chiral initiation for the preparation of chiral polychloral, we decided to concentrate on the embryonic state of chloral polymerization of the preparation identification and characterization of the oligomers from achiral and chiral initiators. This subject will be discussed in a later section of the book.

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### c. Trihaloacetaldehyde Polymers

Polychloral exists only as an isotactic helical polymer. Polyacetaldehyde and polypropylene are known in their isotactic and atactic form. The degree and type of the tacticity in the polymers depends on the type of catalysts and reaction conditions used for their preparation. In our early work on aliphatic aldehyde polymers it had become clear that the bulk of the side chain in the monomer influences the tactic structure of the final polymer. More recent considerations suggest that  $\alpha$ -olefins with bulky groups, such as an isopropyl group produce more readily isotactic polymers.

The literature described briefly the polymers of chloro- and dichloroacetaldehyde. It appeared that a higher amount of insoluble, presumably isotactic polymer, was obtained from dichloroacetaldehyde. We decided not to pursue the question of bulk size with these groups of polymers as examples.

I was convinced that bulk size of the monomer side group alone was responsible for the formation of isotactic polymers in this class of compounds (1-3). As it turned out, the stereospecificity of the polymerization was accompanied by the necessity of conformational specificity and the growth directly into a helical structure.

The polymerization and the polymers of trihaloacetaldehydes provide an ideal example for investigating the influence of the side group size and shape of the stereospecificity of bond opening polymerization to the corresponding polyacetals. The polymerization of the carbonyl group of the aldehyde monomer is well established. Only head to tail polymers can be formed.

Ten trihaloacetaldehydes involving F-, Cl-, Br-atoms are possible. Fluoral and bromal were commercially available and purified. We have synthesized the other trihaloaldehydes.. We expected that the bulkiness of the side group and slightly different electron withdrawing effects influenced the polymerizability of the carbonyl group and the  $T_C$ , which was the case. There is a significant difference in the chemical shift values of the aldehydic proton. The value for fluoral is 9.36 ppm for chloral 8.95 ppm and for bromal 8.45 ppm.

The work on the polymerization of trihaloacetaldehyde was started in my group by Bunichiro Yamada and Richard Campbell. Chlorodifluoroacetaldehyde, dichlorofluoroacetaldehyde bromodifluoroacetaldehyde, dibromofluoroacetaldehyde or fluorochlorobromoacetaldehyde were synthesized by selective reduction of methyl chlorodifluoroacetate, methyl dichlorofluoroacetate, methyl bromodifluoroacetate, and methyl dibromofluoroacetate or methyl fluorochlorobromoacetate with LAH. (4-7)

Dibromochloroacetaldehyde by bromination from chloroacetaldehyde diethylacetal. Bromodichloroacetaldehyde was also made by bromination of dichloroacetaldehyde diethylacetal or from the reaction product of chloral with triphenylphosphine.

Methyl chlorodifluoroacetate and methyl dichlorofluoroacetate were synthesized by fluorination of methyl trichloroacetate. Methyl bromodifluoroacetate was synthesized starting from chlorotrifluoroethylene and methyl dibromofluoroacetate from 1,1-dibromo-2,2-difluoroethylene, methyl fluorochlorobromoacetate in a series of five steps from 1,1,2-trifluoro-2-chloroethylene. It was a key compound in other of our research activities and was carefully characterized by elemental analysis of all the elements.

Bromal as obtained commercially had about 2% to 3% of impurities, which were difficult to remove by distillation. The impurities, believed to be tribromoacetyl bromide, inhibited the polymerization and were finally removed by chemical means.

Homopolymerization of the perhaloacetaldehydes was successfully carried out with anionic initiators but also with some cationic initiators. The rate of polymerization was followed from the disappearance of the NMR signal of the aldehyde proton of the monomers and was determined about 20°C below the threshold polymerization temperature. The thermal degradation behavior of the perhaloacetaldehyde polymerization was also determined. Copolymerizations of individual trihaloacetaldehydes with other trihaloaldehydes, usually chloral, or with aromatic isocyanates were also investigated.

Polyfluoral,  $T_c = +85^\circ\text{C}$ , has been known to exist in a rubbery atactic and a crystalline isotactic form. We found that polyfluoral consists normally as a mixture of a soluble and insoluble fraction. Fluoro substituted trihaloacetaldehydes had a higher rate of polymerization. The ratio depended very much on individual reaction conditions. The soluble part of the polymer mixture, an atactic polymer of reasonable molecular weight, was also characterized.

Chlorodifluoroacetaldehyde was polymerized to crystalline insoluble polychlorodifluoroacetaldehyde,  $T_c = +63^\circ\text{C}$  or to a mixture of amorphous polymers soluble in organic solvents and an insoluble polymer. TPP or antimony pentachloride as initiators gave acetone soluble polymers while triethylaluminum gave insoluble polymers. Soluble polymers of difluorochloroacetaldehyde, by VPO measurements, have a DP in excess of 50. The soluble polymer could be end-capped by acetylation, which substantially improved the thermal stability of the polymer. Chlorodifluoroacetaldehyde could be copolymerized with chloral and dichlorofluoroacetaldehyde (4-7).

Incidentally, and as a sideline, Richard Campbell also tried to synthesize the polymer of tetrachloroethylene oxide, which I believed to be a most desirable polymer now that POM, PEO and recently polytetrafluoroethylene oxide had been prepared. Campbell worked out a very efficient synthesis of tetrachloroethylene oxide. All attempts to polymerize this compound by cationic, and anionic initiators, at elevated and low temperature failed. In most cases trichloroacetyl chloride was obtained in high yield (8).

The polymerization of bromodifluoroacetaldehyde was also investigated. The aldehyde polymerized with both anionic and cationic initiators and has a  $T_c = +48^\circ\text{C}$ . Some initiators produced a soluble polymer of relatively low molecular weight. Most polymers, however, were insoluble. The monomer could also be copolymerized with chloral or with phenylisocyanate.

Initiation of bromodifluoroacetaldehyde with LTB gave completely insoluble polymers. Polymers obtained by TPP initiation were almost completely soluble. Other initiators gave either insoluble or partially soluble polymers. Polymers of bromodifluoroacetaldehydes were acetate end capped which improved their thermal stability significantly.

Dichlorofluoroacetaldehyde had a polymerization behavior similar to that of other trihaloacetaldehydes, and a  $T_c = +41^\circ\text{C}$ . There is one significant difference; most polymers obtained are insoluble. On a few occasions a small polymer portion was soluble but were

not high molecular weight polymers, but oligomers. NMR investigations demonstrated the polyacetal structure with a broad peak centering at 5.3 ppm.

Polydichlorofluoroacetaldehyde was end capped which also improved the thermal stability. Dichlorofluoroacetaldehyde was copolymerized with chloral.

The polymerization of chloral has been extensively investigated and the  $T_c = +14^\circ\text{C}$  accurately determined. The determination of the  $T_c$  of this polymerization was the subject of one example in my Polymer Synthesis lab course and about 20 beginning graduate Students determined the  $T_c$  of chloral polymerization every year with an accuracy of  $\pm 3^\circ\text{C}$ .

Soluble fractions from the polymerization of chloral and bromal have never been isolated. However soluble low molecular weight oligomers have been synthesized and characterized.

Dichlorobromoacetaldehyde was homopolymerized at  $-30^\circ\text{C}$  with anionic and some cationic initiators. The polymer was insoluble and had a  $T_c = -15^\circ\text{C}$ . Alkali metal alkoxides, like LTB, chlorides and fluorides were effective initiators as well as some tert amines and phosphines. Typical cationic initiators were also good initiators for this polymerization. Dichlorobromoacetaldehyde was also copolymerized with aromatic isocyanates, and with chloral.

Fluorodibromoacetaldehyde was polymerized with a  $T_c = -7^\circ\text{C}$ . At elevated temperatures, the polymer vacuum degraded quantitatively to monomer. Fluorodibromoacetaldehyde readily copolymerized with chloral and phenylisocyanate.

Chlorodibromoacetaldehyde polymerization,  $T_c = -40^\circ\text{C}$ , could be initiated with alkoxide such as LTB, but also with amines, acids and Lewis acids. As with other trihaloacetaldehyde polymers, the polymer could be stabilized and vacuum degradation of the polymer gave the monomer dibromochloroacetaldehyde in quantitative yield.

Dibromochloroacetaldehyde copolymerized with chloral and phenylisocyanate to insoluble and infusible polymers, but dibromochloroacetaldehyde was less reactive toward polymerization than chloral.

Bromal was polymerized to polybromal. (8-11) Great skill was required because the  $T_C = -75^\circ\text{C}$ , the lowest  $T_C$  reported. Once the polymer is prepared to an insoluble crystalline polymer, it is stable. The key to a successful polymerization of bromal is the purity of the monomer. Tertiary amines gave polybromal in good yields but TPP was not a good initiator. Polybromal degraded thermally in quantitative yields to monomer. Copolymerization of bromal with chloral with anionic initiators gave copolymers with only small amounts of bromal incorporated. Copolymers of bromal with phenylisocyanate or some aliphatic isocyanates could readily be prepared.

Besides chloral, fluorochlorobromoacetaldehyde was perhaps the most interesting trihaloacetaldehyde (12-15). LTB, tert amines and TPP are very good initiators for the polymerization of fluorochlorobromoacetaldehyde. Polymer grade fluorochlorobromoacetaldehyde also polymerized with sulfuric acid. In all cases crystalline insoluble polymers, without soluble fractions were obtained. The polymer could be vacuum degraded quantitatively to monomer. We were not able to detect a soluble polymer fraction. Fluorochlorobromoacetaldehyde is a racemate of the (R) and (S) form since the trihalomethyl group is chiral. Consequently the polymer could consist of (R) monomer chains, (S) monomer chains or "copolymers" of the (R) and (S) monomer or various compositions. In addition, polymer chains could crystallize in right or left handed helices. It is no surprise that polymers of fluorochlorobromoacetaldehyde were found to have lower crystallinity as polychloral samples.

The objective of this investigation was to prepare and polymerize the enantiomer(s) of fluorochlorobromoacetaldehyde and investigate the chiroptical properties of the polymer. The precursor fluorochlorobromoacetic acid was separated via the strychnine salts into the antipodes. Each antipode was esterified and the (+) and (-) esters reduced with LAH

to the aldehydes. (-) had an optical rotation  $[\alpha]_D = -10.5^\circ$ .

Polymerization of the antipodes of fluorochlorobromoacetaldehyde was accomplished with (+) and (-) Li-2-octanoxide. The optical rotation, of the polymer measured in suspension was slightly enhanced, [to  $23^\circ$ . instead of the  $[\alpha]_D = 10^\circ$  of the monomer], the value is within the error limit of the measurement. We had hoped to demonstrate that the contribution to the value of the optical rotation also included not the value from the monomer but also the optical rotation that was expected from the helicity of the polymer.

### *i. The $T_c$ of Aldehyde Polymerization*

The  $T_c$  of polymerization is the temperature of a 1 molar monomer solution at which the rate of polymerization is equal to the rate of depolymerization. It is the temperature above which a polymerizable monomer is the stable entity and below the polymer is stable. This temperature exists in all addition polymerizations even though the reverse addition may not end up as monomer. The  $T_c$  phenomena is well known in the olefin and also carbonyl polymerization. It depends on the bulkiness of the substituents and the electron contribution of the substituents to the polymerizable double bond (16).

We have experimentally estimated the  $T_c$  of higher aldehyde polymerization, later authors have determined it to be about  $-40^\circ\text{C}$ .

As mentioned before one of the goals of our efforts in studying trihaloacetaldehyde polymerization' was to investigate the thermodynamic driving forces for this polymerization and to determine the  $T_c$ 's of polymerization.

The  $T_c$ 's of trihaloacetaldehyde polymerizations were determined by cooling the initiated trihaloacetaldehyde monomer in an inert solvent until the first cloudiness occurred. The

polymers are insoluble in the medium and precipitate. The cloud point was determined, both visually and by an optical transmission measurement. It was accurate to within  $\pm 2^\circ\text{C}$ . This measurement was much more accurate than any other technique traditionally used to determine  $T_c$ 's. The  $T_c$  for trifluoroacetaldehyde polymerization is  $+85^\circ\text{C}$  with an enthalpy of 13 kcal/mole and an entropy of 37 cal/mole. The corresponding values for chloral were:  $T_c$  of  $14^\circ\text{C}$ , an enthalpy of 9 kcal/mole and an entropy of 32 cal/mole. For polybromal, the  $T_c$  was  $-75^\circ\text{C}$  with an enthalpy of 5 kcal/mole and an entropy of 24 cal/mole. The other mixed haloaldehydes were found to have values somewhere in between.

In the series of trihaloacetaldehydes, the electron withdrawing effect of the substituents was estimated by the chemical shift of the aldehyde protons and the  $^1\text{H}$  NMR spectrum. The frequency of the carbonyl stretching band in the IR spectra also gave an indication of the relative electron withdrawing effect of the trihalomethyl groups.

The effects of the side group bulk in the trihaloacetaldehyde polymers were also investigated. It was concluded that if the entropy and enthalpy of polymerization were plotted as a function of the  $\text{CX}_3$ -radius of the trihaloacetaldehyde we could identify the cause by electronic effects. The increased polymerizability of fluoro- as compared to chloro- or bromoacetaldehydes is largely due to the stronger electronic withdrawing characteristic of the fluoro-containing trihalomethyl groups. The electron negativity difference between fluorine and chlorine is also significant, much greater than that between chlorine and bromine. As a consequence, a much more significant decrease of the DH with increasing  $\text{CX}_3$  group radius was observed.

The behavior of trihaloacetaldehydes under various polymerization conditions was undertaken in order to establish how large a trihalomethyl side group was necessary for the polymer to exist only in isotactic form as is the case with chloral. Also, to establish how large a side group could be in order to have the monomer still polymerizable.

Enthalpy considerations alone indicate that trifluoroacetaldehyde shows the highest and

tribromoacetaldehyde the lowest degrees of polymerizability. The opposite is true if the entropy alone is considered. As the enthalpy factor prevails the  $T_C$  is highest for fluoral and lowest for bromal polymerization while mixed trihaloacetaldehydes have  $T_C$ 's in between.

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## B. Polyamides

At the end of my career at the Polychemicals Department I had spent some time in the Nylon group. The group had been charged to explore and develop new Nylon compositions to strengthen DuPont's leading position in this field. This is how I became involved in the preparation and characterization of polyoxamides and the ring-opening polymerization of c-62. Great strides were made in the Textile Fibers Department. Paul Morgan had discovered the interfacial Polymerization and the aromatic polyamides, Nomex and Keflar were on the way to commercialization. Herman Mark showed

Morgan's Nylon rope trick all over the world. Ten years later at Massachusetts I decided to start my first graduate student H.J. Chang on a simple project that guaranteed success, interfacial polymerization to synthesize regular polyamides.

### a. Regular Polyamides

As a result of our investigation on polyoxamides we had experience preparing diamine diamides (A-B-A). We decided to use the diamine diamides as diamine component for the synthesis of the regular polyamides. It was logical to use the low temperature interfacial polymerization techniques or solution polymerization with another dicy chloride to avoid transmutation and randomization. This method was expected to form A-B-A-C type polymers (1, 2)

The key to this work was to develop efficient syntheses for the synthesis of the A-B-A compounds. A-B-A compounds were not new and a number of routes had been conceived and developed for their synthesis. The method of choice was to develop reliable reaction condition to synthesize the A-B-A diamine directly from the diamine A and the carboxylic acid derivative (B) without the use of intermediates.

The preparation of diamine-diamides (A-B-A where A is an aliphatic or aro-matic diamine and B is a carboxylic acid group) was carried out by direct condensation of diamines with diacid derivatives. This method made these compounds available as monomers for the preparation of regular (Figure 27) copolyamides. It was first demonstrated for the synthesis of

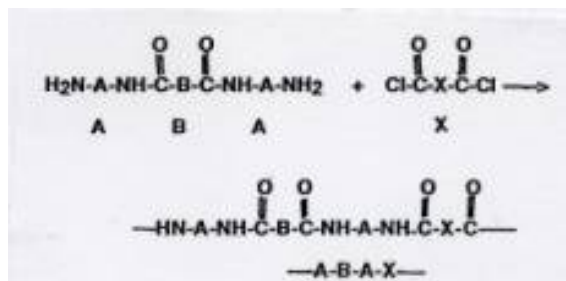


Figure 27: Regular Polyoxamides

N,N'-bis(6-aminohexyl) ox-amide from hexamethylenediamine and diethyl oxalate.

Diaminooxamides were the primary target of our investigations.

$\alpha,\omega$ -Diamine-oxamides with 2-12 methylene groups between the two amino groups were obtained by the reaction of the diamines and diethyl or dimethyl oxalate. Diethyl oxalate was added slowly to a substantial excess of diamine. It was important to optimize the variables for each individual diamine. Diamine-ox-amides were obtained in approximately 80% yield with only small amounts (5-10%) of the corresponding polyoxamides as by-product. Diamine-oxamides from diamines with less than six methylene groups are water-soluble. All diamine-oxamides show an alternation of their melting points and are useful intermediates for the preparation of regular co-polyoxamides (4,5)

Regular co-polyoxamides of the structure  $(A-B-A-C)_n$  have been prepared from aliphatic diamine-oxamides (A-B-A) and diacid chlorides. With the facile preparation of diaminealkylene oxamides, a group of polymers with an interesting combination of properties has become accessible. The principle of the preparation of regular copolyamides has been outlined in a patent by Schlack, but very little systematic work in this area has been done since then.

The preparation of regular co-polyamides requires mild reaction conditions using reactive diacid derivatives in order to avoid rearrangements of the regular co-polyamide structures to random copolyamides. For this reason, melt polymerization of Diaminooxamides and diacid derivatives is not suitable. In addition, the oxamide group is not thermally stable, and decomposition occurs above 280°C. this introduces undesirable links into the polymer chain and furthermore decreases the molecular weight of the desired polyoxamide. In order to prepare regular co-polyoxamides without randomization, di-acid chlorides must be reacted with the proper diamines either by interfacial polymerization or by solution polymerization. Interfacial polymerization was preferred with diaminooxamides where the diamine portion has two to six methylene groups. These diamine-oxamides were readily soluble in water. Regular aliphatic polyoxamides from diamine-oxamides with more than six methylene groups in the diamine portion of the

molecule are better prepared by solution polymer-ization in DMAc.

Regular aliphatic oxamides are soluble in trifluoroacetic acid and hexafluoroisopropanol. They show alternation of the melting point behavior in the di-amine portion of the polyamides with up to five methylene groups. Co-polyoxamides with two and four methylene groups melt higher than the co-polyoxamides with three and five methylene groups. Aliphatic co-poly(oxamides/adipamides) melt at approximately 260°C and show a steady decrease in melting points to about 220°C for polyoxamides with twelve methylene groups. Regular aliphatic/aromatic co-polyoxamides are high melting and generally decompose above 350°C without melting. (IVB 6 - IVB 8) They could be, fabricated from solution and were the basis of our work on desalination membranes.

Aromatic diacid chlorides used included the diacid chlorides of terephthalic acid, isophthalic acid, 2,6-pyridine dicarboxylic acid, two isomeric naphthalene dicarboxylic acid, two cyclo-hexane dicarboxylic acid isomers, as well as 1,1-cyclobutane dicarboxylic acid. A number of these polymers gave dense or asymmetric membranes. Our favored polymer was the regular co-polyamide with isophthaloyl chloride poly(iminoethyleneimino-oxalyliminoethyleneiminoisophthaloyl) (p-222I).

As the number of the methylene groups in the aliphatic diamine portion increased, the polymers became more hydrophobic and the melting point of the polymers decreased from the initial 350°C to near 200°C. Similarly, an increase in the methylene chain length of the diacid portion also decreased the melting point and increased the hydrophobicity of the polymers.

## **b. Polyoxamides as Desalination Membranes**

In the early 70's the United States Government had an Office of Saline Water by now long disbanded. Its objective was to find ways, economic ways to produce, drinkable water from sea water or from brackish water; sea water having 3.5% of salts primarily

sodium chloride and brackish waters with up to 0.8 % of salts. These two objectives clearly required different approaches. I will not discuss the options for large-scale water purifications by distillation, using solar power and favorable solar conditions.

Desalination using membrane technology was in the early 70's an emerging potential technology. Pure water from brackish water and in combination with ultra filtration was also needed for the supply of potable water in Vietnam in the late 60's. Even in Southern California, people needed the technology for "final purification" of water that was slightly brackish and needed final purification to have safe drinking water.

One of the approaches at that time was the use of asymmetric membranes. The first asymmetric membranes were based on cellulose acetate with about 2.5% of acetate groups. In the late 60's, aromatic polyamide membranes were developed, and the patent stated that the amide bonds had to be more than 50% aromatic.

It was clear from our work on regular polyamides, especially polyoxamides that we had potential candidates for desalination membranes that had less than 50% aromatic amide bonds in the polymer. We were determined to optimize the chemical structure of the regular polyoxamides for desalination membrane applications (Figure 28). Asymmetric membranes

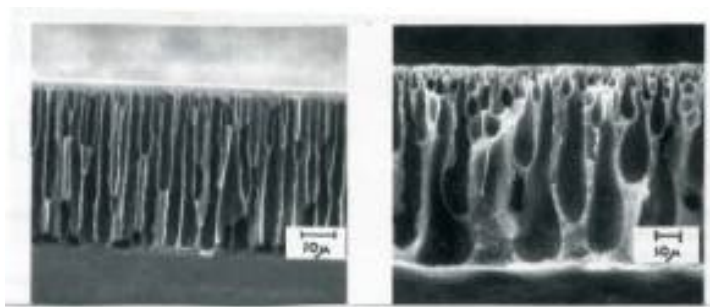


Figure 28: Asymmetric Desalination Membranes

for desalination require not only a desirable chemical structure of the membrane material, but also the mechanical properties for the desalination membranes the proper technology of casting.. The major requirement for the potential polymer were an equilibrium water

absorption of about 20% and a high glass temperature of perhaps 180°C under wet conditions. The preparation of these membranes was a complex process and required controlled evaporation and gelling. Small deviations from optimum conditions resulted in dense rather than the desired asymmetric membranes.

Polymers, which have hydrogen-bonded functionality such as -OH, NH-CO and -NH groups in the macromolecule, have been synthesized and tested as candidates for membrane materials for desalination by reverse osmosis. We have investigated regular co-polyoxamides of the general structure p-A<sub>2</sub>AC where A was an iminoalkylenelmino unit containing 2-6 C-atoms, 2 is the oxalyl unit, and C is a diacyl unit deriving from an aromatic or aliphatic dicarboxylic acid. Our regular co-polyoxamide p-222I. became an excellent candidate. It could be cast from trifluoroacetic acid or DMAc/LiCl solutions into membranes whose structures consist of relatively large pores of various shapes, which had diameters of 50-100 nm. Bound water in p-222I is (a) unable to solvate salts and consequently salt permeation is prevented and (b) able to form ligands with free water. As the amount of bound water per site increased, the flux rate of pure water through the membranes increased.

The morphology of the membranes and the mechanism of water absorption and water retention in the polymeric matrix are factors, which influence substantially the water transport through the membrane. An optimum percentage of water absorption exists for each polymeric material above which the membrane structure loses its mechanical properties and below which the water transfer through the membranes is not sufficiently high.

The equilibrium water absorption ranged from 7% to 30%, varied with the polymer structure and was highest in polymers with high amide concentration. The water absorption was reversible and consisted of a two-step process, rapid absorption of water by polymer followed by a slower second stage as equilibrium is approached. All water is bound to the polymer; it may be freed by heating the hydrated polymer above 100°C, but rebinds completely at room temperature. The water in the regular co-polyoxamides existed in the bound state.

High rates of water transport in polymeric membranes required a high degree of hydrophilicity, while the maintenance of good mechanical properties in the swollen state was favored by a high glass transition temperature or by forming hydrophobic domains. The equilibrium water uptake of selected regular co-polyoxamide was: p-020I: 32%; p-222I:15%; p-222P: 17%; p-2226:14%; p-323I: 8%; p-323P:15%; p-424I:14%; p-424P: 11%; p-4246: 15%; p-626P: 8%; p-6266: 7.%; p-626I 8%; p-22210:12%.

None of the absorbed water froze upon cooling to low temperature. The relative amount of non-freezing water ("bound" water) was found to increase with increasing surface area of the membrane, indicating binding or ordering of water at the membrane surface. The structure of water in membranes, existing in bound or free form had important implications in membrane performance.

In porous polymer films of P-222I, the "skin" is relatively dense "skin" and had a thickness of 500-5000 Å . It is followed by a macro porous substructure, 50-100 mm thick. This asymmetric structure combines the high flux rate of a thin membrane with the -good mechanical properties of a much thicker-film.

All of the water absorbed by the polymer at room temperature and 93% relative humidity is bound to the polymer in such a way that it cannot freeze on cooling. Heating to above 100°C releases this bound water, and a melting endotherm of free water is observed which amounts to 15%, the equilibrium water absorption of p-222I. Already at 50%, rebinding of water occurs and over longer times, complete rebinding occurs.

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## C. Head to Head Polymers

Why did I get interested in head to head (H-H) polymers ? I ultimately wrote over 50 articles on the subject. During our work on the characterization of the thermal stability of the polymer that I was working at

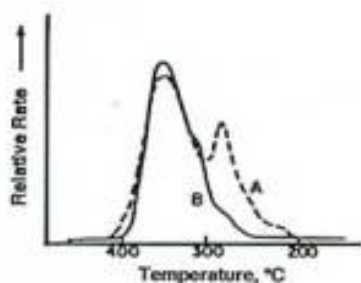


Figure 29 Thermal Degradation Spectrum of PMMA's

DuPont, I had to develop the proper display of the rate of thermal degradation of my polymers. One of the examples of the thermal degradations of polymers was PMMA. It had two perhaps three ranges of depolymerization. Williams and I developed an attachment to the thermal degradation apparatus that displayed not the weight loss of the degrading sample, but the rate of weight loss (Figure 29). – it showed peaks in the degradation spectrum instead of the normal weight loss curves. The peak of lower stability was assigned to the vinyl terminated PMMA chains and the larger to the "saturated" chains, chains that consisted of saturated chains and chains that came from recombination forming a H-H linkage (Figure 30). This inspired me to start to investigate polymers consisting

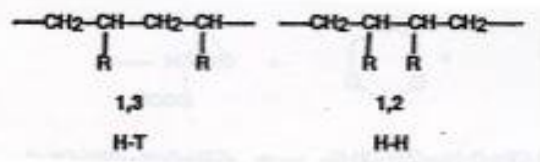


Figure 30: Head to Head Polymers

entirely of H-H linkages - H-H polymers. We could investigate their thermal characteristics, T<sub>g</sub>, thermal degradation, spectral characteristics and see if it would be possible to synthesize them directly.

A second influence was circumstantial. In the early 60's, Monsanto had brought onto the

market alternating copolymers of maleic anhydride with ethylene and styrene. We had already selected these polymers as base polymers for polymer reactions and the study of functional polymers. The ethylene maleic anhydride copolymer was an obvious candidate for the synthesis of H-H polyacrylates.

A third point came into play. In 1968, shortly before I left DuPont for Amherst, I had spent a Semester at Kyoto University in Japan as the guest of the Department of Synthetic Chemistry. My host Professor Furukawa, was by chance the head of the department and arranged that I gave lectures in most important Universities of Japan and major Japanese industrial laboratories. One of them was the research establishment of Mitsubishi Chemicals in Kawasaki, whose Director was Dr. Niwa, a school friend of Furukawa. Two years later, when I was now in Amherst, he asked me if he could send one of his scientists for 2 years to work in my research group. I accepted him and assigned him to work on H-H polyacrylates.

Another aspect of our H-H polymer work is worth mentioning. Since the polymers could not be made directly but required different polymerization techniques. it allowed not only the co-worker who worked on the subject, but the entire research group to be exposed to techniques of polymer synthesis which I thought the student learn to give them a broader understanding of the subject.

## Introduction

Substituted monomers with carbon-carbon double bonds as well as substituted cyclic monomers can be linked in principle in two ways, by the formation of head to tail (H-T) (the normal linking) or by head to head (H-H) linkages (1-5).

The terminology of H-H and H-T linkages applies to "vinyl" monomers, and to "vinylidene" monomers, to mono- and disubstituted substituted oxiranes (ethylene oxides), to substituted butadienes; and to substituted condensation polymers such as polyamides and polyesters. H-H arrangements in condensation polymers are normally not very

important and will not be discussed in this review.

Since vinyl polymers are the best studied cases where H-H linkages play a role, I will briefly comment on the formation of H-H linkages in such polymers. Vinyl monomers are polymerized by successive addition of a vinyl monomer molecule to the growing (usually radical) center, which is normally the substituted part. The monomer adds to the growing by attaching the least substituted part of the monomer (the methylene group in vinyl monomers). This sequence produces a polymer chain bearing the substituents on alternate carbon atoms: H-T linkages.

It has long been realized that flaws can develop in the H-T structure of the polymer chain if an occasional reverse addition occurs. If this type of reverse addition at each step were to continue H-H then T-T, a pure H-H polymer would result.

The question now is: How can H-H linkages actually be introduced in polymer chains? In chain reaction radical vinyl polymerization termination, reactions may occur in two principle ways. One process is by recombination of two growing radical chains as shown, the other is by disproportionation. Disproportionation involves the abstraction of an  $\alpha$ -hydrogen atom by one growing polymer radical from another growing polymer radical forming two terminated polymer chains. One is saturated and one has a vinyl end group. The other type of termination of two polymer radicals occurs by recombination. This type of termination introduces a H-H linkage in the polymer chain.

Recombination of polymer radicals is not the only means of forming H-H linkages in radical polymerizations. Reverse monomer addition in chain reaction radical vinyl polymerization has also been found to occur. Under normal conditions, each monomer molecule is added successively with the predominant formation of H-T structures, but H-T polymerization does not occur exclusively, it depends on the substituent on the vinyl group.

Vinyl chloride has been radically polymerized to PVC. As the polymerization temperature

is increased PVC with H-H linkages of 5% have been detected. Even in vinyl acetate polymerizations 1-2% of H-H placements have been observed at higher polymerization temperatures.

Fluorocarbon polymers have attracted particular attention Poly(vinylidene fluoride) is reported to have 8-10% H-H linkages and poly(vinylidene fluoride), has as many as 32% H-H linkages. Also in these cases increasing the polymerization temperature increased the H-H contents.

In coordination polymerizations of the Ziegler-Natta type, H-H linkages have been found in  $\alpha$ -olefin polymers. Some amorphous polymer fractions of polypropylene (PP) contain H-H linkages. H-H linkages have also been found in polymers obtained from unsymmetrical cyclic ethers, e.g., propylene oxide by ring-opening polymerization, and in polymers prepared from substituted aziridines and oxiranes. H-H linkages have also been observed in polyesters, polyamides and other condensation polymers, where individual difunctional monomer units are asymmetrically substituted. The polymer must, however, be prepared from A-A and B-B monomers and at least one of the monomer units has to be substituted or by ring opening polymerization of substituted lactones and lactams

It was primarily due to the fact that these H-H links occasionally formed in normal chain reaction polymerizations that the study of pure H-H polymers became of interest and highly desirable. Several authors have suggested that weak links in a number of polymers may be caused by H-H linkages, and that the thermal stability of certain polymers might be influenced and their degradation behavior might even be determined by H-H linkages spaced within the polymer structure.

## **a. Synthesis of H-H Polymers**

H-H Polymers with exclusive H-H linkages at the present time cannot be synthesized by traditional polymerization techniques. That does not mean that it could not be accomplished if new concepts could be developed.

Polymerization techniques that allow the synthesis of pure H-H polymers include: a.) Alternating copolymerization; b.) Addition to poly-1,4-butadiene; c.) Diene polymerization followed by hydrogenation; d.) Wurtz or Grignard coupling reactions

### *i. Alternating Copolymerization*

Alternating copolymerization was used early for the preparation of H-H polymers. Copolymerization of ethylene or substituted ethylenes with maleic anhydride (6) or substituted maleic anhydrides, followed by esterification, gave H-H polyacrylates (when ethylene was used). Other H-H polymers such as H-H polycrotonates and H-H polycinnamates, when 2-butene or stilbene, symmetrical disubstituted ethylenes were used as comonomers for alternating copolymerization with maleic anhydride) (7-10). In addition to H-H poly(methyl acrylate), H-H poly(methyl crotonate), and H-H poly(methyl cinnamate) were prepared and characterized.

Attempts to synthesize H-H poly(methyl methacrylate) by alternating copolymerization of ethylene and 1,2-dimethyl maleic anhydride were found to be elusive (11-14). When ethylene and dimethyl maleic anhydride were copolymerized, the best copolymer was of low molecular weight and consisted of three parts ethylene and one part of 2,3 dimethylmaleic anhydride copolymer. Esterification with methanol gave a copolymer with well-established H-H linkages.

### *ii. Addition to the Double Bonds of 1,4 Polybutadienes*

*Hydrogenations of Poly(2,3-Disubstituted-1,4-butadienes):* Another method of synthesizing H-H polymers is by polymerization of 2,3 substituted dienes followed by the reduction of the remaining double bonds in the monomer units in the polymer. This method is the method of choice for preparing normal H-H polyolefins that have hydrogen atoms as one of the other substituents on the carbons atoms.

2,3-Disubstituted dienes must be polymerized to 1,4-polydienes without 1,2 linkages in the polymer. Poly-1,4-(2,3-dimethyl butadiene-1,3) and poly-1,4-(2,3-diphenylbutadiene-1,3) have been successfully and quantitatively hydrogenated to H-H PP and H-H PST respectively.

H-H PP was synthesized starting with the 1,4-polymerization of 2,3-dimethylbutadiene. Poly-1,4-(2,3-dimethylbutadiene-1,3) (15-19). PDMB with pure 1,4 *cis* or 1,4 *trans* structure was obtained with trialkylaluminum-titanium tetrachloride initiator systems. The double bonds of *cis*- or *trans*-poly-1,4-(2,3-dimethylbutadiene-1,3) were catalytically hydrogenated to H-H PP.

H-H polystyrene (20-24) was synthesized from 2,3-diphenylbutadiene-1,3 by radical polymerization with AIBN as the initiator. Poly(2,3-diphenyl-butadiene-1,3) with a 55:45 ratio of *cis* and *trans* double bonds was hydrogenated to H-H PSt by a chemical reduction of the double bonds. Complete hydrogenation gave poly(vinyl cyclohexane (25) H-H poly (1- or 2-vinyl naphthalene) was prepared in an analogous way (26-29)

*Halogenation of the Double Bond of Poly-1,4-butadiene-1,3 for the Synthesis of Poly(vinyl halides):* 1,4-Polybutadiene (PB) has a double bond in each monomer unit, which has either a *cis* or a *trans* configuration. Complete halogenation of these double bonds leads to H-H poly(vinyl halides), PVC and H-H poly(vinyl bromide) (PVB) (30-32).

Chlorine can add to PB either *cis* or *trans* to the double bond. The desired addition of halogen to alkenes (and PB) is by electrophilic addition. The addition of bromine to double bond proceeds in a stereospecific manner, giving the *trans* addition product. Chlorination is not as stereospecific as is bromination.

Chlorination of *cis*-1,4-PB of high molecular weight have partially chlorinated and ultimately completely chlorinated PB.. Their stereochemistry was investigated by NMR.

The synthesis of H-H PVB was also carried out. Bromination of *cis*-1,4-PB of high

molecular weight proceeded readily at low polymer concentration. The bromination of *cis*-1,4-PB including the stereochemistry of the bromine addition was monitored by IR and NMR spectroscopy.

### *iii. Wurtz and Grignard Reactions*

The Wurtz coupling reaction involves the coupling of alkyl halides by treatment with sodium metal or other metals. The Grignard coupling reaction involves a transition metal catalyzed coupling of a Grignard reagent. Using dihalides and di-Grignard reagents and subjecting them to Wurtz or Grignard conditions was expected to give the corresponding polymers (32-37).

Grignard coupling was successfully used for the synthesis of H-H polyisobutylene (PIB). Linear H-H PIB of moderate molecular weight was prepared by Grignard coupling polymerization of 1,4-dibromo-2,2,3,3-tetramethylbutane. The synthesis of 2,2,3,3-tetra substituted-1,4-butanediols starting from  $\alpha$ -bromoesters has general applicability.

Attempts to prepare H-H PIB from 1,4-dibromo-2,2,3,3-tetramethylbutane by the Wurtz reaction gave branched H-H PIB of low molecular weight.

Earlier optimistic reports on the successful synthesis H-H poly( $\alpha$ -methylstyrene) and poly(1,1-diphenylethylene) by oxidative coupling polymerizations of the dimeric dianions (23) could not be verified. The polymers were mixtures, because the dimeric dianions were not stable and were mixtures. Consequently, the low molecular weight polymers obtained by coupling had mixed structures also had structures with some H-H linkages.

## **b. Properties of Head to Head Polymers**

H-T and H-T polymers are similar in overall composition, but different in structure and stereochemistry. When the monomer unit is symmetrical such as in isobutylene, (1,1-

dimethylethylene) or in 1,1-diphenylethylene, the structures are either H-T or H-H. In the mono substitution of ethylenes such as in PP (methyl substituent), PSt (phenyl substituent), PVC (chlorine substituent), PVB (bromine substituent) or poly(methyl acrylate) (carbomethoxy substituent), the individual linkages are subject to various stereochemical linkage possibilities.

A similar situation exists for asymmetric substitutions such as in poly(methyl methacrylate) and poly( $\alpha$ -methylstyrene). In these cases, we have for the H-T polymers, *meso* (*mm*) (*isotactic*), *racemo* (*rr*) (*syndiotactic*) and *heterotactic* (*mr*) linkages as possibilities. For H-H polymers, *erythro-isotactic*, *erythro-syndiotactic*, *threo-isotactic* and *threo-syndiotactic* linkages are the equivalents to H-T polymers (38,39).

### *i. Spectral Properties*

The infrared spectra of all H-H and H-T polymers are generally similar, but have some very specific differences especially in the low wave number region ( $1500 - 600 \text{ cm}^{-1}$ , the fingerprint region). the fingerprint region was important to characterize H-H linkages.

NMR characterization of H-H polymers has also been carried out to differentiate H-H from H-T polymers by both  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift data were used to characterize H-H polymers. NMR spectroscopy was first proven to describe stereospecific *isotactic*, *syndiotactic* polymers or *atactic* H-T polymers.

In H-H polymers, stereochemistry exists also on each of the carbon atoms that can be described by NMR spectroscopy (38-40). The structure of H-H PSt, using high-resolution  $^{13}\text{C}$  NMR spectroscopy was established in detail. The chemical shift lines corresponding to the influence of longer range order, the equivalence of the stereostructure of pentads and hexodes in H-T polymers.

For normal H-T polymers, the stereochemistry has been described for triad structures. The neighboring substituent, which has the same absolute configuration, is called *meso*

(m), the neighboring substituent with opposite configuration is called *racemo* (r). The number of possible stereochemical sequences to consider in H-H polymers is different from the traditional H-T polymers and is not only a function of the *threo* and *erythro* nature of the neighboring unit but also of the respective sites of the two neighboring asymmetric carbons in successive units. If the successive substituents (central sequence) have the same configuration, the structure is defined as *meso* (m), if it is of opposite configuration, it is called *racemo* (r). This analysis could be demonstrated by high-resolution  $^{13}\text{C}$  NMR spectroscopy for H-H PSt (41).

## ii. Glass Transition Temperature

The  $T_g$  behavior of H-H polymers and of the corresponding H-T polymers was investigated. The positions of the substituents in the H-H as compared to the H-T structures of the polymer chains produce two opposite effects: It: a.) increases the flexibility of the polymer backbone caused by the T-T linkages ( $-\text{CH}_2-\text{CH}_2-$  sequences) and b.) stiffens the polymer backbone caused by the H-H linkages. The flexibility increase causes a decrease of the  $T_g$  while the stiffness increase causes the  $T_g$  to increase. If the substituent is a polar group, the H-H linkage can increase the dipole-dipole interaction of the side group, which leads to substantial chain stiffening effects and an increase in the  $T_g$  of the H-H polymer with polar substituents.

Other physico-chemical solution properties of H-H polystyrene and the rheological behavior were also investigated (42-44)

## c. Thermal Degradation Behavior of H-H Polymers

The thermal degradation behavior of polymers is a very important property that is needed to understand the behavior of polymers during fabrication by melt processing. It might ultimately also influence the aging behavior of individual polymers.

The thermal stabilities of H-H polymers are similar to that of the corresponding H-T polymers, when the substituent is an aliphatic, non-bulky group, such as a methyl (PP), or a phenyl (PSt) substituent.

For polymers made from disubstituted monomers, such as poly(methyl crotonate) (PMCr), poly(methyl cinnamate) (PMCi) and poly(isobutylene) (PIB), the MDT of H-H polymers were lower than those of the corresponding H-T polymers. Most strikingly, the MDT of H-H PIB was 65°C lower than that of H-T PIB.

The thermal-oxidative and photo-oxidative degradation studies of H-H PSt and H-T PSt were also carried out. The products of the thermal-oxidative degradation of both H-H and H-T PSt are the same, which indicated a similar degradation mechanism for these two polymers. The rate of the oxidative degradation was faster in H-H PSt degradation than that in the H-T PSt degradation. The degradation of PVC in its initial stage is characterized by the elimination of HCl (32). Depolymerization does not occur to any significant extent at the temperature at which dehydrohalogenation (starting at 230°C) occurs, which ultimately end up in a residual polymer containing a high concentration of conjugated carbon-carbon double bonds which crosslink and produces a char.

#### **d. Blends of Head to Head Polymers**

The blending behavior of H-H polymers has been studied for some time. Blends of H-H or H-T polymers with each other and with other polymers have been investigated.

##### *i. Head to Head and Head to Tail Polymer Blends*

PP blends of H-H ( $T_g = -39^\circ\text{C}$ ) and H-T ( $T_g = -17^\circ\text{C}$ ) of comparable molecular weight were found to be miscible over the entire range of polymer compositions (26). Blends of H-H PSt with H-T PSt, which have nearly the same  $T_g$ . H-H ( $T_g = 97^\circ\text{C}$ ) and H-T ( $T_g = 98^\circ\text{C}$ ) are also completely miscible. H-H PIB ( $T_g = 87^\circ\text{C}$ ,  $T_m = 187^\circ\text{C}$ ) and H-T PIB ( $T_g = -61^\circ\text{C}$ ).

are immiscible and show the  $T_g$ 's of the individual homopolymers. H-H PVC ( $T_g=70^{\circ}\text{C}$ ) and H-T PVC ( $T_g=90^{\circ}\text{C}$ ) are also immiscible almost over the entire range of compositions.

## *II. Blends of Head to Head Polymers with Other Polymers*

Blends of H-H PSt with poly(2,6-dimethyl-1,4-phenylene oxide) showed complete miscibility. over the entire range of compositions, a behavior that is similar to the known blending behavior of H-T PSt with PPO. H-H or H-T PSt were also completely miscible with poly(methylvinyl ether) PMVE . H-H PSt is slightly more miscible.

Blends of H-T PVC were rigorously investigated components. It was found to be miscible with a number of structurally quite different polymers and copolymers, PCL, PMMA, butadiene/acrylonitrile copolymers, and ethylene/vinyl acetate copolymers. In our hands, Blends of H-H or H-T PVH with PCL were completely miscible with PCL When PMMA was used as the blending polymer component for PVC, the tacticity of PMMA also had some effect on the miscibility of PMMA with H-H or H-T PVC With H-T PVC was more miscible with *syndiotactic* PMMA than with *isotactic* PMMA From our work it appeared that the H-H PVC/*iso*-PMMA had a better miscibility.

## *iii. Thermal Co-Degradation of Head to Head Polymer Blends*

Immiscible blends of H-H PIB and H-T PIB showed as a degradation pattern the superimposition of the degradation of the two individual polymers. Immiscible blends of H-H PVC/H-T PVC behaved similarly.

The thermal degradation of miscible blends of H-T PSt with poly(2,6-dimethyl-1,4-phenylene oxide) showed that they degraded quite independently from each other. In the H-H PSt/PPO blend, a decrease in the stability in the PPO fraction of the blends was noticed in the presence of degrading H-H PSt.

The thermal decomposition of the miscible blends of H-H or H-T PVC with PCL is almost a superposition of the degradation processes of the homopolymer of H-H PVC and PCL. The co-degradation of H-T or H-H PVC/PMMA blends showed that the degradation of each individual blend component influenced the degradation of the other.

What did we learn from this work ? We had concentrated on the H-H polymers of commodity polymers, PP, PSt, PVC PIB and polyacrylates. This was a good choice. From PP we learned how to use diene polymerization and polymer hydrogenation, the behavior the  $T_g$  and miscible blends. PSt was the most important polymer. It gave us the first glimpse of polymer degradation, the stereochemistry and long-range order in H-H polymers, rheology behavior miscible blends with H-T polymer but more importantly the miscibility with other polymers. For the first time we could demonstrate the co-degradation behavior of miscible blends. Blends of H-H and H-T polymers of PIB and PVC were not miscible, but we investigated the blends of PVC with other polymers.

We kept away from the more "polar" polymers such as acrylonitrile. We expected that the polarity would be overwhelming and would not contribute to our general interest.

Over a period of 20 years Toru Tanaka, Hiroshi Inoue, Dietmar Helbig, Enikő Földes, Stephen Grossman, Michael Malanga, Haruma Kawaguchi, Takeshi Kondo, Meifang Qin, and Xi Fu were involved in the work on H-H polymers. Henri Benoît, Gilbert Weill, Werner Berger, Albert Zilkha and the late Piero Pino and Ferenc Tüdös contributed to the H-H polymer work.

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## D. Miscellaneous Projects

### a. High Temperature Polymers based on Bis-*ortho*-Esters as Polymer Intermediates

My interest in *ortho*-esters and the use of *ortho*-esters for chemical reactions was spawned when I worked in Princeton and used *ortho*-esters, especially, trimethyl-*ortho*-formate, as cyclization reagent for the direct synthesis of purines, pteridines and other heterocycles.

*Ortho*-esters are reactive carboxylic acid derivatives and used for many reactions where other carboxylic acid derivatives are not suitable. Among the reactions that *ortho*-esters can undergo with amines or amides, are the formation of five- or six-membered heterocyclic rings.

When I began my scientific career in Amherst, I decided – among other polymer projects - to investigate bis-*ortho*-esters as possible polymer intermediates. I had in mind the

direct synthesis of high temperature polymers by forming heterocyclic rings from aromatic tetramines, aminophenols and aminothiophenols. High temperature polymers had been made from a number of diacid derivatives. but not from bis-*ortho*-esters. Consequently we selected some bis-*ortho*-esters, which could be prepared and purified to polymer grade compounds.

*Ortho*-esters are prepared by two methods, the Pinner synthesis from a nitrile, suitable for aliphatic *ortho*-esters. The Williamson synthesis treats a,a,a-trihalomethyl compounds with alkoxides.

In the 1960's hexachloroxylenes, chlorinated in the methyl groups had become available and my old interest in *ortho*-esters arose, this time as polymer intermediates. General interest in DNA and purines in polymers developed and we could see the possibility of making polypurines. It was fashionable at that time to synthesize and investigate high temperature polymers that were "all aromatic." We know now that this also means that they are insoluble and infusible and of limited molecular weight.. Had we thought of using flexible links to make our polymers, we might have produced more useful products.

Ironically, at about the same time, maybe a little later, we started our work on using flexible chains to separate functional carboxylate groups from polymerizable groups which was ultimately very successful - but we did not connect these two observations..

Chuck Dudgeon undertook this project and synthesized three types of bis-*ortho*-esters, hexaalkyl-*ortho*-isophthalates, hexaalkyl-*ortho*- terephthalates, and hexaethyl-*ortho*-oxalate. He made the *ortho*-esters from a,a,a,a',a',a'-hexachloro-m-xylene or hexachloro-p-xylene, and sodium methoxide (1). Transesterification with higher alcohols, for example, ethanol or propanol, gave higher bis-*ortho*-esters. All bis-*ortho*-esters were purified to give monomer grade compounds free of normal esters (Figure 31). *Ortho*-esters have been used as cyclization reagents

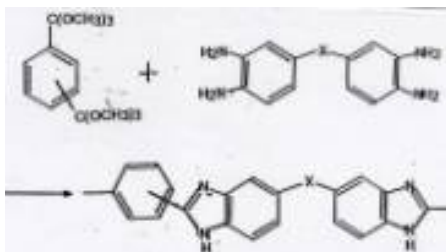


Figure 31: Bis-*ortho*-ester-as Polymer intermediates

for the preparation of heterocyclic ring compounds. In some cases, *ortho*-esters are the only effective cyclization agents. When heated with trimethyl-*ortho*-formate, *ortho*-phenylenediamine or N-substituted *ortho*-phenylenediamines were converted to benzimidazole. We found that bis-*ortho*-esters could be condensed with aromatic tetramines to polybenzimidazoles under mild conditions, and in relatively short reaction time (2,3). Hexapropyl-*ortho*-esters of terephthalic and isophthalic acid, because they are liquids, were the preferred *ortho*-esters because they were relatively easily purified by vacuum distillation to polymer grade *ortho*-esters. Hexaethyl *ortho*-oxalate was also used for condensation reactions.

The three *ortho*-esters were used for polymerizations with 3,3',4,4'-tetraaminobiphenyl, 1,2,3,4-tetraaminobenzene, 3,3',4,4'-tetraaminobiphenyl ether, and 3,3',4,4'-tetraaminobenzophenone. The polybenzimidazoles were obtained in near quantitative yields and fiber forming molecular weights (4).

Almost 20 years ago it was found that triethyl-*ortho*-formate reacted with aminomalonamidamine dihydrochloride to hypoxanthine and aminomalonamidamine dihydrochloride to adenine derivatives in good yields. Triethyl *ortho*-acetate or triethyl-*ortho*-propionate gave the 2,8-dimethyl, 2,8 diethyl- substituted purines.

As a consequence, we decided to use bis-*ortho*-esters with aminomalondiamine or aminomalonamideamidine in order to synthesize polymers with purine moieties in the backbone chain.. Hexa-*n*-propyl-*ortho*-isophthalate, hexa-*n*-propyl-*ortho*-terephthalate, and hexaethyl-*ortho*-oxalate were allowed to react with aminomalondiamine dihydrochloride to poly(2,8-adeninediyl-1,3-phenylene). or aminomalonamideamidine dihydrochloride to

poly(2,8-hypoxanthinediyl-1,3-phenylene) and gave oligomers and low molecular weight polymers (5).

We never placed flexible spacer groups in the monomers, which would have given soluble and fabricable polymers.

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## b. Properties of Esterglycol MDI Polyurethanes

For three years I had been consulting for the Montedison Company in Milan, Italy. One of my responsibilities was to assist in the scientific interaction on an international scale. The President of the Plastics Division, Italo Trapasso, to whom I reported was very interested in the International training of their technical staff. In 1977 the company sent Gianflavio Lunardon, supervisor of the polyurethane group in Porto Marghera, to my laboratory to have some international exposure and to improve his English conversation.

For years I had been teaching the course in Organic Chemistry of High Polymers and I had been intrigued in the specific properties of polyamides. Gian-Flavio was interested in polyurethanes. We found that there was one area in polyurethane chemistry that had not been properly investigated and that was the effects of molecular weight and molecular weight distribution of the polyester based soft segments on the physical properties of linear polyurethane elastomers.

Similar work on polyether based soft segments had been investigated a few years before. Fine points of the mechanical properties of polyurethane elastomers depend on a number of parameters and their interrelationship. Among the parameters are molecular weight and molecular weight distribution of the flexible segments. Comparisons of the properties of polyurethanes having polyester and polyether soft segments have been known. The interest was focused mainly on polyethers because of the relatively weak interaction with the soft segments and the phase separation in these polyurethanes. A clear-cut phase separation exists between the hard and soft blocks with essentially no interaction between the two phases.

We investigated structure, property and morphology of MDI polyurethanes as a function of molecular weight and molecular weight distribution of the polyester segments. The stress-strain behavior of these polymers is primarily effected by the molecular weight of the soft segments. The higher molecular weight polyester segments have a more distinct phase separations than in polymers with lower molecular weight polyester segments.

To summarize: a) All the physical properties of a linear segmented polyurethane elastomers are dependent on the molecular weight of the soft segment. b) The molecular weight distribution of the polyesters soft segment effects the relaxation properties (hysteresis, permanent set dynamic mechanical properties) c) The dynamic mechanical investigations showed a coexistence of three different phases: A soft segment phase, a mixed phase and a crystalline phase of the hard segment. d) The amorphous mixed phase of the polyester diol based polyurethane elastomer is defuse, limited miscibility of the separate phase boundary of the phases of soft and hard segments was also noticed.

e) A super structure was found to be absent.

After about 10 years some samples were remeasured. Some properties had changed. This phenomena could be interpreted as follows: Of the three phases of the polyurethane, the phase that was a mixture of the "hard" phase and the "rubbery" phase, had phase separated to some extent. The driving force is the soft phase, which "pulled" some of the soft segment out of the mixed phase. This naturally caused a slight change of the relevant mechanical properties.

We were very fortunate that at the same time that Lunardon was in my laboratory we had Dr. Sumida from the Kao Company in Japan also in my laboratory. Sumida was an expert in the interpretation of certain properties of polyurethanes.

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### **c. Diketenes as Polymer intermediates**

In our work on the polymerization of chloral, some co-polymerizations were also investigated. It soon became clear that only the copolymerization with isocyanates and ketenes gave real co-polymers. Only the copolymerizations of chloral with aromatic isocyanates and with diphenylketene provided substantial incorporation.

Aliphatic ketenes are quite unstable and undergo readily various reactions on standing, Diphenylketene was relatively stable and it occurred to us that diphenyl substituted diketenes could be interesting polymer intermediates (1). The synthesis of polyester and polyamides on the basis of diphenylketene looked promising. The obvious example for a diphenyldiketene was dihydroanthracene-9,10 diketene. Each ketene functionality was attached to a diphenyl moiety.

Anthracene-9,10 diketene was readily prepared from anthracene.(Figure 32). Dihydroanthracene sodium was easily prepared from anthracene and sodium. Carboxylation with carbon dioxide gave dihydroanthracene-9,10-dicarboxylic which was dehydrated to dihydroanthracene-9,10- diketene.

Reaction of this diketene with glycols gave polyesters, and with diamines gave polyamides. As expected, the polymers of ethylene glycol and butylene glycol gave polymers of low molecular weight. Those of diamines also gave low molecular weight polymers. The molecular weight as judged by the measurements of their inherent viscosity increased as the spacer groups between the ester and amide groups increased. We already had encouraging indication when polyethylene glycol 400 was used as the glycol for the polyester formation. Unfortunately we were unable to

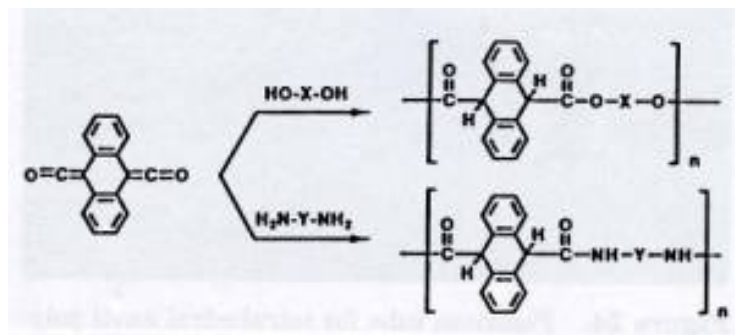


Figure 32: Bis-ketenes as Polymer Intermediates

complete a thorough investigation of making high molecular weight polyester and polyamides from dihydroanthracene-9,10-diketene. Polyaddition of polyethylene glycols, polyethylene oxide capped polypropylene glycols and polyester glycols. The reaction of these glycols with MDI or TDI are the basis of commercial polyisocyanates.

They key reason for this work to make polyesters from diketenes and glycols was that the reaction products were polyesters. Polyesters from primary alcohols have degradation temperature in excess of 300°C. the same is true for polyamides. Polyurethanes degrade thermally already at 150°C. Had we reached our goal, we probably would have had "polyurethane" elastomers with polyester properties and stability.

1. Peter Zarras and Otto Vogl, Ketenes and Bisketenes as Polymer Intermediates, Progress in Polymer Science, 16 (2/3), 173 (1991)

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## E. Functional Polymers

In 1961 I had moved to the Central Research of the DuPont Company from the Polychemicals Department. I had been able to take with me the project that had started in the special research group: polymerization of chloral with the objective of bringing it to commercialization. At that time I was an excellent and very promising polymer but it was insoluble and infusible. As a consequence not only an effective method of polymerization had to be found but also a method of fabrication.. For about 1 1/2 years I worked on the problem without much progress. I was frustrated because I always expected success, I was prepared to undertake something significantly different that had a chance of success.

At that time Monsanto had made and was trying to commercialize alternating copolymers of ethylene/maleic anhydride and styrene/maleic anhydride.

Remembering my early experience with biologically active compounds, steroids, it occurred to me: Would it not be interesting - since some were alcohols to react them with these anhydride copolymers. These polymers were esters of biologically active alcohols. I expected these polymers to either be active by themselves or release the active component by hydrolysis. In this case the polymer acted only as a "carrier." Three of these alcohols were obvious candidates to check this possibility: cholesterol, testosterone and 7-dehydrocholesterol. The reactions with the anhydride copolymers were apparently successful. The isolation of the polymers, they now had acid and steroid functions in the monomer units, was impossible. Work-up by pouring the reaction mixture into water and methanol produced stable emulsions. This was problematic because I carried out the reactions "on the side." My supervisor saw the bottles with the emulsions and frowned: "Why don't you consider changing your job and find a job with a drug company, such as

Merck." I never liked the fellow after this episode.

I did not pursue his suggestion because I had a family to feed and was otherwise happy. By some lucky circumstance the polychloral work started to move , I had discovered the "Cryotachensic Polymerization" and I discarded the emulsions. However, I promised myself that I would at some times work in the field of polymers with bioactive substituents, should the occasion arise.

The occasion did arise after I had joined the University of Massachusetts several years later. It was then that I pioneered the field of functional polymers, polymers with functional groups. We created polymers with carboxylate groups, acids, acid salts, polymers with biologically active groups, polymers as drugs and polymerizable and polymer bound stabilizers. When the functional group was directly attached to the polymer chain, the "polymer effect" became dominant. As a consequence we developed polymers with flexible side chains, to which functional groups could be attached.

Time had come at the University for me to define research projects and objectives. I was committed to start with the regular polyoxamides. The polychloral project was to be my life commitment. But what else?

Again I made a decision to work on subjects of novelty, not on the detailed deliberations of one subject in the greatest detail. In my research group I intended to teach my students to see the exciting kaleidoscope of polymer chemistry and the scientific possibilities in polymer chemistry..

When I was searching for opportunities to conduct research in my early career at the University of Massachusetts, I had to have, as all new academic scientists have, scientific goals, students and funding to support the students.

By chance I met on some occasion, the key person at the Army Office of Scientific Support. He was interested in my fundamental idea of preparing functional polymers (1-

5). But now to the practical side of the problem. He told me he had "a little bit" of money left and was interested in longer lasting, perhaps one week-end-UV protection, for combatants in desert conditions. I told him we could handle it with polymeric and polymerizable UV absorbers. We received \$18,000 for the first year.

I assigned my second graduate student, Dave Bailey, to the project. He was an excellent student and skilled experimenter. He opened this new area of our research on functional polymers. We started with polymers with N,N'-dimethylaminobenzoate groups end capped or attached to polymer chains. For me, this was the beginning of our 25-year commitment to functional polymer chemistry.

My initial interest was not in polymers that can protect us from UV radiation but in functional polymers as drugs. In the mid-70,s we contributed to the very early development of polymeric drugs and even edited a book on "Polymeric Drugs" with Guy Donaruma. which I will describe in the next section in this book (6,7)

In the late 70's I decided to step out as a major contributor of this field.. The "set-up" at the University of Massachusetts was not conducive for this kind of research. We would have needed access to a hospital or at least medical research teams, would have had to cooperate with a major pharmaceutical company. I would have had to restrict my other research activities and concentrate entirely on polymers in pharmacy and medicine. I did cooperate with Merck on bile acid sequestering and with the Alcon Company on inter ocular and soft lenses.

## **a. Polymeric Drugs**

We define polymeric drugs as polymers, which consist of synthetic polymers with functional groups of known or potential biological activity. Such drugs are defined to include any agents, which, upon introduction into a living system, cause a physiological response. Not only curative but also prophylactic agents are included in this definition.

Polymeric materials, which are biologically active, have, potentially, both advantages and disadvantages in comparison with low molecular weight compounds. The activity of a polymeric drug may be related to the functional group present in the structure, or to the polymeric nature of the substance. An important area for biologically active synthetic polymers is the applications outside of the human body (e.g. topical application), as little is known at the present time about the long -term effects of synthetic polymers in the body. The retention of synthetic polymers in tissues, the mechanism of the action of polymeric materials with biological activity, and the metabolic fate of polymers, especially synthetic polymers, are still not well understood. There are two highly desirable objectives in the development of new drugs: to enhance the drug specificity and to increase the duration of its actions. Enhanced specificity requires an increase in the therapeutic effect of the drug without a proportionate increase in side effects. Systematic chemical modification of known drugs was an accomplished goal to a varying extent in several classes of compounds. A different kind of specificity is achieved if one can restrict the drug's penetration into undesirable parts of the system or limit the movement of the drug in the system. It is also desirable to be able to increase the duration of a single dose of the drug to increase the patient's tolerance. The establishment of this knowledge is important for prophylactics and the treatment of diseases in inaccessible areas of the world. The increase of the duration of drug action can be accomplished by slow delivery, through slow dissolution from a crystalline depot, through diffusion from or dissolution of a matrix material, or through cleavage of the drug, from a carrier molecule. These techniques potentially can avoid important undesirable side effects, particularly those associated with toxicity.

After the turn of the century the effect of organic dyes on curing diseases was studied; the basic concept of chemotherapy, the treatment of infections with synthetic chemicals was developed. Enormous and continued progress has been made over the years; it has included the discovery of sulfa drugs, antibiotics and other synthetic materials for use against virtually all infectious diseases. Only the virus diseases as a group have not been treated successfully by chemotherapy. Viruses are in general much smaller than bacteria and only selected viruses can be treated by chemotherapy, while bacteria and fungi both

can be effectively destroyed. The drug action is effected by agents affecting bacterial and other infectious diseases in various ways, (a) Acting on the cell wall. (b) Affecting the cell membrane. (c) Modifying replication or protein synthesis (d) Affecting nucleic acid metabolism. (e) Affecting intermediary metabolism. Many antibiotics or synthetic materials are effective by acting in one or more of these individual points.

A number of polymers have been tested for their biological activity and polymers have been found with antibacterial, antifungal, interferon inducing, antiviral and antiparasitic activity. Polymeric materials effective as gastrointestinal, dermatological and antiulcer compositions have also been studied, as well as polymers which affect the immune response or act as antiinflammatory agents. Other polymers, which were studied, exhibited the following properties and activities: anthelmintic, narcotic, antitussive, hypotensive, hypnotic, tranquilizing, analgesic, antisecretory antispasmodic, antineoplastic, appetite depressing, motor activity depressing, and muscle relaxing. Polymers, were also found which are useful in treating circulatory, cardiac and blood diseases. Steroids and vitamins have been incorporated into polymeric systems and the larger group of herbicides and pesticides was and is being even more extensively investigated.

Polymers with biological activity are expected to differ from drugs of low molecular weight with respect to both effectiveness and toxicity. Of particular importance is the possibility that the polymeric drug has prolonged activity either directly or by sustained release, but greatly diminished toxicity.

The activity of a polymeric drug can be influenced by the characteristics of the macromolecular chain itself and is probably very readily influenced by the molecular weight and molecular weight distribution. Since some of the most interesting polymers are actually copolymers, modification of the activity can be visualized by manipulating the copolymer composition. In addition to the molecular weight and molecular weight distribution of the copolymer, the run number indicating randomness or blockiness of the polymer is very important. The stereospecificity or tacticity of the polymer or the co-

tacticity of copolymers has to be taken into account. The know-ledge of design of polymers with hydrophilic and hydrophobic groups as part of the chain or attached to the polymer chain also changes significantly the character and utility of a polymeric drug. Distribution of groups with hydrophobic/ hydrophilic character, or transformation of the polymer into a polyelectrolyte by proper dis-tribution of charges along the chain may play important roles in developing the optimum characteristics for biological activity (8-11). If synthetic polymers in crosslinked' form are used as polymeric drugs, the degree of crosslinking and the swelling behavior of such materials are also of importance.

We decided to start with the synthesis of polymerizable salicylates. Why salicylates ? We were still involved with the aminobenzoate polymer project. Salicylate esters, methyl and phenyl esters, where at that time commonly used as UV stabilizers. Aspirin, acetylsalicylic acid, is the most common pain reducing agent

It was 1972 and I was teaching in Freiburg, Germany for about six weeks. At the end of my stay I had developed a toothache involving my crowned molar tooth. I had only two more weeks before I had to go home and I did not think it was sensible to bother with a new dentist in Germany. In order to control the constant and increasing pain I took aspirins tablets to control the toothache. I came home just before Christmas and I had to wait to schedule the tooth extraction. I was given codeine. What I did not know was that the big codeine pill consisted of 90% aspirin. The continued and excessive use of aspirin caused stomach bleeding and I had to be placed for a few days in the hospital. 30 years ago this problem was neither recognized nor accepted by the medical profession. Dave Bailey had been joined by Dave Tirrell in our research group and we decided to synthesize a safe aspirin and started our work on polymerizable vinylsalicylic acid derivatives.

#### *i. Poly(vinylsalicylates)*

We synthesized 3-, 4-, and 5- derivatives of vinylsalicylic acid and polymerized them (Figure 33). For the synthesis of the 5-vinylsalicylate, methyl salicylate was the starting

material. It was acetylated, the acetyl group reduced, dehydrated and the vinyl compound polymerized. The 3-, and 4-vinylsalicylate isomers were synthesized from 3-ethyl and 4-ethyl methyl salicylate. The compounds were brominated dehydrobrominated to 3- and 4-vinyl methyl salicylates and polymerized (12-14).

Vinylsalicylic acids and vinylsalicylic acid derivatives, their polymers and some of their copolymers were investigated for their antimicrobial and cytotoxic properties. Making homopolymers and especially copolymers increased one property and decreased another. Homopolymers were not very active because of limited solubility's, soluble copolymers showed much more activity. Most of the compounds were more cidally active toward bacteria than toward fungi. Homo and copolymers were very active against *S. aureus* but not against *E. coli*. the monomers were active to both bacteria and fungi. Homopolymers and especially copolymers of biologically active monomers increased their specificity. Some copolymers were found to have very high activity against one bacterium but not to another. Cytotoxicity was high for monomers and homopolymers but not for copolymers with methacrylic acid (15)

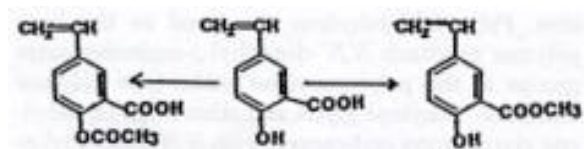


Figure 33: Poly((Vinylsalicylates)

Salicylic acid esters, (both low molecular weight and polymeric) not unexpectedly have an optical density of about one half of that of 2,4-dihydroxybenzophenone, which will be discussed later. They are good UV absorbers and much less costly. In the effectiveness as UV absorbers, there is essentially no difference between low molecular salicylic acid esters and the polymers.

## ***ii Polymeric Antitumor Agents***

Synthetic pharmacologically active polymers as compared to low molecular drugs have

become of increasing interest in recent years. As mentioned earlier, a polymeric drug can be capable of overcoming the problem of toxicity and can have increased activity and effectively. it can also increase the durability for drug activity. and for anticancer drugs an affinity for tumor cells.

5-Fluorouracil has shown remarkable antitumor activity but also strong side effects. In order to overcome these effects, 5-fluorouracil was attached in Professor Ouchi's laboratory to D-glucofuranose and other sugars. An acryloyl group attached to the furanose part. These acrylic monomers are now capable of polymerizing and copolymerizing. The most convenient class of copolymer were those with acrylamide, because it provided polymers of different degrees of water solubility.

When Ouchi was an Assistant Professor at Kansai University in Japan he decided to spend some time in my laboratory as Research Associate. When he returned to Japan, he decided to work on polymeric cancer drugs. He had good relations with a hospital, He had learned from my interest on polymeric drugs and we collaborated on the 5-fluorouracil project. I functioned mostly as an advisor.

The extent of release of 5-FU residues from the copolymer was investigated in the enzyme or non-enzyme system *in vitro*. Poly(ethylene glycol) monomethoxy ether attached through ester, amide, and ether bonds were also attached to 5-fluorouracil. The hydrolysis was investigated *in vitro* in the presence and absence of enzymes. Furthermore, the antitumor activities of the water-insoluble homopolymer and water-soluble copolymer obtained were tested *in vivo*. The hydrolyses of the end ester, amide, and ether bonds in the presence or absence of enzymes was studied. The rate of hydrolysis of the ester bond decreased and the antitumor activity increased as a function of the degree of polymerization of the ethylene oxide units 16-20).

The methyl ether or stearyl ether show respectable antitumor activity in mice cells. The copolymers of the copolymer of the acryl compound with acrylamide was active.

### iii. Degradable Polymers with Biologically Active Groups

Condensation polymers with repeat units that are pharmacologically active in their monomeric form had attracted attention as possible polymer drug systems. It was considered for sustained drug delivery at optimal rates. Sustained delivery of herbicides and insecticides with minimal effect on the environment was of additional interest. Our interest was to prepare polymers that can hydrolyze either at physiological pH of 7.4 or with enzymatic assistance. The basic principle was in polymers that only release a biologically active agent and carbon dioxide, ammonia or phosphoric acid.

As a test case we decided to use bithionol [2,2'-thiobis(4,6-dichlorophenol)], an antibacterial agent and a bisphenol to prepare the polycarbonates and other polyesters. We synthesized a number of bithionol polyesters, as well as poly(bithionol phenylphosphate), poly(bithionol phenyl-phosphonate), and poly(bithionol phenylphosphinate). They were prepared from bithionol and the diacid chlorides, respectively. With excess phosgene, bithionol gave the bischloroformate, which was a very versatile intermediate for the synthesis of polycarbonates and polyurethanes of polycarbonates and alternating polycarbonates, polyurethanes and terpolymers (21-23) (Figure 34).

In the 70's, bithionol was a frequently used as antibacterial agent especially after delivery. "Overuse" and "overdose", just like in the case of DDT, made the safety of this chlorinated bisphenol questionable..

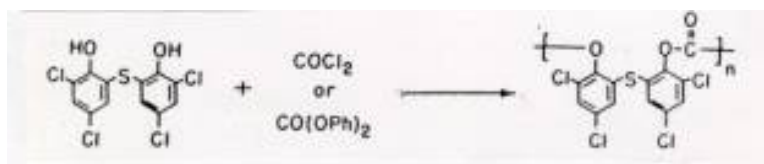


Figure 34: Condensation Polymers with Biologically Active Units

Our ultimate objective was to study the hydrolysis, under conditions resembling physiological systems, of those bithionol polymers and co-polymers. The hydrolysis

depended primarily on the water solubility or hydrophilicity. Favorable hydrolysis conditions were found with alternating bithionol/PEG 4000 co-polycarbonates. The hydrolysis rate of the polymer at 37°C was satisfactory.

On a different subject, we prepared biuret oligomers from primary aliphatic amines and diisocyanates. Aliphatic primary amines were used as bifunctional monomers to form biuret type condensation polymers. They included n-propyl, n-hexyl-, n-octyl-, n-dodecylamine, and adamantylamine (an antiviral agent) and primaquine [8-(4-amino-1-methylbutylamino)-6-methoxyquinoline], an important antimalarial agent. As diisocyanates, the aromatic methylenedi-p-phenyl diisocyanate, and the aliphatic 1,6-hexamethylene diisocyanate were used.

## **b. Polymerizable and Polymeric Stabilizers**

In 1960 at Du Pont I had as one assigned task to explore and identify new and more effective antioxidants and UV stabilizers POM. It was then recognized that such stabilizers must be "soluble" in the amorphous phase of the polymer that had to be stabilized. I have described this work in an earlier section.

Drawbacks of all low molecular weight stabilizers were their volatility in the fabrication step; and their leachability during use, leaving surface regions of the object with lower amounts of protective agents.

### *i. Polymerizable UV Stabilizer*

When I started in academia and began my research activity on Functional Polymers, we started with N,N'-dimethylaminobenzoates, effective sunscreens for the skin. We prepared polymeric esters from the reactive alkyl halides epichlorohydrin and tetraethylammonium-N,N'-dimethyl-p-aminobenzoate. End capping of ethylene glycol and other oxyethylene glycols was done by transesterification with di-N,N'-dimethyl-p-aminobenzoate gave mono-, di-, tri-, and poly(oxyethylene)-di-N,N'-amino-p-

aminobenzoate) (25-27)

30 Years ago, the most common group of UV stabilizers were salicylates. We synthesized methyl 5-vinylacetylsalicylate, as described earlier and polymerized it and copolymerized it with acrylic acid methacrylic acid (28).

*2,4-dihydroxybenzophenone*: Other effective UV stabilizers for plastics were 2,4-dihydroxybenzophenones. We synthesized 2,4-dihydroxy-4'-vinylbenzophenone. polymerized it and copolymerized it. A specialist in 2,4-dihydroxybenzophenones. was Professor Pinazzi of the University of Le Mans, France (29). I sent Dave Bailey to his laboratory for 3 months to learn the chemistry but more importantly to expose him to science in the International world.

We also made 2,4-dihydroxybenzophenone esters from the tetraethylammonium salt of poly(methacrylic acid) and 4-(2-bromoethoxy)-2-hydroxybenzophenone. We used n-butylbromide to form the copolymer with n-butyl methacrylate (30).

*Ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate*: Esters of  $\alpha$ -cyano- $\beta$ -phenylcinnamic acid have been used in the past as UV stabilizers when free phenolic groups were undesirable. Polyacetals are sensitive to phenol groups, which decrease their thermal stability during fabrication.

$\alpha$ -Cyano-- $\beta$ -phenylcinnamate esters are quite volatile and significant losses of stabilizer during extrusion had been noted. Attempts were made to decrease the volatility by using bisesters of glycols such as that of 1,10-decanediol and  $\alpha$ -cyano- $\beta$ -phenylcinnamic acid.

Ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate was synthesized in a sequence of five steps from 4-ethylbenzoyl chloride and benzene followed by condensation with cyanoacetate. The compound was brominated and dehydrobrominated and gave ethyl 4-vinyl- $\alpha$ -cyano- $\beta$ -phenylcinnamate. It was polymerized and copolymerized.

*2(2-Hydroxyphenyl)2H-benzotriazoles*: In the 1980's 2(2-hydroxyphenyl)2H-benzotriazole

UV stabilizers have become the most prominent and effective stabilizers for polymers especially in automotive coatings (31). The technology was base coat and topcoat, Mercedes-Benz pioneered a new era of automotive coatings. In their expensive vehicles they could also afford the best stabilizer. 2(2-Hydroxyphenyl)2H-benzotriazoles were first synthesized in the mid 20's, but it was not until the mid-fifties that it was realized that 2(2-hydroxyphenyl)2H-benzotriazoles were unusually stable compounds in photo physical processes.

We started to work on polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles in 1978 with the arrival of Shohei Yoshida from Asahi Glass in Japan. The syntheses of 2(2-hydroxyphenyl)2H-benzotriazoles involves the diazotization of o-nitroanilines to o-nitro-benzenediazonium chloride and reacting it with phenols. The diazo compound is then reduced, which causes reductive cyclization to the 2(2-hydroxyphenyl)2H-benzotriazole (32-34) (Figure 35).

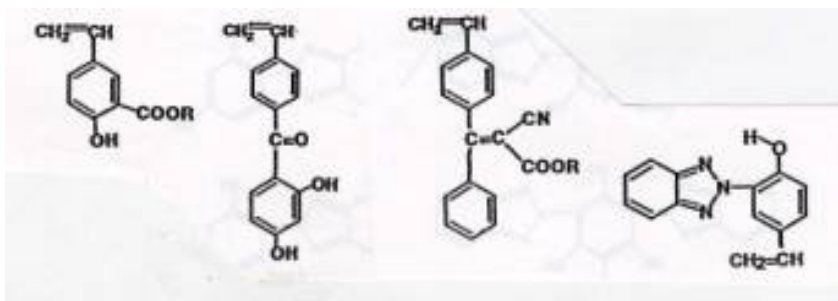


Figure 35: Polymerizable UV Stabilizers

Over the next 15 years we investigated the following categories of 2(2-Hydroxyphenyl)2H-benzotriazoles: A.) Vinyl (Styryl) Derivatives; B.) Substitution on the B-ring; C.) Multisubstituted Benzotriazoles D.) (Meth)acrylate Polymerizable Monomers; E.) 2(2-Hydroxyphenyl)2H-bis-benzotriazoles for Condensation Polymers; F.) Reaction on Polymers Involving 2(2-Hydroxyphenyl)2H-benzotriazoles, including chemical and photo grafting.

Soon after we had succeeded in the synthesis of the first and simplest vinylbenzotriazole, we were approached by the Jet Propulsion Laboratory and NASA. Dr. Amitava Gupta, a

photo physicist, was the manager in charge of photostabilization of polymers. He asked us to join the Jet Propulsions efforts to design and synthesize efficient UV stabilizers that could be used in the vacuum of space. We were supported by them for over 10 years.

The work on polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles was started in Amherst but much of the significant later work was done at the Polytechnic University in Brooklyn. Consequently, I will describe the details in our section on Polytechnic University.

### *ii. Polymerizable Antioxidants*

For many years selected hindered phenols have been used as effective antioxidants for polymers. Unlike aromatic amines they are not toxic and do not form color on autoxidation. We have decided to see if some hindered phenol could be made into a polymerizable antioxidant. We synthesized 2,6-di-tert butyl-4-vinyl (and 4-isopropenyl) phenol polymerized and copolymerized it with butadiene and isoprene by radical emulsion polymerization (35-37). The presence of a free phenolic hydroxyl group was always suspected as a possible chain-stopping reagent for radical initiated polymerizations. This is not the case with highly hindered phenols.

Hydrogenation of the butadiene copolymers gave phenol-ethylene-copolymers and those with isoprene gave phenol-ethylene/propylene-copolymers. Blends of co-polymeric antioxidants with polyolefins were tested for their antioxidant activity. They were found to be active, but weak antioxidant.

### *iii. Polymeric Flame Retardants*

This work was undertaken, when Professor Janovic of the University of Zagreb in Croatia, spent a year with me in Amherst. He was interested in the flammability of polymers. Years before at DuPont, in my "polychloral" period, I knew what really non-flammable polymers were.

Most polymers burn when exposed to a flame and oxygen, mostly under the condition of

the natural composition of the air (18% oxygen/82% nitrogen), which is called an oxygen index of 18. In order to increase the use of polymers under conditions where burning can occur, low molecular weight halogen containing primarily bromine compounds, have been added. They are volatile or not always soluble in the polymer matrix. Janovic was associated with the Company INA in Zagreb, a polystyrene producer and we decided to add flame-retardants to our work program on "polymeric stabilizers" (38-46)

Styrene polymers and copolymers with acrylonitrile have a number of applications, which require resistance to burning, in other words higher oxygen index. With Janovic we prepared copolymers of brominated (meth)acrylic esters of 2,3-dibromopropanol, 2,4,6-tribromophenol, or pentabromophenol with vinyl mono-mers. For uniform co- and terpolymers we studied reactivity ratios of the monomers. The reaction rates for both homopolymerizations and copolymerizations increased in the order styrene < 2,3-dibromopropyl acrylate < 2,4,6-tribromophenyl acrylate < pentabromophenyl acrylate. The incorporation of the acrylates in the co- and terpolymers decreased the thermal stability but improved the flame retardance of the co- and terpolymers.

Acrylonitrile was similarly copolymerized with the three brominated acrylate esters. The reaction rates for both homo-polymerizations and copolymerizations increased in the order pentabromophenyl acrylate > 2,4,6-tribromophenyl acrylate > 2,3-dibromopropyl acrylate > acrylonitrile.

The limited oxygen index of the co- and terpolymers of 10% incorporation in the blends showed an increase of the limited oxygen index. For styrene copolymers the oxygen index rose to was 22 (which is significant) and for acrylonitrile copolymers and acrylonitrile/styrene terpolymers from a LOI of 24 to 27.

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## c. Polymers with Carboxylic Acid Functions

### i. Copolymers of Ethyl Glycidate with Cyclic Ethers

Functionally substituted polymers became very important when it was recognized that certain groups have a profound influence on the bulk properties of polymers. Polymers of acrylates, acrylonitrile, vinyl acetate, vinyl halides, acrylamides, polyesters, polyamides, polyurethanes, and polybutadienes, which have been prepared, are typical examples.

I had started the work on polyoxymethylene ionomers, initially with Ken Martin at Du Pont (in which he played a major role). The work was concluded by Larry DeMejo at UMass. The synthesis was carried out by mixing TO and ethyl glycidate in the gas phase and polymerizing the mixture with boron trifluoride (cationically) to the POM copolymer with pendent carboxylate units.

From this work we had ethyl glycidate on hand and had had experience handling it. He knew that ethyl glycidate was quite unreactive under these copolymerization conditions and had to be used in large excess to obtain proper incorporation into the POM.

It was then logical to check out the homopolymerization of ethyl glycidate and the copolymerization with cyclic ethers. We had hoped to make some copolymers with the carboxyl group from the ethyl glycidate (1). Our ultimate objective was to prepare copolymers that could be transformed into polyether-based ionomers.

To understand our circumstances I would like to mention that I had a highly qualified graduate student who was ready to finish his thesis work before his allotted time. I wanted him to spend a short period of time as a "post doctorate" research fellow abroad. He was destined to pursue an academic career. At the same time, I had become very involved with Professor Saegusa of Kyoto University in research and professional activities. We had secured funds for a cooperative program. Saegusa was interested in oxirane polymerization. I proposed to Dave that he go to Japan to Saegusa's laboratory

for one semester. I could afford to pay part of his subsistence and Saegusa paid the rest. By accepting this "window of opportunity," Dave had a head start his up-coming academic career. In close cooperation with Shiro Kobayashi, an Instructor in Saegusa's laboratory, he undertook the project of polymerization of ethyl glycidate and the copolymerization with cyclic ethers.

We investigated the polymerization of ethyl glycidate with cationic Initiators (2) and with a variety of organometallic initiators. Cationic homopolymerization with triethyloxonium tetrafluoro-borate or triflate (trifluoromethylsulfonic acid) esters produced polymers of relatively low molecular weight, paste-like materials. Both head-to-head and head-to-tail linkages are present in the polyether backbone. The homopolymerization of ethyl glycidate with several organometallic initiation systems, including  $\text{AlEt}_3/\text{H}_2\text{O}$ ,  $\text{ZnEt}_2/\text{CH}_3\text{NO}_2$ ,  $\text{Al}(\text{O}-i\text{Pr})_3$  and  $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$ , were tried but without success.

The cationic homopolymerization of ethyl glycidate and its copolymerization with THF were examined, using triethyloxonium tetrafluoroborate and super acid ester as initiators. Relatively low molecular weight polymers were obtained at that time. Elastomeric copolymers of ethyl glycidate were obtained with propylene oxide, butylene oxide, and oxetane. Conversion of the pendant ester groups of propylene oxide/ethyl glycidate copolymers to the sodium carboxylate and carboxylic acid forms produced the first oxyethylene-based ionomers and carboxylic acids.

While glycidates can be polymerized with typical cationic initiating systems, or the cationic modified aluminum alkyl systems, functional epoxides with spacer groups, that will be discussed in the next section. required a significant modification of these aluminum alkyl systems.

Copolymerization of ethyl glycidate with tetrahydrofuran was also examined. The copolymers were also of low molecular weight ( $< 4000$ ). but an interesting phenomenon was detected. The polymer compositions were exact alternating copolymers with an ethyl glycidate: tetrahydrofuran ratio of 1:2. This result seemed to have been caused by a

penultimate effect as this copolymerization proceeded.

In contrast to the results obtained with cationic initiators, the use of organometallic initiators prepared from  $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$  (1:0.3:0.5) initiator system provided ethyl glycidate copolymers of high molecular weight (3,4). Ethyl glycidate was relatively unreactive in homopolymerizations. Tough copolymers of ethyl glycidate with propylene oxide or n-butene oxide with up to 5 mole percent of ethyl glycidate were prepared. Ester substituted alkylene oxide copolymers of ethyl glycidate and cyclic ethers were also prepared using the  $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$  (1.0/0.3/0.5) initiating system. Copolymerizations of ethyl glycidate with other epoxides, such as epichlorohydrin and isobutylene oxide were also briefly investigated. With oxetane as comonomer, ethyl glycidate gave white, leathery copolymers.

The carbethoxy groups of polyether/ethyl glycidate copolymers were hydrolyzed with sodium hydroxide to the sodium salts, the ionomers of the copolymers. Neutralization of the polymeric sodium salts gave the free polymeric acids.

In connection with the cooperative work with Saegusa he sent one of his former students, Kondo, now employed by UNITICA Co., to my laboratory. In view of my interest in vinylsalicylates, we assigned him to prepare oxiranes of methyl salicylates. He epoxidized methyl 5-vinylacetyl salicylate with our preferred epoxidation reagent 5-Epoxyacetylsalicylate did not homopolymerize but readily co-polymerized with propylene oxide and styrene oxide with the  $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiating system (5).

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## F. Spacer Groups in Macromolecular Structures

### Introduction

My interest in spacer groups in macromolecular architecture had its origin in a number of events, which occurred during my research in polymer chemistry. a.) Polymerization of aliphatic polyaldehydes; b.) Reactions on polymers; c.) Various other observations during our research on polymers and their reactivity.

**a. Side Chain Crystallization:** During my research on isotactic polyaldehydes I recognized that crystalline, isotactic polyaldehydes showed unusual melting behavior. Polyacetaldehyde melted at 165°C and poly(n-butyraldehyde) at 225°C (polyformaldehyde melted at 178°C). As the aliphatic chain length of the polyaldehydes increased, double melting points were observed for poly(n-valeraldehyde, poly(n-hexaldehyde) and poly(n-heptaldehyde). We later substantiated that these polyaldehydes behaved as if they were immiscible mixtures of two components. Over 10 years later, in academia, I had the possibility and continued interest to investigate this phenomena in detail.

Indeed two melting regions were detected for poly(n-valeraldehyde, poly(n-hexaldehyde)

and poly(n-heptaldehyde). The higher melting point is related to the helical POM backbone chain of the isotactic polyaldehyde.

During my research on isotactic polymers of higher aliphatic aldehydes, I had observed dual melting points. The dual melting points started to appear with poly(n-valeraldehyde) representing the melting of the POM helix at about 120°C and a "paraffin" melting point in the 40-50°C range. After the poly(n-heptaldehyde) there was only the "paraffin" melting but no more POM melting point.

We directed our polyaldehyde research into determining the side chain crystallization of the isotactic polyaldehydes. In fact we had determined the structure of poly(n-heptaldehyde). The polymer structures were known as rigid chains. We attempted to determine how long a methylene "spacer" group between the main chain and the crystallizable aliphatic group was needed for the aliphatic paraffin crystallization to occur.

For our polyaldehydes we calculated the spacer length of the methylene groups before side chain crystallization could occur. We needed only to measure the heat of fusion of the isotactic polyaldehyde of the melting range of the "paraffinic" melting. Knowing the heat of fusion as 6.1 cal/g per methylene unit we could "count" how many methylene units had crystallized.

When I had just started in my academic career Nicolai Platé, of Lomonosoff State University in Moscow gave a talk in the early 1970's in which he described a crystalline polymer of alkyl methacrylate with long aliphatic ester side chains. He studied n-dodecyl methacrylate in detail. This was the time of stereospecificity and stereoregular polymers and methacrylates were of major interest. Platé's polymers melted in the 40-50°C range. It is now clear that what they had been an atactic amorphous methacrylate chain with a long enough aliphatic paraffin side chain, which was capable of paraffin type crystallization.

By chance, as a result of our work on head to head polymers we had also worked out a

general synthesis for 2,3- dialkylbutanediols-1,4. We prepared selected polyesters of long chain 2,3-dialkylbutanediols-1,4 and found that paraffinic side chain crystallization could be observed. We determined how long the paraffin side chain had to be when crystallization occurred. We measured the heat of fusion of the methylene groups and used the formula that we had used earlier to calculate how many methylene units were involved in the crystallization.

**b. Fluorocarbon polymers:** At DuPont my laboratory was close to the laboratories where the development for NAFION was carried out and I also well knew the scientists who worked on the project. NAFION, the polyfluorocarbon sulfonate or carboxylate, ultimately became a commercial success. It is a co-polymer of tetrafluoroethylene with a fluorocarbon co-monomer. The co-monomer has as a flexible spacer a hexafluoropropylene oxide oligomer of about 2-3 units between the perfluoroethylene polymerizable group and the terminal sulfonyl fluoride group.

Functional groups in polymers, when attached directly to the polymer chain have been known to react differently than functional groups in low molecular molecules. This different behavior had sometimes been called "polymer effect." Early in my polymer career, I learned how difficult it was to hydrolyze poly(methyl methacrylate) with bases, how complicated it was to dehydrohalogenate PVC and how complicated it was to react poly(vinyl alcohol) with n-butyraldehyde quantitatively. - and all that because of the dominating influence of the polymer chain.

**c. Natural Polymers:** Nature has carefully selected spacer groups in their structures. Proteins are convincing examples of how flexible spacers, methylene spacer groups, dominate the conformation of the tertiary and quaternary structure of large protein molecules. Most consist of complicated structures,  $\alpha$ -helices of poly( $\alpha$ -amino acids) connected with random  $\alpha$ -amino acid chains.

The  $\alpha$ -amino acids units have spacer groups, methylene units, between the peptide chain and the functional group. i.) A carboxylic group for glutamic acid, ii.) An amino group for

lysine and ornithine, and c.) The short hydrocarbon chain in leucine and isoleucine (whose "function" is to provide the hydrophobic interactions that stabilize tertiary structure in proteins.

Some of the basic amino acid units have functional groups, such as amino, thio, and carboxylic acid groups. They are attached to the chiral  $\alpha$ -carbon atom of the amino acid with 2 or 4 methylene units. Examples are lysine, ornithine, arginine, threonine and glutamic acid. Having the advantage of flexible links, they are now free to interact with other parts of the macromolecule, not necessary with a monomer unit in their vicinity. Other groups provide hydrophobic portions for the macromolecule, such as leucine, isoleucine and phenylalanine.

I still remember a lecture by Professor Bayer, when I was at the Free University of Berlin in 1975, as a recipient of the Senior Humboldt Award. He showed that HEM, the key protein in our blood cells, had a ferrous ion at the center of what is called the prosthetic group. It has as a complexing link an amino group at the end of a 4-methylene lysine unit of the protein chain. The three-dimensional protein structure places the lysine unit on top of the ferrous ion and the bottom is a histidine unit. This structure absorbs, complexes and releases the oxygen molecule reversibly our whole life long and allows us to breathe and live. When the amino group from the lysine unit, is attached with 3 or 5 methylene groups instead of the 4-methylene units, in the side group, the oxygen absorption is less reversible and the ferrous oxidizes irreversibly.

I have mentioned the hydrophobic interactions using leucine in proteins. Nature has also used other hydrophobic, paraffinic side groups for different functions. Polysaccharides, carbohydrates, are used for nutritional purposes such as cellulose, starches and sugars. To prevent water from evaporating from fruits and vegetables, the skin of several fruits and vegetables are composed of esters of high aliphatic fatty acids of cellulose. Examples of fruits are apples, pears, cherries and the vegetables tomatoes, peppers and cucumbers.

### a. Polymers from $\omega$ -Epoxyalkanoates and $\omega$ -Alkenoates

When I was becoming interested in spacer groups, the overall scientific directions were toward the development of "ultimate properties" of polymer. Usually they could not be fabricated in convention ways because of these "superior" properties.

First came Nomex the aromatic polyamide from m-phenylene diamine and isophthalic acid. 10 Years later came Kevlar, the aromatic polyamide from p-phenylene diamine and terephthalic acid. Vespel, the polyimide resin from pyromellitic dianhydride and bis( 4-aminophenyl) ether and Econol, the polymer of p-hydroxybenzoic acid. A number of years later it was recognized that one, two or three methylene groups in the stiff polymer backbone can bring the range fabrication or use temperature into a manageable range. See also crystallization rate between poly(ethylene terephthalate) and the better crystallizing poly(propylene terephthalate) and poly(butylene terephthalate).

In 1972 I started to consult for Tennessee Eastman in Kingsport, Tennessee. Tennessee Eastman was heavily involved in research on polyesters. Jerry Jackson's research group transesterified poly(ethylene terephthalate) with various dicarboxylic acids and glycols but also with hydroxy acids. Among these hydroxyacids was p-hydroxybenzoic acid. Co-polymer with ~about 30% p-hydroxybenzoic acid incorporated peculiar properties. Everybody (including me as the consultant) were puzzled. It turned out to be the first liquid crystal polymer. Being under contract with Tennessee Eastman, I could not become involved in my own research in liquid crystalline materials, especially in backbone liquid crystalline polymers, but my interest in liquid crystalline polymers remained over the years. As indicated earlier, we had carefully studied the homopolymerization of ethyl glycidate under cationic conditions. It did not proceed easily. The copolymerization of TO with ethyl glycidate under normal conditions gave only in low molecular weight unless it was carried out in our flow apparatus.

We also accomplished the co-polymerization of ethyl glycidate, which was accomplished with propylene oxide, 1--butene oxide, and oxetane when a specially prepared and aged but traditional initiating system of triethylaluminum/water/acetyl acetone (1.0/0.3/0.5) was

used. Still, the incorporation of ethyl glycidate into the copolymers was low.

We concluded that the low incorporation of ethyl glycidate into the copolymer was caused by the electron withdrawing influence of the carbethoxy group on the polymerizable oxirane ring. We proposed a simple working hypothesis: (a) to separate the polymerizable oxirane ring from the functional group by methylene spacer groups with an increasing number of methylene groups and (b) to study the polymerizability of the functional epoxide (for example, by determining the yield of polymer formation at standard times or molecular weight and molecular weight distribution).

By the mid 70's my scientific interests were broadening, the size of my research group was increasing and my research activities required additional funding. I decided to create a program that was specifically tailored to study the effect of the spacer on the polymerization behavior. This approach required the a.) Synthesis of monomer, b.) Polymerizability and c.) Reactions on the final polymers.

This program was closely connected with our program on functional polymers of POM and polyethers. Here we had prepared initially the (co)-polymeric esters and ionomers and hydrolyzed them to the polymeric carboxylic acids (ionomers). Our other interest came from our work on functional polymers. We had in mind to attach mesogenic groups on the end of a flexible side chain to achieve liquid crystalline portions in our polymers. Such structures had become fashionable. Nonlinear optical properties became to be in vogue. - and potential sources of funding.

This approach was directed toward "side chain crystallinity." In order to provide polymers with these possibilities, we had to make comb like polymers with reactive groups at the end of the side chain of each monomer unit. We concentrated on mesogenic groups to synthesize polymers with liquid crystallinity in the "side chain".

We decided on a dual approach: The preparation monomers for epoxy- (oxirane) or olefin polymerization (1-5).

We prepared and submitted this proposal, sent it to NSF. It was rejected. We rewrote the proposal and again it was rejected. We could never identify any interest group(s), but several years later we found that two groups in refereeing capacities had similar ideas. The proposal was finally funded. I assigned 2 students to the initial thrust to investigate epoxy-terminated aliphatic carboxylic ester from one to eight methylene groups.

## b. Synthesis of $\omega$ -Alkenoates and $\omega$ -Epoxyalkanoates

The initial approach was to synthesize the methyl  $\omega$ -alkenoates from the  $\omega$ -alkenoic acids. Some of them,  $n=0$ , acrylic acid,  $n=1$ , 3-butenic acid,  $n=2$  4-pentenoic acid and  $n=8$ , 10-undecenoic acid were commercially available. The others had to be synthesized by methods that were known. They were synthesized by decarboxylation of the corresponding dicarboxylic acids. As later work progressed, two of the  $\omega$ -alkenoic acids became our favorites: 5-hexenoic acid ( $n=3$ ) and 10-undecenoic acid. 5-Hexenoic acid was readily prepared by pyrolysis of caprolactone and 10-undecenoic acid, made from castor oil could be purchased (6) (Figure 36).

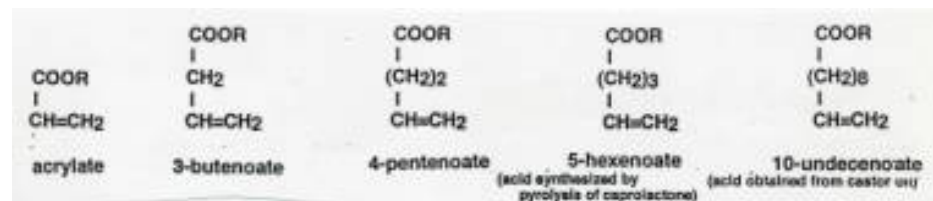


Figure 36: Esters of  $\omega$ -Alkenoic Acids

The acids were esterified with methanol in high yields and epoxidized. We used the reliable epoxidation method using *m*-chloroperbenzoic acid. The epoxidation of the higher  $\omega$ -alkenoates proceed in nearly quantitative yield. 4-pentenoate reacts much slower but after several hours high yield is also obtained. Methyl acrylate epoxidized extremely slowly and other epoxidation methods were preferred (Figure 37).

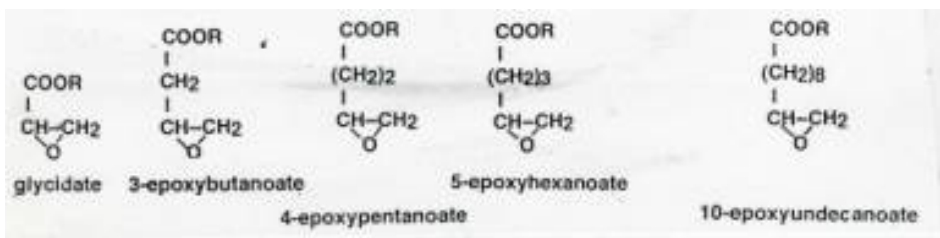


Figure 37: Esters of  $\omega$ -Epoxyalkanoic Acids

The relative ease of epoxidation of 5-hexenoate, which is essentially the same as olefin epoxidation, makes these  $\omega$ -alkenoic acid derivatives an attractive monomer and we have used it later on numerous occasions.

One important surprise occurred when we recognized the cause of the difference in the reactivity between methyl acrylate and other methyl  $\omega$ -alkenoates..  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra showed remarkable chemical shift changes of the methine C-atom as methylene groups were added between the oxirane ring and the carboxylate group. While ethyl glycidate ( $n=0$ ) has a  $^{13}\text{C}$  chemical shift value of 47.7, methyl 3-epoxybutanoate ( $n=1$ ) of 48.0, methyl 4-epoxypentanoate ( $n=2$ ) of 51.5 and methyl 5-epoxyhexanoate ( $n=3$ ) of 51.7, the chemical shift values of epoxy esters with longer methylene spacer groups level off at about 51.8, demonstrating the higher electron density on the methine carbon atom.

We found a similar behavior with the  $^1\text{H}$  signal of the vinyl group and the oxirane groups. After 3 methylene groups are added between the vinyl (or oxirane) group, the NMR signals were identical with those of simple  $\alpha$ -olefins or oxiranes.

The answer was simple: If the polymerizable group and the functional carbomethoxy group were separated by about 3 methylene spacers, they would function independently of each other.

For the polymerization of vinyl-terminated alkanoates we had earlier found that the methyl esters cause problems. I had decided earlier that the polymerization of the  $\omega$ -

alkenoates must be accomplished with catalyst systems traditional for propylene polymerization. We were not going to be involved with designing, new and complicated catalyst research. As a consequence we decided to modify the ester group to be adaptable for the system  $\text{TiCl}_3\cdot\text{AA}$  and  $(\text{C}_2\text{H}_5)_2\text{AlCl}$ . After some tries we settled on the 2,6-dimethylphenyl ester.

It was not enough to just have the 2,6-dimethylphenyl ester of the  $\omega$ -alkanoic ester as an ester group for successful polymerization, the ester had to be complexed. By chance we found that the simplest complexing agent was  $(\text{C}_2\text{H}_5)_2\text{AlCl}$ . When the monomers, the 2,6-dimethylesters of the  $\omega$ -alkenoic acid were "precomplexed" a mild exothermic interaction occurred and the "now" true monomer had been formed. We never took the time to identify the structure of the complex, we only knew it worked for the polymerization. It had to be a more than equimolar complex.

## **b. Polymerization of $\omega$ -Epoxyalkanoates and $\omega$ -Alkenoates**

### *i. $\omega$ -Epoxyalkanoates*

We decided to study first the polymerization of oxiranes. For the polymerization of epoxides, cationic polymerization initiators had been favored and successfully used. In the middle to late 50's catalysts that were produced in mysterious ways from aluminum alkyls of zinc alkyls have provided unusual initiating systems. Their structure has not been known, only their effectiveness after the mixing of the components, possibly aging and use in the presence of the monomer. Even today the structure of the initiating systems are unknown. Prepared by adding the individual ingredients in an optimal way, produced initiating systems that not only polymerized ethylene oxide, but propylene oxide or other epoxides. Some combinations influenced and determined the stereospecificity of the polymerization of propylene oxide. It was known that aluminum alkyl/water or alcohol systems provide cationic initiator. Others that include acetyl acetone are more anionic initiator.

We have early recognized that the aluminum alkyl/acetyl acetone/water sys for one set of

condition and sometimes ineffective for other systems.. We developed our own aluminum alkyl/acetyl acetone/water system, which was very effective for the polymerization and copolymerization of w-epoxy alkanoates.

We investigated the polymerizability of the oxirane monomers as a function of the number of methylene groups between the oxirane ring and the carboxylate group. Not only did we want to study the homopolymerization of individual functional oxirane monomers, but also the copolymerization of oxirane carboxylates with other nonfunctional oxiranes and especially with ethylene oxide.

We first needed to develop initiating systems that are suitable for the polymerization of such epoxides. We found that a specially prepared triethylaluminum/water/acetyl acetone initiating system of the composition (1.0/0.5/1.0), a member of the family of the Furukawa/Van-denberg initiating systems, but prepared in a different way, was effective. Particularly, aging was important. The system polymerized very effectively and to high molecular weight oxiranes from ethylene oxide to 1-dodecene oxide, and oxetane, but not THF.

We could now investigate the polymerizability of oxiranes with functional ester group by inserting methylene between the oxirane and the ester group. This system also immobilizes the monomer by complexation of the carboxylate with part of the initiator system. The most important influence on the oxirane ring is the insulation of the withdrawing electrons from the ring. As the methylene spacer group reaches a critical length those factors become less important. Three methylene groups were necessary to effectively separate the oxirane ring from the carboxylate group. The polymer yields of homopolymerization for  $n=0$ , 1, and 2 were very low and ranged up to 10%, but the yields in the polymerization of functional epoxides of  $n=4$  and higher were in excess of 60%.

The series of methyl w-epoxyalkanoates, with 0 to 8 methylene spacer groups, were homopolymerized with the  $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$  (1.0/0.5/1.0) initiator. The rate of the polymerization also increased as the number of methylene groups between the

polymerizable group and the carbomethoxy group increased. It became constant when more than three methylene groups separated the polymerizable group from the carbomethoxy group. After hours or even days of polymerization reactions, high molecular weight polymers were obtained in all cases.

Based on yields and molecular weight of the polymer we have concluded that about 1-3% of the aluminum is the active initiator and much of the initiating system is inactive or functions as complexing agent for the carboxylic function.

The lower members of the epoxyalkanoate series gave polymers of lower molecular weights and broader molecular weight distributions ( $M_w/M_n > 2$ ). The higher members of the series ( $n > 3$ ) had molecular weight distributions between 1.5 and 2.

The glass transition temperatures, melting temperatures and melting ranges of the polymers were also investigated. The  $T_g$ 's decreased as the number of methylene spacer groups increased. Poly(methyl 3,4-epoxybutanoate ( $n=1$ )) showed a  $T_g$  of  $-26^\circ\text{C}$  while poly(methyl 8,9-epoxynonanoate) had a  $T_g$  of  $-56^\circ\text{C}$ .

Methyl w-epoxyalkanoate homopolymers with longer methylene spacer groups were semicrystalline showing multiple melting peaks, which were attributed to the crystallization of the paraffinic side chain.

Poly(methyl 10,11-epoxyundecanoate), the most investigated w-epoxyalkanoate, showed a  $T_g$  of  $-40^\circ\text{C}$ ; a low temperature endothermic transition with a peak maximum of  $-7^\circ\text{C}$  is attributed to the melting of the microphase separated systems and the crystallization of the  $\text{C}_8$  aliphatic side chains (7-15).

## *ii. Copolymerization of (w-Epoxyalkanoates with Cyclic Ethers*

Methyl 3,4-epoxybutanoate, methyl 4,5-epoxypentanoate ( $n=2$ ) and methyl 7,8-epoxyoctanoate were copolymerized with a number of oxiranes (propylene oxide, 1,2-

butylene oxide, 1,2-hexene oxide, epichlorohydrin, phenylglycidyl ether and with oxetane).

Three methylene groups are also necessary to separate the influence of the carboxylate group of  $\omega$ -epoxyalkanoates on the polymerization of the oxirane group with oxiranes and oxetanes. Methyl 4,5-epoxypentanoate copolymerized with propylene oxide, 1-butene oxide, 1-hexene oxide, and other oxiranes. It gave copolymers with less methyl 4,5-epoxypentanoate incorporated than was added to the polymerization feed mixture. However, with methyl 7,8-epoxyoctanoate and methyl 10,11-epoxyundecanoate as the comonomer, the amount of comonomer incorporated into the co-polymer with various oxiranes was the same as that of the comonomer mixture in the feed. With 30 mol % of methyl 7,8-epoxyoctanoate in the feed, approximately 30 mol % of the comonomer units were in the comonomer.

Tetrahydrofuran did not take part in the attempted methyl  $\omega$ -epoxyalkanoate-tetrahydrofuran copolymerizations and only acted as a solvent. It strongly indicated that the polymerization of  $\omega$ -epoxy monomer proceeds by an anionic but not by a cationic polymerization mechanism. Tetrahydrofuran only polymerizes under cationic conditions.

Methyl 3,4-epoxybutanoate produced copolymers in very low yields. Methyl 4,5-epoxypentanoate gave comonomers, in much higher yields (20 to 60%). The copolymers of methyl 4,5-epoxypentanoate with propylene oxide or butylene oxide were amorphous. Copolymers of methyl 7,8-epoxyoctanoate with the cyclic ethers oxetane or 1,2-epoxyhexane comonomers produced copolymers in good yields and high molecular weights. These copolymers were semicrystalline, had  $T_m$ 's in the paraffinic crystallization range and had sharp  $T_g$ 's.

As mentioned before methyl 10,11-epoxyundecanoate became our favored monomer because it was easily available. It was copolymerized with ethylene oxide, propylene oxide, 1-butylene oxide, 1-hexene oxide, phenyl glycidyl ether, epichlorohydrin, and 4,4,4-trichloro-1-butane oxide. The polymerizations were carried out on a small scale at room

temperature in vacuum sealed polymerization tubes with 5 mol % of the  $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$  (1.0/0.5/1.0) as a initiating system.

Poly(methyl 10,11-epoxyundecanoate) of high molecular weight had an  $M_w/M_n$  of about 2. 1,2-Dodecane oxide with an aliphatic chain, similarly to that of methyl 10,11-epoxyundecanoate) polymerized initially twice as fast, but had ultimately the same high yield.

In copolymerizations with ethylene oxide, methyl 10,11-epoxyundecanoate is much more reactive and gave only about 5 mol% incorporation. Higher levels of incorporation of methyl 10,11-epoxyundecanoate were obtained (at a feed ration of 70:30) with the less reactive 1-butylene oxide (25 mol%), epichlorohydrin (17 mol %), and others. Copolymers with ethylene oxide, and phenylglycidyl ethers were semicrystalline elastomers, but all other copolymers of methyl 10,11-epoxyundecanoate were amorphous.

The  $T_m$  of the copolymers with ethylene oxide depended upon the level of the incorporation of methyl 10,11-epoxyundecanoate. The  $T_m$  was directly related to the  $T_m$  of poly(ethylene oxide) ( $59^\circ\text{C}$ ) and depended on the amount of comonomer incorporation. With 4 mol %, the  $T_m$  was  $56^\circ\text{C}$  but with 15 mol% it was  $43^\circ\text{C}$ . This copolymer was made with a larger excess of methyl 10,11-epoxyundecanoate in the feed. The melting point represents the length of the ethylene oxide segments in the copolymers.

Cationic copolymerization of TO with a methyl 10,11-epoxyundecanoate or methyl 7,8-epoxyoctanoate was also accomplished. Terpolymerization with 1,3-dioxolane was also carried out.

11,12-Dihydroxyundecanoate was synthesized and the two vicinal hydroxy groups were transformed into the corresponding DO. It was copolymerized with TO and

terpolymerized with DO with triflic anhydride as the initiator.

### *iii. Poly( $\omega$ -Epoxyalkanoate) ionomers*

We were interested in preparing and studying the ionomer properties of alkylene oxides. This was not completely new to me because my laboratory at DuPont was located near the laboratory where the ionomes (based on ethylene and methacrylic acid) were conceived, but not were they were actually developed. I did some work on polymers that were ionomers of POM and also of polymeric acids(and salts) of polyethers.

Our interest had changed. We were not interested any more in ionomers whose carboxylic acid function was directly attached to the polyethylene (or other) backbone chains. Our interest had changed to the preparation and characterization of polymeric acids whose acid function was separated from the polymer backbone by methylene spacer groups. From our earlier work on the copolymerization of  $\omega$ -epoxyalkanoates we knew that copolymers of ethylene oxide with  $\omega$ -10-epoxyundecanoate were undesirable. The copolymerization ratio (although not established) favored the polymerization of ethylene oxide and the few percent of "comonomer" was probably a terminal sequence.

With Phillip and Koetz in Berlin, we studied "structure of side-chain branching on the composition of polyanion-polycation complexes (17-19).

We concentrated on copolymers of propylene oxide or butylene oxide with 10,11-epoxyundecanoate. We started a cooperative project with our friend Adi Eisenberg, a compatriot of my Princeton period, who is an expert on ionomers and was now at McGill in Canada. He advised us that such copolymers with 5-10 mole % of our 10,11-epoxyundecanoate would be desirable for investigations. The poly(oxy ethylene) backbone would not crystallize (as did with polyethylene oxide copolymers). We successfully prepared the copolymers and hydrolyzed them to the "ionomers" An accident in the transfer of the samples from my lab to Eisenberg's lab at McGill caused the loss of these very carefully prepared samples. We will never know the properties of

these most interesting ionomers (15).

#### iv. Polymerization of $\omega$ -Alkenoates

The polymerization of epoxides with a functional carbo-methoxy group was now accomplished and the more difficult task of polymerizing terminal olefins with ester groups lay ahead.

Some olefins polymerize with free radical initiators: ethylene, styrene, and olefins, which do not have a hydrogen atom, attached to the carbon atom alpha to the olefin double bond. When such olefins are treated with free radicals (initiators), hydrogen abstraction from the alpha methylene group of the monomer occurs. The generated allylic radicals are unreactive, can only recombine (but not add to the vinyl double bond) and only low molecular weight compounds are formed.

The only polymerization of choice for olefins with methylene groups in the side chains is the polymerization with Ziegler-Natta type coordination initiators. When functional carboxylate groups are attached at the end of such a side chain, the problem becomes more complicated because the polar group interfered with the initiating systems.

It was our policy to use traditional initiating systems and try to adapt them. rather than to get involved in catalyst research. We expected that polymerization with Ziegler-Natta-type initiators could be carried out if the carboxylate group of the monomers were separated by inert, flexible methylene spacer groups from the olefin group and could be deactivated by precomplexation.

We had already established that the  $^{13}\text{C}$  NMR chemical shift values of the methine carbon atom and/or the carbonyl carbon atom could be used to identify critical groups. The carboxylate group influences the polymerizability of the vinyl group. The decreased electron density in the vinyl group caused by the direct attachment of the carbomethoxy group was the reason for the failure of common functional  $\alpha$ -olefins in the coordination

polymerizations.

We approached the problem of polymerization of  $\omega$ -alkenoates with coordination initiators as follows: We investigated the (a) variation of type of carboxylate derivatives, (b) complexation of carboxylate derivatives, (c) type and amount of reducing agent for the transition metal compounds, (d) spacer length of the methylene groups between the polymerizable vinyl group and the functional carboxylate group, (e) polymerization time, polymerization temperature, type of complexation, with attention to initiator preparation, (f) type of transition metal compounds in the initiator system, and (g) copolymerization behavior of  $\omega$ -alkenoates under optimized polymerization conditions.

Initially we concentrated on the esters of *n*-undecenoic acid. Our first objective was to prepare esters of  $\omega$ -alkenoic acids that might undergo coordination polymerization with Ziegler-Natta initiators. A number of esters were prepared including the methyl, trifluoroethyl, 2,6-dimethylphenyl, and the 2,6-diphenylphenyl esters of *n*-undecenoic acid.

We synthesized a number of carboxylic acid derivatives: the methyl and ethyl esters but also the trichloroethyl, trifluoroethyl, phenyl, 2,6-dimethylphenyl, and 2,6-diphenylphenyl ester; in addition, two oxazolines were also prepared. It was found that the phenyl esters, particularly the 2,6-dimethylphenyl ester and also the 2,6-diphenylphenyl ester were suitable for coordination polymerization.

We also prepared a series of 2,6-dimethylphenyl  $\omega$ -alkenoates with methylene spacers of one, three, six, and eight units, the methyl and 2,6-dimethylphenyl esters of 6-heptenoic acid ( $n=4$ ), 7-octenoic acid ( $n=5$ ), and 8-nonenoic acid ( $n=6$ ). These four monomers were polymerized using  $\text{TiCl}_3$ .AA/ $\text{Al}(\text{iso-Bu})_2\text{Cl}$  as the initiator. Polymers were obtained in good to excellent yields. A spacer of less than three methylene units does not sufficiently insulate the double bond from the electron withdrawing effects of the ester group and  $\omega$ -alkenoates of  $n < 4$  did not polymerize.

As a starting point for the development of an efficient initiating system, we used the

activated titanium trichloride system, which is used commercially and often referred to as "Stauffer catalyst"; this initiating system proved to be effective in our research. As reducing agent for titanium trichloride, we found that diethylaluminum chloride was effective, but even better was diisobutylaluminum chloride when used in 3 to 4 times the molar amount. Under these conditions, polymer yields of the 2,6-di-methylphenyl 10-undecenoate of about 60-90%, were obtained. Without monomer precomplexation, no or essentially no polymer was obtained (19-24).

Complexation of the ester group with excess dialkylaluminum chloride gave by precomplexation a "new monomer" that was readily polymerizable. The monomer required about 2-3 moles of the dialkylaluminum chloride for complexation. Diisobutylaluminum chloride was also found very effective as the complexing agent as well as the reducing agent for the titanium trichloride catalyst.

No polymer was formed without complexation. A 60% yield with 2 moles excess of diisobutylaluminum chloride, and an over 90% yield with about a 5 moles excess of diisobutylaluminum chloride complexing agent. No polymer was obtained with our titanium chloride initiating system from complexed ethyl acrylate or from complexed ethyl w-butenate; when at least four methylene groups were the link between the ester group and the olefin double bond, a nearly quantitative yield of homopolymer was obtained with our initiating system with 8-nonenoate ( $n=6$  or  $n$ -undecenoate ( $n=8$ ) methylene groups.

The molecular weight of poly(2,6-dimethylphenyl undecenoate) MW's between 1 and  $2 \times 10^5$ ; the polymer samples were rubbery to leathery.

The polymerization of esters of  $n$ -undecenoic acid other than the hindered substituted phenyl esters was not easily accomplished. and the yield of methyl 10-undecenoate polymer was less than 20%. The polymerization of 8-nonenoic acid esters ( $n=6$ ) 7-octenoic acid esters ( $n=5$ ) and 6-heptenoic esters ( $n=4$ ) was also accomplished. Polymerization of w-alkenoates with  $n < 4$  methylene groups did not polymerize under these conditions.

We have concluded that the number of methylene groups used as spacers between the polymerizable olefin and the carbomethoxy group must be greater by one methylene unit than the corresponding oxiranes.

After our work was nearly completed, I met with the director of polyolefin research at DuPont, Bob Arnold and told him our results. I had become a DuPont consultant. I offered him the research results before publication. He brought to our next meeting Dick Jones, who reported that our work could not possibly be correct. He had tried something similar in 1967 and did not obtain any polymer. --- But then he admitted that he had used only the stoichiometric amounts of the aluminum alkyl chloride - and never bothered complexing the functional group of the monomer;

#### v. Copolymerization of $\omega$ -Alkenoates with $\alpha$ -Olefins

2,6-Dimethylphenyl undecenoate also served as a very suit-able comonomer for the coordination polymerization with various  $\alpha$ -olefins and ethylene. The copolymerization with 1-dodecene, 1-hexene and 1-butene proceeded very well. We used most frequently 2:1 ratios of monomer and comonomer.

Copolymerization with propylene, gave only about 7-10 mol% incorporation. With 1-butene it was much better. Because of its much higher activity, it was difficult to incorporate more than 5 mol% of 2,6-dimethylphenyl undecenoate into the ethylene copolymer. Large excess of the less reactive monomer is required to achieve satisfactory incorporation.

Copolymerization of 2,6-dimethylphenyl 10-undecenoate with 1-dodecene, 1-octene, 1-hexene, propylene, and ethylene using the coordination initiation system  $\text{TiCl}_3\text{AA/Al}(\text{dialkyl})_2\text{Cl}$  was accomplished. Copolymers were obtained in high yields and with high inherent viscosities.

Terpolymerizations of 2,6-dimethylphenyl 10-undecenoate with ethylene and propylene were also carried out. Up to 6 mol% of 2,6-dimethylphenyl 10-undecenoate units were incorporated.

The co- and terpolymerization of ethylene, propylene, and 2,6-dimethylphenyl undecenoate was of interest because this kind of polymer is of potential interest as an elastomer. The 2,6-dimethylphenyl undecenoate units were expected to provide a novel method of curing (cross-linking) reaction for ethylene/propylene rubbers.

Very recently, we have studied more exotic monomers for incorporation into functional polyolefins, 10-undecenoate derivatives that could function as polymeric antioxidants or UV stabilizers.

### **c. Reactions on Poly( $\omega$ -epoxyalkanoates) and Poly( $\omega$ -alkenoates)**

Poly( $\omega$ -epoxyalkanoates) and poly( $\omega$ -alkenoates) and their copolymers have earlier been prepared in sealed tubes. The polymerization required hours and days. It was most conveniently carried out at or near room temperature, easily controlled and reproducible. As the project unfolded, larger quantities of polymers were needed and we were able to carry out the polymerizations in reaction vessels in liter volumes.

The two most accessible  $\omega$ -alkenoic acids, 5-hexenoic acid and 10-undecenoic acid were utilized for our studies of the reactions on polyethylene-based copolymers. 5-Hexenoic acid was prepared by pyrolysis of  $\omega$ -caprolactone and 10-undecenoic acid was commercially available. The two acids were esterified with 2,5-dimethylphenol. After the esters were properly complexed, they were polymerized in high yield to high molecular polymers. Improved polymerization techniques using improved titanium based coordination polymerization initiating systems. The polymeric esters were hydrolyzed with base to the acid salt, which were converted to the acids. Reactions with 1,1-carbonyldiimidazole gave polyethylene based polymeric imidazolides.

The two  $\omega$ -undecenoic acids, 5-hexenoic and 10-undecenoic acid were esterified with methanol and the methyl esters epoxidized to the corresponding 5,6-epoxyhexanoate and 10,11-epoxyundecanoate. The epoxy esters were polymerized with  $\text{AlEt}_3/\text{H}_2\text{O}/\text{AcAc}$  systems. Quantitative hydrolysis made the polyethylene oxide based polymeric acids available for their transformation with carbonyldiimidazole to the highly reactive polymeric carboxylic acids imidazolids.

Polymeric esters and amines were prepared from the imidazolids of poly(10-undecenoic acid, poly(10,11-epoxyundecanoic acid), poly(5,6-epoxyhexanoic acid). Initially the reaction was studied with simple aliphatic and aromatic amines, phenols and alcohols (25) Our ultimate objective was, however, to synthesize polymeric liquid crystalline polymers with mesogenic groups at the end of the side chain, but separated with a flexible spacer group from the main chain.

The mesogenic polymers include polymeric reaction products of 4-hydroxybisphenyl, 4-cyano-4'-hydroxybisphenyl, 4-aminobisphenyl, cholesterol, carbazole, and also others. The reactions were carried out via the imidazolids of the polyacids and gave yields between 75 % to quantitative with conversions from 60-100%. Aliphatic and aromatic amines gave nearly quantitative conversion; phenols gave also high yield reaction products. For quantitative substitution using alcohols such cholesterol their alkali salts should be used. The polymeric esters and amides were briefly studied for their thermal and mesogenic properties (Figure 37).

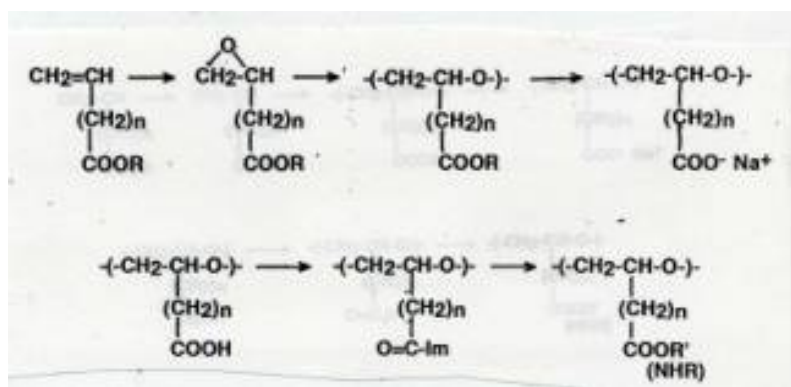


Figure 37: Reactions of Poly( $\omega$ -Epoxyalkanoates) and Poly( $\omega$ -Alkenoates)

We had synthesized "comb" polymers that have poly(ethylene oxide) or polyethylene chains. Attached to each monomer unit is a short aliphatic chain with terminal functional groups. We have especially prepared, polymeric carboxylic acid, carboxylic acid esters, mesogenic esters and amides and various other polymers

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## V. Polytechnic University

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On a day in January of February 1982, I received a phone call from the Provost of the Polytechnic Institute of New York (in Brooklyn), - Brooklyn Poly. He told me that the Polytechnic Institute had created anew position, an endowed Chair named after the well known Herman F. Mark, a Professor and Dean of Science at the Polytechnic Institute. He mentioned that the Institute was considering me for this position and would I be interested. My immediate reaction was - NO.

In Amherst I was the co-director of CUMIRP and had just finished my chairmanship of the Gordon Research Conference on Polymers I was also the Vice Chairman of the upcoming 34th IUPAC Symposium on Macromolecules, a meeting that I had worked very hard to bring to Amherst. I had my hands full with the organization of the Symposium.

My research group was sizable and very productive. New results were pouring in. I had planned a trip abroad for the end of March. I had another, now more urgent phone call and was persuaded to visit in Brooklyn on March 9, 1982, just before our trip abroad, The offer was made more formally and our negotiations went well. The position (at a substantial increase of salary) had to be taken later in the year. The position had been held on a 3-month temporary basis by Ephraim Katchaski-Katzir from the Weizman Institute after he had completed his term as President of the State of Israel. The offer was modified and I as the holder of the endowed Chair would report directly to the

Provost. It was a Research Professorship but I was encouraged to teach some courses. By September I had accepted the offer of the Polytechnic Institute. Since I was the appropriate age, I could retire from the University of Massachusetts at that time. I will discuss the move in more detail later in the book

In January 1983 we moved to Brooklyn to an apartment in Brooklyn Heights. At that time, parts of New York and especially Brooklyn was not as safe place to live as Amherst and the situation required some adjustment. Ultimately we got used to it.

My research activities moved to Brooklyn. Some of my coworkers came with me, some students remained in Amherst and finished under my direction but under someone else's guidance. I had run a fairly simple laboratory in Amherst. As a basically organic laboratory, it did not need more than glassware and some instrumentation. Much of the equipment had been given to me by the University and I was able to take it with me to Brooklyn.. The laboratory and office facilities in Brooklyn were excellent and modified to my specifications. I had a nice office complex directly connected to one large laboratory.

I had funding from several sources. I was committed to the work with the Jet Propulsion Laboratory. Consequently, much of the effort at the Polytechnic involved the work on polymerizable and polymer-bound UV stabilizers. Some "head to head polymer" work was brought to conclusion. The work on "Spacers in Polymer Structures" was revived, and the work on the polymerization of trihaloacetaldehyde was redirected. Much of our new thrust was focused on **macromolecular asymmetry** and **helicity**. Some work directly related to industry was undertaken. My work at the Polytechnic University, (previously called Brooklyn Poly), is recorded in this section of the book (1-7)

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## A. The Genesis of Polymerization

Cryotachensic polymerization allowed the smooth polymerization of chloral to isotactic and helical polychloral. Chiral initiation gave polychloral with optical activity, optical activity based on macromolecular asymmetry. We had been wondering why this kind of optical activity was not always perfect. Why was the optical rotation of polychloral films different from run to run and from day to day? Why was one time the optical rotation of the polymer film higher when the film was made immediately after the addition of the chiral initiator. Why was the optical rotation of the films different when the initiated monomer was "incubated" for some time prior to polymerization.

Everything had an explanation but what was the right one? We decided to look for the answer by investigating the embryonic state of chloral polymerization. We had an unusual handle for this study, which no other polymerization had, the  $T_c$  and cryotachensic polymerization. Other investigators had studied other systems. The "beginning" of the chain growth was the subject of extrapolations and implications.

With chloral as the monomer, we could follow the first time, step by step, the oligomerization of a monomer. Granted chloral was not the most common monomer but it was in many ways the perfect monomer. Using the chloral system allowed us to understand the genesis of polymerization. It also provided individual compounds (oligomers) that could be isolated, characterized and in some cases their absolute configuration determined. Furthermore, this approach allowed us also to understand chiral initiation, which produced stereospecific and conformational specific chiral polychloral. Ultimately it provided the basis for the design of experiments to synthesize the single helix (8)

### a. Chloral Oligomers, LTB Initiated

The oligomerization of chloral was accomplished by mixing 0.5 mole percent of LTB

with chloral in toluene above the polymerization temperature ( $T_C$ ). With agitation, the mixture was slowly cooled. It is cooled through the temperature of the  $T_C$ , and chloral polymer starts to precipitate. At this point the mixture contains insoluble polychloral, and, in solution, soluble oligomers of chloral. The polychloral probably also contains small amounts of insoluble higher oligomers of chloral. This mixture is in equilibrium depending on the temperature. In order to freeze the equilibrium, the mixture must be end capped. End capping was achieved by treating the mixture with acetic anhydride. The suspension was filtered and the insoluble polychloral separated. The mixture of soluble oligomers was worked-up and the low oligomers characterized (9-13) (Figure 39).

The chloral oligomers from dimers to the tetramer were isolated by distillation and by GPC fractionation. The dimer fraction was a diastereomeric mixture of the

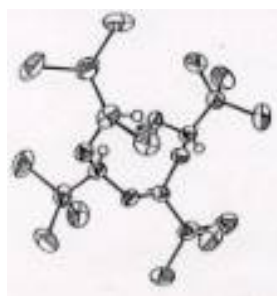


Figure 39: Model of Lithium *tert* Butoxide, Acetate Terminated Chloral Tetramer

racemo- (14-16) and meso- isomers while the trimer, tetramer, and pentamer fraction, each contained essentially one single diastereomer.

$K^+$ IDS mass spectrometry (useful to mass numbers up to 2000 Da) was used to identify the individual oligomers (Figure 40). Oligomers with mass numbers of the [unimer] $K^+$  (301 Da) to the mass of 1187 Da), the [heptamer] $K^+$  could be identified. Individual oligomers were also characterized by their chlorine isotope calculations. It could also be used for semi-quantitative estimates of individual compound in mixtures.

The stereo structure of linear chloral oligomers was determined by X-ray single crystal analysis. Single crystals were grown from methanol and their space group was identified. The X-ray analysis showed that the acetal backbone consisted of meso dyad arrangements. The backbone arrangements are identical with the repeat gauche(+)-skew(-) sequences from the tertiary butyl group to the acetal terminal group.

The conformation of the 4m, (S,S,S,S) is very similar to the unit sequence of an approximate 4/1 helical structure of isotactic polychloral with left-handed helicity. The repeat distance was 4.81Å.

The dimer was found to be triclinic, the trimer and the tetramer monoclinic and the pentamer orthorhombic; the melting points were 73°C, 116°C, 255°C and 225°C respectively.

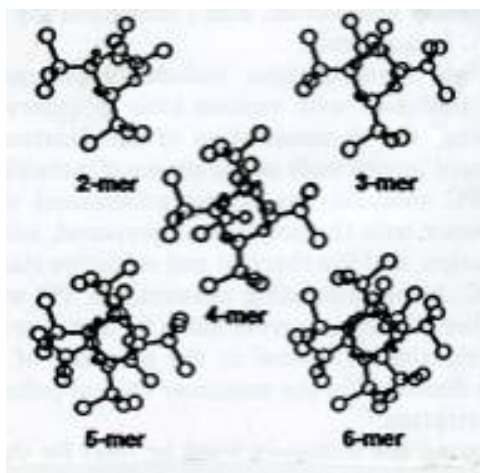


Figure 40 Models of Chloral Dimer to Hexamer

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of chloral oligomers was intensely investigated. The signals to the unimer, meso and racemo isomers of the dimer (2-m), (m,m,r,r) and the most abundant stereoisomers of the trimer and tetramer were identified. The meso/racemo assignment of the dimers, the signals due to the trimer and tetramer were assigned to the structure of 3mm and 4mmm structures respectively. The NMR spectrum of the dimer showed that the diastereomeric ratio for the dimer was 75 to 25. The two diastereomers of the dimers were also resolved into enantiomers on a chiral

(cellulose tri(3,5-dichlorophenylcarbamate) and cellulose tri(3,5-dimethylphenylcarbamate) HPLC column (17,20).

The predominant conformation of the acetal backbones in solution is the alternating g\*s- over the S arrangement. That is the helical conformation of the chloral oligomers was maintained even in solution.

In all these cases we had been analyzing chloral oligomers that had one initiating end group and a different end group from the end capping reagents because this was convenient.

## b. Dimethyl Capped Chloral Oligomers

Our work on the oligomerization of chloral was carried out in close cooperation with Hatada's group in Osaka. In much of our early work, somewhat bulky tert butoxide anion (LTB) was used as initiator. The result was that the acetate end capped oligomers, even the unimer, had rigid structures as shown by their NMR behavior.

The advantage of a smooth scientific and congenial cooperation is that criticism is available when needed. Hatada said: We need the oligomers "without an end group". Since it was not possible to have "just a hydrogen" end group, we decided on a methyl end group. Hatada's group synthesized methoxide initiated, methyl terminated oligomers of chloral. The initiation was relatively easy but the methyl end capping could only be done with methyl triflate. Oligomers up to the pentamer and the hexamer were isolated (21-22) (Figure 41).

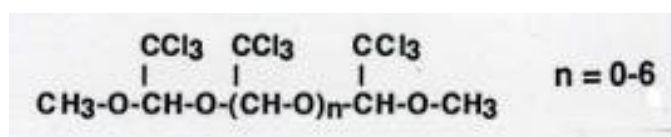


Figure 41: Methyl Capped Chloral Oligomers

The purely isotactic and symmetrical pentamer carrying a methyl group on both ends which is the (R,R,S,S)-(+/-) isomer was analyzed for their non-equivalence. The signals due to the methyl group coalesce at 72°C. In a similar manner the coalescence temperature for the methyl group of the tetramer was determined as +4°C and that of the hexamer of +140°C. These experimental results showed that the low polymer chain of isotactic chloral is not "inherently" inflexible, but is locked by the tert butyl end group in LTB initiated chloral oligomers. Once the length of one and a half turns of the helix are available, the rigidity of the conformation is established.

### c. Amine initiation of Chloral Polymerization

For a long time we were interested in the initiation, propagation and termination of chloral polymerizations. We used alkoxides and TPP (actually the reaction product of TPP with chloral which is a phosphonium counter ion) extensively as initiators. We also initiated with tertiary amines. This polymerization proceeded readily but the resulting polychloral samples were relatively unstable. Furthermore, when the polymerization was carried out between glass plates (to prepare films or sheets) the polymer stuck tenaciously to the glass and the plates had to be broken to retrieve the desired objects.

With our recent experience in the oligomerization of chloral with LTB initiation, we felt that we should investigate more precisely the tertiary amine initiated chloral oligomerization. The tertiary amine initiated chloral was cooled below the  $T_c$  until 20-30% polymer was produced and the mixture was end-capped with acetic anhydride (Figure 42). A number of tertiary amines were used for this chloral oligomerization, from triethylamine and pyridine to the chiral strychnine.

After isolation, the oligomer mixture was subjected to GC and showed several peaks that were indicative of the expected oligomers. The oligomer mixture was then

subjected to the  $K^+IDS$  mass spectrometry. To our surprise the mass spectrum of the mixture consisted of diacetyl capped chloral oligomers (23-25). We had to conclude that tertiary amine initiation

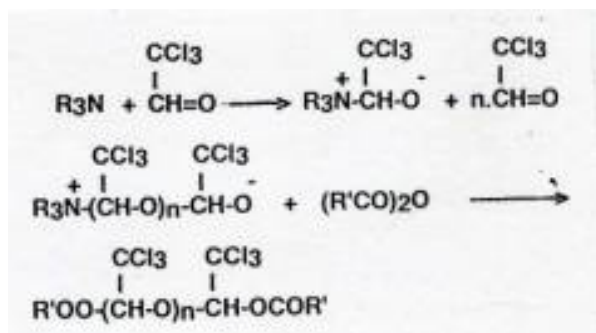


Figure 42: Amine initiation of Chloral Polymerization

occurred directly and one mole of chloral was added to produce a Zwitterion ion. Acetylation of the oligomer mixture not only acetylated the "growing" alkoxide, formally with the acylium ion, but the acetate part replaced the ammonium end to form the oligomeric diacetate. For triphenylphosphine (TPP), and other tert phosphines initiation, one mole of chloral reacted with the phosphines and formed the chloride of a phosphonium salt. The chloride was the actual anionic initiator.

According to our  $K^+IDS$  analysis, similar oligomer diacetate mixtures were obtained independent of the type of initiating tert amine used. Strychnine did not produce chiral chloral oligomer diacetate.

The chloral oligomeric alkoxides initiated with triethylamine were also acylated with the following anhydrides: Propionic acid anhydride, n-butyric acid anhydride, isobutyric acid anhydride, pivalic acid anhydride and benzoic acid anhydride. They gave the diacylated chloral oligomers. Capping with acetic anhydride proceeded very rapidly and effectively. Capping with less reactive anhydrides was more sluggish. Diphenylacetic acid anhydride and adamantane carboxylic anhydride are not sufficiently reactive and gave only chloral unimer diacetates.

### c. Chirally Initiated Chloral Oligomers

The oligomerization of chloral with the lithium salts of (1S,2R,4S)-(-)-borneol as the initiator was studied. The unimer and dimer fractions consisted of 2 and 4 diastereomer respectively. The individual isomers were isolated from the fraction by crystallization from methanol and by high performance liquid chromatography. The X-ray single crystal analysis showed that the major isomer of the unimer fraction is the (R) form, which has the acetal carbon in (R) configuration. The diastereomeric ratios were determined by  $^1\text{H}$  NMR spectroscopy. The R/S is 57 over 43 for the unimers and RS/SR/RR/SS = 34/25/23/18 for the dimers. The conformation of the meso dimer [(R,R)- and (S,S)-isomers] in the crystalline form corresponds to a half turn of the 4/1 helix of isotactic polychloral whereas the conformations of the racemo dimer [the (R,S) and (S,R)-isomers] was different from the helical structure in the crystal and in its solution. The trimer fraction consisted of six of the eight possible diastereomers; among these isomers the mm [the (R,R,R) and (S,S,S)-isomers] were pre-dominant. The amount of the (R,R,R)-trimer form, was only slightly larger than that of the (S,S,S)-isomer. For the dimer and trimer fraction, the assignments of each oligomer structure were made by  $^1\text{H}$  NMR spectroscopy (26-28).

The results of the oligomerization of chloral with bornyloxide is slightly different from that of the dimerization and oligomerization of chloral with tertiary butoxide. The trimer fraction as mentioned before consisted of 6 isomers. Among the 6 isomers, the isotactic trimer mm-(R,R,R) and mm-(S,S,S) were predominant and largest in quantity (82%). On the other hand, the syndiotactic trimers, rr, were not found.

Polychloral prepared under these conditions contains nearly equal amounts of both left handed and right-handed helices and shows low optical activity. That means that a much bulkier chiral alkoxide was needed to approach the requirements for a single helix. We actually investigated the stereospecificity of addition of chloral to bulky alkoxides by characterizing dimers. Tricyclohexylmethyl methoxide did not add chloral (it was too crowded. Dicyclohexylmethyl methoxide gave a highly stereoselective chloral dimer addition product.

Characterization of linear bornyloxide initiated acetate end capped chloral oligomers was done with  $K^+IDS$  mass spectrometry exclusively. Ions from the [unimer] $K^+$  with a mass of 381 Da to the [hexamer] $K^+$  with a mass of 1119 Da were observed. Analysis of the isotope patterns supported their structural assignment. The individual oligomers were of course, also analyzed by GC and NMR spectroscopy.

#### **d. Other Trihaloacetaldehyde Oligomers**

The oligomers of fluoral, bromal and the co-oligomers of chloral/bromal proved to be an interesting and most desirable addition to our investigation of the genesis of trihaloacetaldehyde polymerization. Capillary gas chromatography and  $K^+IDS$  were essential for the analysis and characterization of the individual components of the oligomer mixtures.

*Fluoral Oligomers:* Linear fluoral oligomers were prepared by initiation of fluoral with LTB but also with bornyloxide; the oligomers were acetate capped (29). A series of oligomers up to the undecamer could be identified. Analyzing the fluoral oligomerization it could be seen that some stereospecificity was developing even with the small trifluoromethyl group as the side group. The oligomer fraction responsible for the meso addition product increased and became constant at about 60% to 70% meso addition.

*Bromal Oligomers:* The oligomerization of bromal was accomplished by initiation with LTB or bornyloxide. It was concluded by acetate end capping. Oligomers up to the pentamer could be identified. The oligomerization of bromal was more complicated because bromal was quite reactive and could undergo side reactions; furthermore, and the  $T_C$  was much lower.

Similar results were found when the bornyloxide initiated bromal oligomerization was analyzed by  $K^+IDS$  mass spectrometry. The two diastereomeric unimers of the

bornyloxide initiated acetate end capped bromal unimers were subjected to single crystal X-ray analysis and confirmed by their  $^1\text{H}$  NMR spectrum. The structure of the bromal unimers was quite similar to that of the corresponding chloral unimer. By NMR spectroscopy it was shown that the two diastereomers exist in a ratio of 53 % to 43 % (30-32).

**Co-oligomers:** We also analyzed the co-oligomerization of bromal and chloral. Co-oligomers of chloral and bromal were synthesized by initiating one to one mixtures of chloral and bromal with LTB or lithium bornyloxide followed by acetate capping. Co-oligomers up to the pentamers were characterized by  $\text{K}^+\text{IDS}$  mass spectrometry and GC analysis (33-37).

**Optical Activity of Trihaloacetaldehyde Oligomers:** The optical activity of diastereomeric bornyloxy terminated trihaloacetaldehyde unimers was investigated. Bornyloxide initiated acetate end capped unimers of fluoral, chloral and bromal were prepared and the optical rotation measured. Bornyloxy initiated trihaloacetaldehydes consist of two diastereomeric unimers. The cases of the chloral and bromal unimers initiated with bornyloxy groups and terminated with acetate groups have been isolated and characterized (38-39). One diastereomer of the chloral unimers was crystallized and the absolute structure was determined. The optical rotation of the unimers was plotted as a function "side group" size of the unimer. Two series of values were obtained which seem to follow a linear relationship, the (R) series had a lower and (S) a higher negative value of the optical rotation.

In conclusion. The oligomerization of trihaloacetaldehydes gave an amazing amount of information of how trihaloacetaldehydes of different reactivities, as represented by their  $T_c$ , behave, and how chloral and bromal behave in co-oligomerizations.

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## B. Chiral Pentatomic Molecules

The way we became involved in chiral pentatomic molecules consists of a combination of my early interest, an interest in the chiral carbon atom and an accidental discovery. Tom Doyle was working on the synthesis of fluorochlorobromoacetic acid and its perfection. The five-step synthesis was successful. Fluorochlorobromoacetic acid is a racemate and he simultaneously started on the separation of the acid into its enantiomers. This was to be done using optically active bases. After a few tries Tom and I decided that the separation should be done via the strychnine salt. I was not too happy to have to handle a considerable amount of strychnine in the lab, but, after a few tries, we found that it was the best method.

After a while, Tom learned to handle the crystallization of the salts. For some of you who might have used this technique to separate enantiomers, sometimes it work, and sometimes well. We needed a considerable amount of the enantiomeric acid for esterification and reduction to the aldehyde.

Tom found that when the crystallization was done quickly and in larger quantities, the purity of the salt, as judged by its optical rotation, changed. It appeared that the salt became more and more impure and had more and more free strychnine in the salt. This was very enjoyable and I asked Tom: Why he did not sweep the system and pass the gases through a trap cooled in dry ice/acetone bath when he recrystallized the strychnine salt. He actually heated a dry strychnine salt. After 30 minutes, he had obtained in 10 % yield a low boiling liquid that was, by GC, 99 % pure and proved to be fluorochlorobromomethane (Figure 43). The synthesis was ultimately

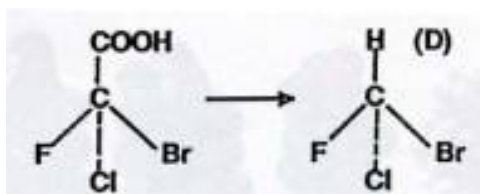


Figure 43: Chiral Fluorohlorobromomethane

perfected. The reaction from the trihaloacetic acid salt to fluorochlorobromomethane was carried out in ethylene glycol at 140°C and gave in 50-70 % yield b.p.= - 31°C,  $[\alpha]_D=2.8^\circ$  . The chiral deuterofluorochlorobromomethane was synthesized from the chiral acid salt in boiling heavy water,  $[\alpha]_D=4^\circ$ .

We have not only synthesized the trihalomethane using the "iodoform" reaction, but we also carried out this reaction using the nearly pure enantiomers of the acid. The fluorochlorobromomethane and deuterofluorochlorobromomethane were also chiral. This proves that the reaction is specific and does not involve any inversion of the fluorochlorobromomethyl anion intermediate. Since we have published our results our colleagues in Lyon, the group of André Collat, used our convenient synthesis of fluorochlorobromomethylacetic acid and the separation into the antipodes. After preparing the sodium salt of the enatiomeric acid his group determined the absolute configuration by x-ray structure analysis. Since the fluorochlorobromomethane results from the sodium salt without racemization. their work also established the absolute configuration of fluorochlorobromomethane and deuterofluorochlorobromomethane, the known absolute configuration of a pentatomic molecule.

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## C. Measurement of Optical Activity in Powdered Solids

The optical activity of compounds containing asymmetric (carbon) atoms is generally measured in solution. What is actually measured is the optical rotation of a solvated individual molecule. For this reason the optical rotation is reported "in the solvent". Many types of crystals also exhibit optical activity in the solid state. These structures are of two major types: a.) Crystals of small molecules, which are themselves molecularly dissymmetric and show optical activity in solution, b.) Compounds, whose optical activity is produced only by the dissymmetry of the crystal structure itself but which disappears upon destruction of the crystal structure.

Measurements of solids in suspension had been attempted in the past. The suspension value of the optical rotation of sodium chlorate was determined but only unreliable values (about 1/3 of the actual value) were detected.

We have now developed and perfected the general method for measuring the optical activity of inorganic crystals in suspension (in addition to the single crystal measurement) (1). We also measured synthetic macromolecules in solution and suspension, found excellent agreement of the data, when all the conditions of measurements were optimized (2-5).

Polychloral is insoluble in all known solvents. We had to devise alternate methods for measuring its chiroptical properties in the solid state. The measurements of polychloral film disks gave high quality solid-state measurements.

Not all solid samples can be prepared in disk or thin film form. Thus, we sought to develop a general method, which could employ suspensions of finely divided powders.

Our general method to measure optical rotation in the solid state (in suspension (Figure 44) and in some cases also in film form) allows the determination of the optical

rotation of: a.) Inorganic (isotropic) crystals, and b.) Organic macromolecules (including polymers whose optical rotation is caused by macromolecular asymmetry (helicity)). The measurements require attention to most of the factors that are necessary for optical measurements. Matching of the refractive index of the crystals and the suspending medium to 0.005 and sufficient light transmission through the sample cell are primary requirements. Other important factors are: particle size and surface, orientation, uniformity of refractive index, type of suspending media, homogeneity of the suspension and possibly density. In semicrystalline samples, the compromise matching of the refractive indices of the crystalline and amorphous phases is also significant.

We found that the selection of a proper suspension medium is critical. The densities and refractive indices of the sample and medium must both be closely matched. Moreover, particle size must be small and the sample particles must not be oriented. These rather stringent conditions limit rotation measurements to solids that are isorefractive in all three dimensions. Highly crystalline materials and polymers that exhibit birefringence are not amenable to this technique. Birefringence is

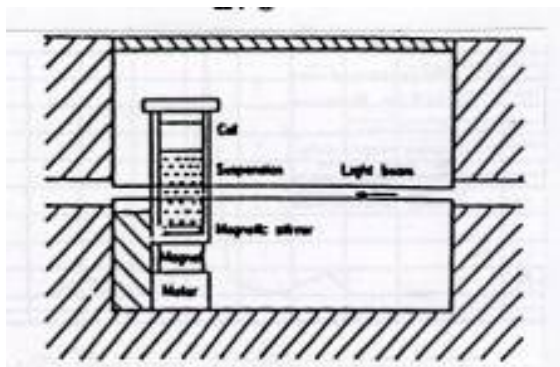


Figure 44: Measurements of Optical Rotation of Polymer Powders in Suspension

caused by differences of the refractive index, which may be caused by orientation, grinding, or the difference between amorphous and crystalline phase. If a measurement is in question birefringence is easily recognized by checking the solid powders with an optical microscope. The data of the optical rotations are erratic and

differ widely. Under the microscope various color patterns show inhomogeneity.

We have further found that samples should be stirred by placing a small stirring device directly under the optical cell. Stirring rates can be conveniently monitored with the aid of a stroboscope. Excessive stirring rates can cause cavitation while too slow a rate will not produce the proper suspension.

The refractive index of the suspending medium should be checked at the beginning and at the end of optical rotation measurement to insure that no change has occurred. The optical rotation of the suspension should be measured as a function of both the changing refractive index of the medium and as a function of the polarimeter's photo current to insure that measurements are gathered in a region of maximum transparency. For a given sample, we have found that chiroptical measurements can be made within 30 minutes with a precision ranging from  $\pm 3\%$  to  $\pm 5\%$ .

It is with this technique that chiroptical measurements were made on a variety of different solids including inorganic salts, organic compounds, and polymers. Sodium chlorate and sodium bromate both crystallize from aqueous solutions to give chiral, D- and L-crystals. These crystals are isotropic with refractive index and optical rotation being the same in each of the three crystallographic directions. These salts were thus ideally suited for the development of our techniques for suspension measurements. Sodium chlorate as the single crystal gave (+) or (-) values of  $121^\circ$  to  $124^\circ$  in all three directions of the crystal axes. Our suspension measurements had an  $[\alpha]_D$  of  $122^\circ$  (6). The powders of a particle size below 40 m were suspended in a mixture of carbon disulfide and carbon tetrachloride having a matched refractive index with the salt.

We also repeated earlier measurements of Pino's for the poly-(S)-3-methylpentene in suspension with a sample obtained from Pino and were able to closely replicate reported optical rotation data for this polymer. Optical rotation measurements were also performed on a variety of other polymers as well. For optically active poly

(triphenylmethyl methacrylate), suspension and solution measurements are in remarkable agreement. They gave values of  $[\alpha]_D = +340^\circ$  to  $+450^\circ$ , in solution and suspension, depending on the solvent or the suspending media. Poly-(S)-3-methylpentene, also in spite of considerable birefringence gave a value of  $[\alpha]_D = +154^\circ$  (3). In other cases, we have observed significant differences, however. For example, measured specific rotations (sodium D-line) for poly-(R)-lactide are  $[\alpha]_D = +245^\circ$  in suspension,  $[\alpha]_D = +170^\circ$  in film form, and  $[\alpha]_D = +162^\circ$  in solution (9). For RNA, we noted rotations  $[\alpha]_D$  of about  $+201^\circ$  in suspension and  $[\alpha]_D = +115^\circ$  in solution (10). "Zero" measurements for about 15 polymers have been made on amorphous, but also semicrystalline materials (11,12).

Not only could we measure the optical rotation of solids in suspension but we found also one example where we could measure the Circular Dichroism of sodium thioantimonate nonahydrate in powder form (13).

Although it was our initial objective to measure optical rotation of polychloral samples in powder form, it did not succeed because of birefringence.

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## D. Polycationic Salts

In the late 1980's I was approached by the Senior Vice President of Merck, Sharpe &

Dome in Rahway to consider working with his Division. He wanted me to consult with them, set up a Polymer Groups of about 8 people and to play an active part in their program of bile acid sequestering agents. The latter project was for me very intriguing. I had worked on steroids during my thesis days, had some knowledge of the cholesterol metabolism but at that time nobody cared about the cholesterol level in the blood. This was, of course, long before the possible importance of the cholesterol level became known for its potential life threatening effects.

The Pharmaceutical Companies knew that about 70% of the cholesterol is produced in the liver, by liver enzymes from acetate. The remaining 30% comes from bile acids present in the intestines by "biochemical" reduction. In order to control the cholesterol metabolism there are two possible approaches: a.) The "medical" approach: To develop a drug that interferes with the cholesterol-producing enzyme in the liver. This approach in various modifications is now the basis of cholesterol reducing drugs. b.) the other approach is to sequester the bile acids in the intestines.

I decided to join the Merck effort to find a way to reduce blood cholesterol by trying to find efficient bile acid sequestering polymers. I agreed that, under Merck's guidance, I would design and synthesize the polymers in my laboratory. Peter Zarras joined my group and fulfilled with dedication the task of monomer and polymer synthesis and characterization. Some ground rules were established that guided our research. Since time was an important factor we had to produce 100-150 g every 6 weeks. We knew that the polymers would have to be prepared from monomers that could be simply synthesized from available chemicals. In order to sequester bile acids it was essential to prepare polymeric cations, not amines but ammonium salts. The polymers had to be of high quality and free of oligomers or other low molecular weight compounds such as amines or ammonium salts that had the tendency to cause bleeding in the intestines of the test animals.

Once delivered, the polymers would be used directly by Merck for three week long

feeding studies on large dogs. The dogs were in the 20-30 kg range and had been trained for cholesterol testing. This meant, that they were very valuable, believed to be worth \$ 20,000. My goal was to develop a polymeric sequestering agent that could be readily formulated for the feeding studies and could reduce the blood level of cholesterol from 300 to 210 with a daily application of about 2-5 g (similar to one tablet of Maalox).

We decided to select styrene based or MMA based polymeric cations. We checked the synthesis of MMA based polycationic resins but soon abandoned the MMA approach. The styrene approach provided more flexibility.

We used as our primary starting material commercially available chloromethylstyrene. The chlorine atom in chloromethylstyrene is very reactive and can undergo readily the Menshutkin reaction with tertiary amines to give quaternary ammonium salts. We prepared a number of these monomers by reacting chloromethylstyrene with trimethylamine, triethylamine, tri-n-butylamine, dimethyl-n-ethylamine and dimethyl-n-dodecylamine (1).

The synthesis of the vinylbenzyl tri-n-alkyl ammonium salts proceeded by a straightforward synthesis. Vinylbenzyl chloride was allowed to react with trimethylamine, triethylamine, and tri-n-butylamine, N, N-dimethyl-n-octylamine, N, N-dimethyl-n-dodecylamine and N-methylimidazole and gave in nearly quantitative yields the desired monomers. A novel crosslinking agent was also prepared. The reaction of vinylbenzyl chloride with N,N,N',N'-tetramethylethylene-diamine gave N,N-(divinyl benzyl)-N,N,N',N'-tetramethylethylene diammonium dichloride (Figure 45).

It became soon clear that the simplest compound, trimethylammoniummethylstyrene, was also the most interesting. Zarras made a major invention. He found that this monomer could be polymerized

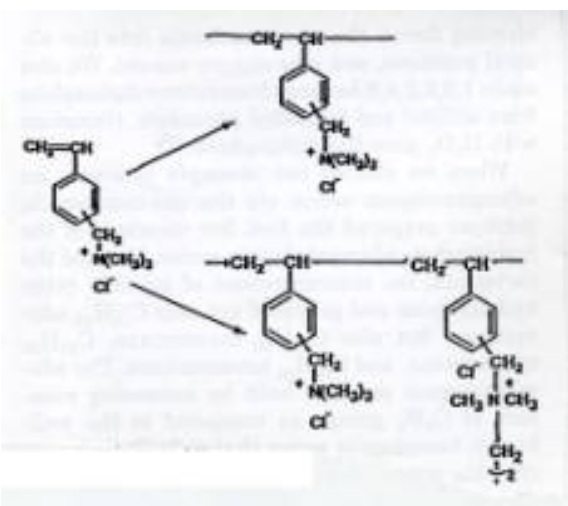


Figure 45: Polycationic Salts as Bile Acid Sequestering Agents

With water-soluble 4,4'-azobiscyanovaleric acid as the initiator, he could obtain polymers with molecular weights of over a million (2,3). Styrene ammonium salts with longer aliphatic chains had to be carried out in methanol. By copolymerizing several vinylbenzyl tri-*n*-alkylammonium chloride monomers we could control and fine-tune the hydrophilicity. whether the polymerization was done in water or methanol, we used azo-initiator 4,4'-azobiscyanovaleric as the initiator (2).

The crosslinking agent *N,N*-(divinyl benzyl)-*N,N,N',N'*-tetramethylethylene diammonium dichloride was used extensively for the homo- and copolymerization of various vinylbenzyl tri-*n*-alkylammonium chloride monomers. *N,N*-(divinyl benzyl)-*N,N,N',N'*-tetramethylethylene diammonium dichloride copolymerized with the following monomers: vinylbenzyl trimethyl ammonium chloride, vinylbenzyl triethylammonium chloride, vinylbenzyl tri-*n*-butylammonium chloride and vinylbenzyl *N*-imidazolium chloride. Although not directly relevant with the actual objective, the homopolymerization of the interesting *N,N*-(divinyl benzyl)-*N,N,N',N'*-tetramethylethylene diammonium dichloride was also investigated

Methacryloethyl trimethylammonium chloride was also prepared and was then polymerized in an aqueous solution using ACVA at 60° C to give a white polymer in high yield, which was water-soluble, and of high molecular weight ( $M_{\text{W}} > 1,000,000$ ).

Methacrylamidopropyl trimethyl-ammonium chloride, a commercial sample, was polymerized in aqueous solution in high yield to a white polymer of high molecular weight.

The analysis of the styrene monomers was accomplished by  $^{15}\text{N}$  NMR spectroscopy.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy was found to be of limited value. With 400,000 acquisitions (spectra taken by pulsing) we were even able to produce an  $^{15}\text{N}$  NMR spectrum of a completely insoluble gel of highly swollen vinylbenzyl trimethylammonium chloride polymer lightly crosslinked with N,N-(divinyl benzyl)-N,N,N',N'-tetramethylethylene diammonium dichloride.

Our objective had been established, we had demonstrated that vinylbenzyl trimethylammonium chloride polymers and their lightly crosslinked satellites were the most effective polymers for bile acid sequestering. This was demonstrated in the dog feeding experiments.

We had additional ambitions. The ammonium groups in the styrene polymers were located at the end of the methylene groups of the polystyrene and the simple trimethylammonium group was the most effective.

A very important polycationic group that had been developed in the 60's were the ionomers. Ionomers are polymers with ammonium groups regularly spaced along the polymer chain. They were made from a,w-aliphatic dihalides and a,w-aliphatic diamines. Polymers with long aliphatic methylene groups can easily be prepared with reasonably high molecular weight. Those with only 2 methylene groups form only the cyclic compound. Only the compounds with the shortest aliphatic chain would provide polymer structures of the highest hydrophilicity.

## **a, Side Chain Ionen Polymers**

We had decided to make 2-ionenes, even if it meant making only short chains, and attaching them to the vinylbenzyl structures, as we had attached tert amines (5,6). Structurally speaking this meant that we would ultimately make a polystyrene structure, of which each individual phenyl ring was linked by a methylene chain to an ionene side chain. We expected that such structures would provide additional "hydrophilicity" and the hydrophilic groups would be even more readily available for binding the bile acids.

Mono-amino terminated 2-ionene oligomers were synthesized from a stepwise Menshutkin reaction of N,N,N',N'-tetramethylethylene diamine and 1,2-dibromoethane. Mono-amino terminated 2,2- dimer and 2,2,2-ionene trimer chlorides were also prepared and reacted with chloromethylstyrene. The Styryl monomers were polymerized as described above. They were also copolymerized with other monomers and with the crosslinking agent.  $^{15}\text{N}$  NMR spectroscopy proved to be invaluable tool for the characterization of the ionene derivatives.

Our vinylbenzyl tri-n-alkylammonium and 2-ionene derivative compounds, both monomers and polymers, were investigated for their potential use as bile-acid sequestering agents. In-vitro studies were conducted using a Sigma Bile Acid Diagnostics Test Kit and a Visible Spectrophotometer set at 530 nm for absorbency readings ( under strict quality assurance guidelines) to record activity of prepared polymers as compared to commercial bile acid sequestering resin (Cholestyramine). Results indicated greater activity of our linear, water-soluble polymers and crosslinked polymers.

The percent of water uptake and the knowledge of water extractables were examined for the homopolymers and copolymers. Water extractables are important features for this type of application. The swellabilities of our best slightly crosslinked polymers were in the thousands of percent water uptake.

The sequestering use of the cationic polymers can be quickly summarized (7). These

dog-feeding tests were made directly on "cholesterol" trained dogs of about of 30 kg weight. After 3 weeks of exposure to our best Cationic polymers the cholesterol level in the blood of the dogs was reduced by 30%.

The ultimate result of sequestering vs treatment by the medical approach of reducing the enzyme activity in the liver was clear. The enzyme blocking was a more efficient and practical way of reducing the cholesterol level. Each person might have their personal problems with side effects of drugs administered.

The promising and safer sequestering method to reduce cholesterol levels in blood was abandoned, after a few years of work with moderate to significant success. Our best candidate, poly(vinylbenzyl trimethyl-ammonium chloride was by a factor of about 3 times more effective a than cholesterylamine, the compound that had been used for sequestering bile acids. Our candidate still required a daily dose 3 times the amount of one pill of Maalox.

Since Merck had lost interest, we did not pursue this effort of bile acid sequestering any longer and terminated our research on poly(vinylbenzyl tri-n-alkylammonium) salts.

We concluded that we have contributed significantly to polycation research. We have established that the monomers are readily prepared, the salts can easily polymerized in water to very high molecular weight. An efficient, not actually new crosslinking agent, was recognized. It is a much better crosslinking agents than divinylbenzene and should be considered more broadly, because the two vinyl groups polymerize independently from each other, and less crosslinking agent is required.

We feel that we have established to our satisfaction, that efficient bile acid sequestering with polycations does not require a magic structural arrangement of the polymer chain and a possible "push-pull" hydrophilic-hydrophobic polymer configuration. It requires the proper hydrophilicity, high water absorption that means

availability of the ammonium group. In other words it means a trimethylammonium group attached to the end of a spacer group in this case a phenyl group that is attached to the polymer chain.

Merck abandoned the chemical, sequestering approach and we concluded our very significant research. One important conclusion came to light, years later, and justified the conclusion for the "medicinal" approach. This approach interferes with functioning of the liver enzyme (which produces about 70% of our cholesterol) and reduces the production of the cholesterol thereby controlling the blood cholesterol levels. Bile acid sequestering agents could have reduced cholesterol levels for persons whose level was below 300. However, the bile acids are not only intermediates for the reduction to cholesterol, they are also essential for the production of the steroid hormones, testosterone etc. The body needs the bile acids for this reason It was later found that reducing the bile acids by sequestering only induces the body to major more bile acids.

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**2(2Hydroxyphenyl)2H-**

group.. The synthesis was not considered a problem, but the radical polymerization was a potential problem. To be an efficient UV stabilizer, the molecule has to have a phenolic hydroxyl group. Phenols, as in most antioxidants, are radical stoppers. Fortunately for us the hydrogen bond to the benzotriazole ring was sufficiently strong and the 2(2-hydroxyphenyl)2H-benzotriazoles did not act as "free" phenols.

Shortly after our first communication on polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles we were approached by Amitava Gupta, a photophysicist and manager at NASA's Jet Propulsion Laboratory in Pasadena. He asked me to consider working with them on polymer-bound 2(2-hydroxyphenyl)2H-benzotriazoles. For space application they needed a UV absorber that did not evaporate in the vacuum of space. I gladly agreed and our cooperation lasted for nearly 12 years.

We synthesized styrenic and acrylic 2(2-hydroxyphenyl)2H-benzotriazoles. 2(2-Hydroxyphenyl)2H-benzotriazoles, with hydroxy, carboxy and amino groups for incorporation in polyesters and polyamides. 2(2-Hydroxyphenyl)2H-benzotriazoles whose polymerizable group was removed from the UV stabilizing group by spacers, we grafted and even photografted polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles and attached 2(2-hydroxyphenyl)2H-benzotriazoles to polymers with reactive groups. With Gupta and Ghiggino we worked on the photophysics of the stabilization involving 2(2-hydroxyphenyl)2H-benzotriazoles.

Another approach led us to develop novel 2(2-hydroxyphenyl)2H-benzotriazole structures. We synthesized 2(2-hydroxyphenyl)2H-benzotriazoles with halogen substituents, with methoxy groups, and structures with more than one 2(2-hydroxyphenyl)2H-benzotriazole ring in the molecules. Most of these structures were also synthesized in polymerizable form.

This work brought us in contact with the Alcon Co. of Fort Worth, TX, an organization that manufactured optical lenses: contact lenses, soft lenses and interocular lenses. They were

interested in lenses with UV stabilizers permanently incorporated in the polymeric systems. We had already made a composition that with polymer bound UV stabilizer, which was of potential use as soft lenses. As in space where low molecular weight UV stabilizers can evaporate, in lenses they might be leached out. Hence the interest on permanently incorporated UV stabilizers.

## Introduction

Ultraviolet stabilizers are prone to evaporation from the surface of polymeric materials upon exposure to sunlight. The surface is the location where the stabilizing action is needed. As a consequence, efforts have been made for over 20 years to prepare polymerizable ultraviolet stabilizers. The first attempt was made at DuPont but was not effective as UV stabilizer..

Typical ultraviolet stabilizers are UV screens, UV absorbers, excited state quenchers, free radical scavengers, or hydroperoxide decomposers. For polyolefins, hydroperoxide are first formed by autoxidation. To stop this deterioration the decomposition is important to protect polyolefins from degradation. UV stabilizers are very important for the photodecomposition of hydroperoxide. They include hindered amine (HALS) stabilizers and are needed for ultraviolet protection of polyolefins. Most other stabilizers belong to the category of screens (absorbers or excited state quenchers). Compounds that are active have a phenolic hydroxyl group attached either to a carbonyl group or to a triazole ring. Year ago, polymerizable salicylic derivatives were investigated and found to be effective. Polymerizable 2-hydroxybenzophenones were also found effective.

With the recognition that 2(2-hydroxyphenyl)2H-benzotriazole derivatives were the most effective ultraviolet stabilizers, a concerted effort was started in the development of polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles.

2(2-Hydroxyphenyl)2H-benzotriazoles are now the most effective type of ultraviolet

light stabilizers among stabilizing additives that include 2-hydroxybenzophenones, phenyl salicylates and hindered amine light stabilizers. They are prominent and effective for plastics materials, especially automotive coatings.

The first 2(2-hydroxyphenyl)2H-benzo-triazole were synthesized by K. Elbs in the 1920 but were not recognized as UV stabilizers until the 1950's.

The general syntheses involve the diazotization of o-nitroanilines, condensation of the diazonium salt with a 4-substituted phenol and reductive cyclization of the azo-compound. If the 4-position is not blocked, the condensation will take place in this position; 4-hydroxyphenyl-benzotriazoles are not UV stabilizers.

We have synthesized polymerizable 2(2-hydroxyphenyl)2H-benzo-triazoles with vinyl and isopropenyl groups as "styrene" type monomers. We have introduced (meth)acrylate groups for radical co-polymerization. Epoxides and phenolic hydroxyl groups were used for incorporation in reactive polymers. With the appropriate polymerizable 2(2-hydroxyphenyl)2H-benzo-triazole monomers we carried out radical polymerizations, condensation polymerization, grafting and reactions on polymers. The synthesis and use of the individual 2(2-hydroxyphenyl)2H-benzo-triazoles will be described in the subsequent section.

### **a. "Styrene" Type 2(2-hydroxyphenyl)2H-benzo-triazoles**

*Vinyl or Isopropenyl Group in the Phenol Ring:* The synthesis of 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole had first been accomplished by Yoshida (8-15). He started by the diazotization of o--nitroaniline. The diazonium salt was condensed with p-ethylphenol and the azo compound reductively cyclized with zinc and sodium hydroxide to 2(2-hydroxy-5-ethylphenyl)2H-benzotriazole. The compound had to be acetylated to 2(2-acetoxy-5-ethylphenyl)2H-benzotriazole, brominated in the a-position with N-bromosuccinimide. The bromo-compound was dehydrobrominated with tri-n-

butylamine to 2(2-acetoxy-5-vinylphenyl)2H-benzotriazole. Hydrolysis gave 2-(2-hydroxy-5-vinylphenyl)2H-benzotriazole. 2-(2-Hydroxy-3-vinylphenyl)2H-benzotriazole and 2-(2-hydroxy-4-vinylphenyl)2H-benzotriazole could not be obtained by a similar condensation and was directed to the 4 position and gave 2-(4-hydroxy-2-vinylphenyl)2H-benzotriazole and 2-(4-hydroxy-3-vinylphenyl)2H-benzotriazole (16).

Instead of bromination with NBS in a-position of the phenyl ring and dehydrobromination to introduce the vinyl group it could be introduced by dehydration of a secondary alcohol.

2(2-Hydroxy-5-vinylphenyl)2H-benzo-triazole was prepared by condensing p-hydroxyacetophenone with the diazonium salt of o-nitroaniline. Reductive cyclization gave 2(2-hydroxy-5-acetylphenyl)2H-benzotriazole and acetylation 2(2-acetoxy-5-acetylphenyl)2H-benzotriazole. Reduction with sodium borohydride resulted in 2(2-acetoxy-5-[2-hydroxyethyl]phenyl)2H-benzotriazole. The compound was dehydrated and hydrolyzed to 2(2-hydroxy-5-vinylphenyl)2H-benzo-triazole. Reaction of the 5-acetyl group with methyl Grignard gave the 2(2-acetoxy-5-[2-hydroxy isopropyl]phenyl)2H-benzotriazole which, on dehydration, resulted in 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole. The same compound could also be prepared from the condensation of the diazonium salt of o-nitroaniline and p-isopropylphenol. After reductive cyclization and acetylation, 2(2-acetoxy-5-isopropylphenyl)2H-benzotriazole. was brominated and the bromo compound dehydrobrominated and hydrolyzed to 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole (17-19).

The two types of 2(2-hydroxy-5-vinyl (or isopropenyl)phenyl)2H-benzotriazole monomers were polymerized and copolymerized with styrene and methyl (meth)acrylate with AIBN as the initiator (20,21). With this initiator system, the radical polymerization could be readily carried out without interference by the phenolic hydroxyl group, because it is not free and strongly hydrogen-bonded to the triazole ring of the benzotriazole moiety.

*Vinyl Group in the Benzotriazole Ring:* Starting with the diazonium salt of 3-ethyl-o-nitroaniline and reacting it with p-cresol allowed us the synthesis of 2(2-hydroxy-5-methylphenyl)2H-4'-vinylbenzo-triazole. The initial cyclization product of the condensation, 2(2-hydroxy-5-methylphenyl)2H-4'-ethylbenzo-triazole was acetylation, brominated with NBS, dehydrobrominated and hydrolyzed to 2(2-hydroxy-5-methylphenyl)2H-4'-vinylbenzo-triazole (22). As the other vinyl 2(2-hydroxyphenyl)2H-benzo-triazoles the compound could be readily polymerized with AIBN.

## **b. 2(2-Hydroxyphenyl)2H-benzotriazoles from Multiphenols and the UV Spectra of these Compounds**

*Benzotriazolized Resorcinol or Phloroglucinol:* Resorcinol or phloroglucinol turned out to be excellent examples for the coupling reaction with diazonium salt of o-nitroaniline or substituted o-nitroanilines. The ease of condensations allowed the preparation of mono-substituted but also of di- and tri-benzo-triazole substituted phenols. Reductive cyclization of the azo compounds gave the benzotriazoles (23,24,33).

The condensation of resorcinol with the diazonium salt required careful control of the molar ratio of the two reactants. In acidic  $p_H$  at a 1:1 ratio, the monosubstituted product, 2(2,4-dihydroxyphenyl)2H-benzotriazole, was obtained. When phloroglucinol was condensed, also in acidic  $p_H$  the monosubstituted product, 2(2,4,6-trihydroxyphenyl)2H-benzotriazole, was obtained. Condensation of the diazonium salt with resorcinol in basic media and a 2:1 ratio results in 2,6-bis(2,4-dihydroxyphenyl)2H-bis benzotriazole and with phloroglucinol at a high ratio of diazonium salt in strongly basic media results in 2,4,6-tris(2,4,6-trihydroxyphenyl)2H-tris-benzotriazole. Condensation of phloroglucinol in neutral media in the appropriate ratio results in 2,4-bis(2,4,6-trihydroxyphenyl)2H-tris-benzotriazole (Figure 47). We had also turned our

attention to the

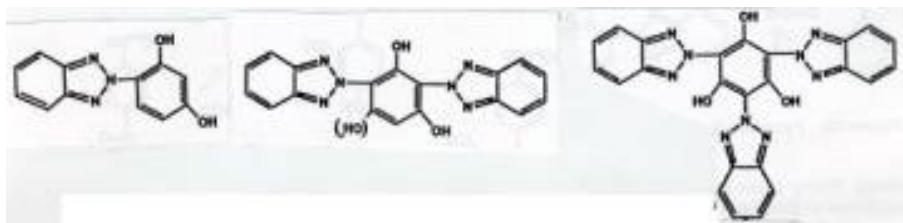


Figure 47: Di and Tri-Substitution of 2(2-Hydroxyphenyl)2H-benzotriazoles

incorporation of polymerizable UV stabilizers into co- and ter-polymers that would lead us into the preparation of UV-stabilized polymers that could be used for contact lenses and implant applications. In this case it was important to synthesize polymers with permanently incorporated (polymer-bond) UV stabilizers, low molecular weight UV stabilizers in UV stabilized polymer compositions where they must be colorless, i.e., must have a sharp cut-off at about 380 nm. Polymers for some ophthalmologic applications had to be hydrophilic with an equilibrium water up-take of about 33-35%, and they must have a high absorbency at 400 nm, be hydrolysis resistant, and not influence the equilibrium water absorption of the polymer and not toxic (allergy causing).

We have reported on the synthesis of 2(2-hydroxyphenyl)2H-benzotriazoles with the same characteristics. The objective of this work was to synthesize some of these compounds and to study their structure/UV behavior in nonpolar medium and to compare their spectral behavior in protic media to simulate the situation in the eye.

Substituted resorcinol or phloroglucinol-based 2(2-hydroxyphenyl)2H-benzotriazole derivatives were investigated with special emphasis on UV absorption characteristics that were expected to be useful as polymer-bound UV stabilizers especially in optical lens applications. Ultraviolet spectra of a number of 2(2-hydroxyphenyl)2H-benzotriazoles were studied in nonpolar, polar, and hydrogen bonding solvents.

We compared the UV spectral data of the substituted 2(2-hydroxyphenyl)2H-

benzotriazoles to the spectral data with the unsubstituted 2(2,4-dihydroxyphenyl)2H-benzotriazole, for which  $\epsilon$  is 23,600 L/mol x cm at a  $\lambda_{\text{max}} = 340$  nm.

2(2,4-Dihydroxyphenyl)2H-5-fluoro-benzotriazole was prepared from the diazonium salt of 4-fluoro-2-nitroaniline and resorcinol. The UV absorption spectrum in chloroform showed an absorption band  $\lambda_{\text{max}}$  at 341 nm with a molar extinction coefficient,  $\epsilon = 21,830$  L/mol x cm. and a shoulder at 295 nm with  $\epsilon = 7600$  L/mol x cm. The ratio of the intensities of the peak and shoulder, Abs(341)/Abs(295), was 2.87. In this nonpolar aprotic solvent, this absorbency ratio demonstrates to what extent the hydrogen-bonded [H] form predominates over the nonhydrogen-bonded, non-planar conformation.

*UV Spectra of 2(2,4-dihydroxyphenyl)2H-benzotriazoles (34,35):* The UV spectrum of 2(2,4-Dihydroxyphenyl)2H-5-fluoro-benzotriazole (from 4-fluoro-o-nitroaniline and resorcinol) was also measured in a methanol/phosphate buffer solution because this solution, at a  $\text{pH}$  of 7.8, simulates the pH and salinity of the human eye. It showed absorption bands at 325 and 291 nm with molar extinction coefficients of  $\epsilon = 12,270$  and 10,510 L/mol x cm, respectively. The polar solvent has a hypsochromic effect on the longer wavelength absorption band, causing a hypsochromic shift of the band of 16 nm to lower wavelength. On the other hand, a polar solvent has a hyperchromic effect on the band at  $\lambda_{\text{max}} = 290$  nm. The same type of solvent effect has been observed for 2(2-hydroxy-5--methylphenyl)2H-benzotriazole *in hydrogen bonding protic solvents*. The polar solvent shifts the equilibrium favoring the [N] form and *inhibiting* the formation of the hydrogen-bonded form.

2(2,4-Dihydroxyphenyl)2H-5'-chloro-benzotriazole (from 4-chloro-o-nitroaniline and resorcinol) showed an absorption band  $\lambda_{\text{max}}$  at 346 nm (a hypsochromic shift of 14 nm) with  $\epsilon = 23,470$  L/mol x cm.

2(2,4,6-Trihydroxyphenyl)2H-5'-chloro-benzotriazole (from 4-chloro-o-nitroaniline and phloroglucinol) with three hydroxyl groups showed a single absorption band  $\lambda_{\max}$  at 355 nm with an  $\epsilon$  of 25,560 L/mol x cm and a significant molar extinction coefficient,  $\epsilon = 850$  L/mol x cm at 400 nm.

2(2,4-Dihydroxyphenyl)2H-5-morpholino-benzotriazole (from 4-morpholino-o-nitroaniline and resorcinol) showed an  $\lambda_{\max} = 364$  nm with  $\epsilon = 20,900$  L/mol x cm. The tail of the absorption band extended well into the visible region.

2(2,4-Dihydroxyphenyl)2H-5,6-dichloro-benzotriazole (from 4,5-dichloro-o-nitroaniline and resorcinol) in chloroform showed an  $\lambda_{\max}$  at 338 nm with  $\epsilon = 29,320$  L/mol x cm.

In the methanol/phosphate buffer solution the 338 nm band was hypsochromic shifted to a  $\lambda_{\max}$  of 324 nm and the intensity was lowered to  $\epsilon = 16,510$  L/mol x cm.

2(2,4-Dihydroxyphenyl)2H-1,3-bis(5'-chloro)-benzotriazole (from two moles of 4-chloro-o-nitroaniline and one mole of resorcinol) showed an intense absorption band at an  $\lambda_{\max}$  of 341 nm with  $\epsilon = 36,780$  L/mol x cm. 2(2-Hydroxy-5-[2-hydroxyethylphenyl])2H-benzotriazole showed a major absorption band at an  $\lambda_{\max}$  of 335 nm with  $\epsilon = 16,660$  L/mol x cm.

2(2-Hydroxy-5-[3'-carboxypropyl])2H-benzotriazole showed an absorption band with an  $\lambda_{\max} = 340$  nm and  $\epsilon = 17,480$  L/mol x cm.

2(2-Hydroxynaphthalene)2H-benzotriazole (from 2-naphthol) and 2(4-hydroxynaphthalene)2H-benzotriazole (from 4-naphthol) are isomers. 2(2-Hydroxynaphthalene)2H-benzotriazole has the hydroxyl group in the *ortho*-position to the benzotriazole ring system. Its UV spectrum should show absorption maximum at 330-360 nm. 2(4-

Hydroxynaph-thalene)2H-benzotriazole has the hydroxyl group *para* to the benzotriazole group and should show no  $I_{\max}$  between 330-360 nm.

The UV spectrum of 2(2-hydroxynaphthalene)2H-benzotriazole in chloroform showed several absorption bands. The major absorption band has an  $\lambda_{\max}$  at 354 nm with a  $\epsilon = 11,750 \text{ L/mol} \times \text{cm}$ . A second band has an  $\lambda_{\max}$  at 320 nm with a  $\epsilon = 11,290 \text{ L/mol} \times \text{cm}$  and a shoulder at 310 nm with  $\epsilon = 10,070 \text{ L/mol} \times \text{cm}$ .

The  $I_{\max}$  in the UV spectrum of 2(4-Hydroxynaph-thalene)2H-benzotriazole in chloroform showed one single  $\lambda_{\max}$  at 316 nm with an  $\epsilon = 15,860 \text{ L/mol} \times \text{cm}$ . Not unexpectedly, 2(4-hydroxy-2-methylphenyl)2H--benzotriazole is a UV absorber but not a UV stabilizer.

The  $I_{\max}$  and the molar absorptivity coefficients,  $\epsilon$ , of the compounds. The values have been related to the "base" compound. The intensity of the absorption an  $I_{\max}$  330-350 nm could be enhanced by increasing the number of hydroxyl groups in the 2(2-hydroxyphenyl)2H-benzotriazole molecule as well as by the presence of a second benzotriazole ring system. An increase in the number of benzotriazole moieties and *ortho*-hydroxyl groups in one molecule is one way to enhance the photo-stabilizing capability of the basic chromophor.

We also explored the effects of the electron-donating groups in the benzotriazole ring. The absorption data for the individual compounds with respect to BDH changed when an electron-donating substituent such as a fluoro, chloro, methoxy, or morpholino group was introduced into the 4-position of the benzotriazole ring. The absorption maxima,  $I_{\max}$ , were shifted to longer wavelengths by 5 up to 25 nm, which indicates the effectiveness of a more efficient intramolecu-lar hydrogen bond.

The molar extinction coefficient was even more significantly enhanced by the addition of a second benzotriazole moiety as is evident in 2(2,4-dihydroxy-phenyl)2H-1,3-bis-benzotriazole. The value of the molar extinction coefficient was more than doubled to over  $\epsilon = 40,000 \text{ L/mol} \times \text{cm}$ .

UV Spectra for various 2(2-Hydroxyphenyl)2H-benzo-triazole derivatives in chloroform: 2(2,4-dihydroxyphenyl)2H-benzotriazole:  $\lambda_{\text{max}} = 340 \text{ nm}$ ,  $\epsilon = 23,600 \text{ L/mol} \times \text{cm}$ , 2(2,4-dihydroxyphenyl)2H-5'-fluorobenzotriazole  $\lambda_{\text{max}} = 341 \text{ nm}$ ,  $\epsilon = 21,830 \text{ L/mol} \times \text{cm}$ , 2(2,4-Dihydroxyphenyl)2H-4'-chlorobenzotriazole:  $\lambda_{\text{max}} = 346 \text{ nm}$ ,  $\epsilon = 23,470 \text{ L/mol} \times \text{cm}$ , 2(2,4-dihydroxyphenyl)2H-4-methoxy-benzotriazole:  $\lambda_{\text{max}} = 345 \text{ nm}$ ,  $\epsilon = 26,650 \text{ L/mol} \times \text{cm}$ , 2(2,4-dihydroxyphenyl)2H-4-morpholino-benzotriazole  $\lambda_{\text{max}} = 364 \text{ nm}$ ,  $\epsilon = 20,900 \text{ L/mol} \times \text{cm}$ , 2(2,4-dihydroxyphenyl)2H-1,3-bis-4'-chlorobenzotriazole:  $\lambda_{\text{max}} = 338 \text{ nm}$ ,  $\epsilon = 29,320 \text{ L/mol} \times \text{cm}$ , 2(2-hydroxynaph-thalene)2H-benzotriazole  $\lambda_{\text{max}} = 354 \text{ nm}$ ,  $\epsilon = 11,750 \text{ L/mol} \times \text{cm}$ , 2(4-hydroxynaph-thalene)2H-benzotriazole  $\lambda_{\text{max}} = 316 \text{ nm}$ ,  $\epsilon = 15,860 \text{ L/mol} \times \text{cm}$ , 2(2,4,6-trihydroxyphenyl)2H-4-methoxy-benzotriazole  $\lambda_{\text{max}} = 349 \text{ nm}$ ,  $\epsilon = 24,860 \text{ L/mol} \times \text{cm}$ , 2(2,4,6-trihydroxyphenyl)2H-4'-chlorobenzotriazole:  $\lambda_{\text{max}} = 355 \text{ nm}$ ,  $\epsilon = 25,560 \text{ L/mol} \times \text{cm}$ , DBDH:  $\lambda_{\text{max}} = 325 \text{ nm}$ ,  $\epsilon = 32,835 \text{ L/mol} \times \text{cm}$ , MDBDH  $\lambda_{\text{max}} = 344 \text{ nm}$ ,  $\epsilon = 41,400 \text{ L/mol} \times \text{cm}$ , 2(2,4-dihydroxyphenyl)2H-1,3-bis-4'-chlorobenzotriazole  $\lambda_{\text{max}} = 341 \text{ nm}$ ,  $\epsilon = 36,780 \text{ L/mol} \times \text{cm}$ , HHEPB  $\lambda_{\text{max}} = 335 \text{ nm}$ ,  $\epsilon = 16,660 \text{ L/mol} \times \text{cm}$ , 2(2-hydroxy-5-3'-carboxyethyl-phenyl)2H-benzotriazole:  $\lambda_{\text{max}} = 340 \text{ nm}$ ,  $\epsilon = 17,480 \text{ L/mol} \times \text{cm}$ , 2(2-hydroxy-5-methylphenyl)2H-benzotriazole  $\lambda_{\text{max}} = 337 \text{ nm}$ ,  $\epsilon = 16,390 \text{ L/mol} \times \text{cm}$ ,

### c. (Meth)acrylate Monomers from 2(2-hydroxyphenyl)2H-benzotriazoles

Meth)acrylate monomers from 2(2-hydroxyphenyl)2H-benzotriazole derivatives usually utilized the unhindered 4-hydroxy group of the 2(2,4-dihydroxyphenyl)2H-benzotriazoles or the dibenzotriazolized resorcinol or phloroglucinol. They were treated with acryloyl or methacryloyl chloride, often by the Schotten-Baumann technique. They gave phenyl ester type stabilizers. When aliphatic esters were desired as for example in the case of 2(2-hydroxy-5-[2'-hydroxyethyl]phenyl)2H-benzotriazole, the methacrylate groups was conveniently incorporated by reaction of hydroxyl group with glycidyl methacrylate, or by transesterification with methyl methacrylate (25-28).

*Benzotriazole derivative of 10-undecenoic acid:* We have paid increasing attention to the incorporation of flexible spacer groups into polymerizable UV stabilizers. We selected 10-undecenoic acid for a reactive group. The imidazolyl derivative of 10-undecenoic acid was reacted with 2(2,4-dihydroxyphenyl)2H-benzotriazole and gave 2(2-hydroxy-4-undecenoxophenyl)2H-benzotriazole. With 2(2,4,6-trihydroxyphenyl)2H-benzotriazole, 2(2,6-dihydroxy-4-undecenoxophenyl)2H-benzotriazole was obtained. The two dibenzotriazolized esters of 10-undecenoic acid were prepared in the same manner from the imidazolids of n-undecenoic acid. 2(2,4-trihydroxyphenyl)1,3-di(2H-benzotriazole) gave 2(2-dihydroxy-4-undecenoxophenyl)1,3-di(2H-benzotriazole) and 2(2,4,6-trihydroxyphenyl)1,3-di(2H-benzotriazole) gave 2(2,6-dihydroxy-4-undecenoxophenyl)1,3-di(2H-benzotriazole) (29).

*UV Stabilizers for Oriental Lacquers:* Ultraviolet stabilizers suitable for protecting coatings of oriental lacquers against the damaging effects of UV radiation were synthesized (30,31). 2[2-Hydroxy-3-tert-butyl-5(3'-hydroxypropyl)phenyl]2H-benzotriazole was prepared by reduction of polyethylene glycol 2(2-hydroxy-3 tertiary-butyl-5[proprionato-phenyl]2H-benzotriazole, a commercially available UV stabilizer with LAH. The white crystals showed a molecular peak  $[M]K^+$  of 364 Da, which corresponds to a molecular weight of 325. 2[2-Hydroxy-3-tertiary-butyl-5(3'-hydroxypropyl) phenyl]-2H-benzotriazole was allowed to react with several imidazolids of aliphatic acids or by direct classical esterification using p-toluene sulfonic acid as the

catalyst. Esters of stearic, oleic, linoleic and linolenic were synthesized. 2[2-Hydroxy-3-tertiary-butyl-5(3'-hydroxypropyl) phenyl]-2H-benzotriazolyl linoleate and linolenate were co-cured (copolymerized) with urushiol of high triene [3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl)catechol] content. Simulated testing by exposing the films of cured oriental lacquer containing these polymerizable UV stabilizers to UV light showed an increase of the lifetime of these coatings by a factor of 3 as compared to the stability of unstabilized films.

#### **d. 2(2-Hydroxyphenyl)2H-benzo-triazoles with more than one Type of UV Absorbing Groups**

*Compounds containing benzotriazole and aceto- or benzophenone chromophors:* 2,4-dihydroxy-benzophenone and 2(2-Hydroxyphenyl)2H-benzotriazole are chromophors that are used for commercial UV stabilizer formulations. We thought it might be interesting to combine these two chemical structures and observe the effect. We intended to use 2,4-dihydroxyacetophenone and 2,4-dihydroxybenzophenone as our "resorcinol derivatives." Coupling of the diazonium salt of o-nitroaniline in a 1,1 ratio with 2,4-dihydroxyacetophenone and reductive cyclization gave 2(2,4-dihydroxy-5-acetyl-phenyl)2H-benzotriazole and with a 2:1 ratio 2(2,4-Dihydroxy-5-acetyl-phenyl)2H-1,3-bis-benzotriazole (36,37) was obtained. A similar reaction sequence starting from the diazonium salt of o-nitroaniline and 2,4-dihydroxybenzophenone gave 2(2,4-Dihydroxy-5-benzoyl-phenyl)2H-benzotriazole and 2(2,4-Dihydroxy-5-benzoyl-phenyl)2H-1,3-bis-benzotriazole, respectively.

#### **e. Bisphenols and Biscarboxylates of 2(2-hydroxyphenyl)2H-benzo-triazole Derivatives**

The incorporation of 2(2-hydroxyphenyl)2H-benzotriazole UV stabilizers into polyesters, polycarbonates and polyamides, in other words into common condensation polymers, was another objective of our research on polymerizable 2(2-hydroxyphenyl)

2H-benzotriazole) stabilizers. We first prepared the appropriate bisphenols. 4-methoxy-2-nitro-benzenediazonium chloride was condensed with resorcinol. At a 1:1 ratio it gave 2(2,4-dihydroxyphenyl)2H-5'-methoxy-benzotriazole) and at a 2:1 ratio 2(2,4-dihydroxyphenyl)2H-1,3-bis-5' methoxy-benzotriazole. Both were desirable intermediates for our objective. Demethylation gave 2(2,4-dihydroxyphenyl)2H-5'-hydroxy-benzotriazole and 2(2,4-dihydroxyphenyl)2H-1,3-bis-5'-hydroxy-benzotriazole, respectively. The hydroxyl compound could be acetylated and gave the diacetates, desirable for transesterification reactions on aromatic polyesters.

Co-polyesters were prepared with sebacic, isophthalic and terephthalic acids and with ethylene glycol, butanediol-1,4, hexanediol-1,6, decanediol-1-10, 2,2-dimethylpropanediol, and *trans*-cyclohexane-1,4-dimethanol. About mole 10 % of either 2(2,4-dihydroxyphenyl)2H-5'-hydroxy-benzotriazole) or 2(2,4-dihydroxyphenyl)2H-1,3-bis-4'-hydroxy-benzotriazole were efficiently incorporated into these polymers (38-41).

2(2,4-Dihydroxyphenyl)2H-1,3-bis-4'-hydroxy-benzotriazole was also acetylated to 2(2,4-dihydroxyphenyl)2H-1,3-bis-5'-acetoxy-benzotriazole.

This compound was incorporated into poly(butylene terephthalate) by the common technique of transesterification (Figure 48).

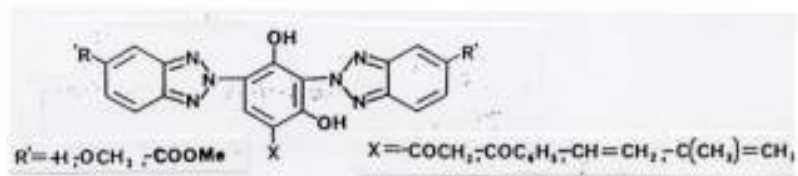


Figure 48: Bisphenol and Carboxylic acids of 2(2Hydroxyphenyl)2H-benzotriazoles

2(2,4-Dihydroxyphenyl)2H-4'-hydroxy-benzotriazole) or 2(2,4-dihydroxyphenyl)2H-1,3-bis-4'-hydroxy-benzotriazole were also efficiently incorporated into polycarbonates. This was accomplished by direct incorporation of the 2 UV stabilizers into polycarbonate recipes. We have chosen using the route of

diphenylcarbonate and bisphenol A for the synthesis of the polycarbonate, rather than the phosgene route. The incorporation could also be accomplished by transesterification of 2(2,4-dihydroxyphenyl)2H-1,3-bis-5'-acetoxy-benzotriazole with the already formed polycarbonate.

For the synthesis of 2(2,4-dihydroxyphenyl)2H-5'-carbomethoxy-benzotriazole and 2(2,4-dihydroxyphenyl)2H-1,3-bis(5'-carbomethoxy-benzotriazole the diazonium salts of 3-nitro-4-amino methyl benzoate or 3-nitro-4-amino benzoic acid were made. Depending on the ratio of the reactants and the reaction condition either of the 2 salts could be obtained; in the case of the free acid it was esterified. polyesters or polycarbonates were prepared by substituting part of the diester for the synthesis of the polymer. For polycarbonates, part of the diphenylcarbonate was substituted by our "stabilizer" dicarboxylate. Similarly the esters of the dicarboxylic esters were replaced by the "stabilizer" dicarboxylate. The polymers showed good incorporation of the 2(2,4-dihydroxyphenyl)2H-1,3-bis(5'-carbomethoxy-benzotriazole into the polyesters and polycarbonates.

## **f: Surface Active Monomers and Polymers**

Another technique is presently in the advanced stages of development: morphology control, which brings the ultraviolet stabilizer to the surface of a coating. In the photografting case the polymeric film is extruded or molded and the film is then soaked with the stabilizer and photograft-ing is accomplished. The present case is more applicable for a coating application where the material goes from a liquid state to a solid glassy state. In this case the photo-stabilizers, primarily 2(2-hydroxy-5-[2-carboxyethyl]phenyl)2H-benzotriazole, are esterified with fluorocarbon alcohols, hydrocarbon alcohols of long aliphatic chain length, or silicone alcohols. The compounds are then allowed to react with (meth)acrylomidomethylol to give the final 2(2-hydroxyphenyl)2H-benzotriazole derivatives. The typical perfluoro-structure is 2(2-hydroxy-3-methyleneacrylamidomido-5-{3'-1,1,2,2-H-perfluoroalkyl}-phenyl )2H-benzotriazole (46). The monomers are then copolymerized. On casting of these

polymers, the fluoro-carbon chain of 12-14  $\text{CF}_2$  groups or silicone group help bring the stabilizing groups to the surface. ESCA measurements show that the fluorocarbon and silicone groups are substantially at the surface of the film, thus bringing the stabilizer to the surface of the film where it is needed most (Figure 49).

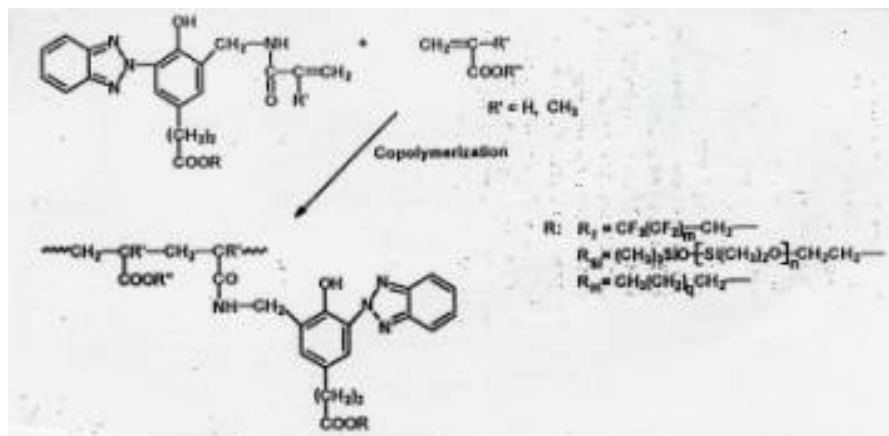


Figure 49: Surface Active 2(2Hydroxyphenyl)2H-benzotriazoles Derivatives

**Emulsion Polymerization:** N-maleimide derived monomers were of interest because they can conveniently be incorporated into copolymers. We decided to synthesize 2(2-hydroxy-3-methylenemaleimido-5-methylphenyl)-2H-benzotriazole. As starting material we used the commercially available Tinuvin P, 2(2-hydroxy-5-methylphenyl)-2H-benzotriazole and N-methylolmaleimide. We had used a similar procedure to introduce the (meth)acrylamidomethylene group into 2(2-hydroxyphenyl)-2H-benzotriazoles using (meth)acrylamidomethylol as condensation agent. 2(2-hydroxy-3-methylene maleimido-5-methylphenyl)-2H-benzotriazole was obtained in nearly quantitative yield. Emulsion polymerization was carried out successfully in an ABS type recipe with acrylonitrile, styrene and N-phenylmaleimide with 4,4'-azobis(4-cyanovaleric acid) as the initiator (47,48). Sometimes N-(2,6-dimethylphenyl)maleimide was used as a termonomer instead to increase the  $T_g$  of the final polymer. The radical emulsion polymerization was successful, in spite of the free (but hydrogen bonded) phenolic hydroxyl group which when "free" would act as radical inhibitor.

Polymerizable 2(2-hydroxyphenyl)-2H-benzotriazoles were also incorporated in

unsaturated polyester recipes, successfully polymerized and characterized (49, 50).

### **g. Grafting of 2(2-hydroxyphenyl)2H-benzotriazole Monomers**

*Regular grafting:* We had earlier reported that we had successfully grafted methyl 5-vinylsalicylate onto 1,2 and *cis*-1,4-polybutadiene. We have also successfully grafted 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole onto polybutadiene. It was important to carry out the grafting at 60°C with AIBN or benzoyl peroxide with a satisfactory grafting efficiency (51,52).

*Photo Surface-grafting of Polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles:* Polyolefins are notorious for their relatively poor stability when exposed to the environment. Polymer degradation due to aging and weathering may cause the loss of physical, mechanical or surface properties. Consequently these polymers must be stabilized with antioxidants and photo-stabilizers (53). Photo-stabilization is of primary interest for outdoor use.

Films of low-density polyethylene and high-density polyethylene and polypropylene have been surface photografted with different polymerizable 2(2-hydroxyphenyl)2H-benzotriazole monomers 2(2-hydroxy-4-acryloxyphenyl)2H-benzotriazole, 2(2-hydroxy-4-methacryloxyphenyl)2H-benzotriazole, 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole and 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole in the presence of benzophenone as the photo-initiator using 254 nm ultra-violet irradiation. Photografted films of polyethylene have much higher resistance towards photo-aging (tested in a Weather-0-meter) than non-stabilized samples.

The mechanisms of photodegradation and photo-stabilization of polyolefins have been the subject of a number of intensive investigations during the past decades. In spite of substantial efforts to protect polyolefins against photo-oxidative degradation by use of antioxidants and photo-stabilizers, the desired results have generally not been

realized. For this reason, new concepts of polyolefin stabilization against light are under active investigation. One new concept is photo-stabilization of polyolefins by surface photografting with monomeric photo-stabilizers. In all cases, 2(2-hydroxyphenyl)2H-benzotriazole monomers were efficiently photografted on polyethylene. Easier to low density than to high density polyethylene which suggested the grafting occurs in the amorphous phase. Irradiation times of one to two minutes under nitrogen were sufficient. The surface of photografted polyolefin films exhibit the characteristic absorption of 2(2-hydroxyphenyl)2H-benzotriazoles of 335 nm or 350 nm, depending of the class of 2(2-hydroxyphenyl)2H-benzotriazole monomers. From a slight shift in the UV frequency we can conclude that grafting caused the formation of shorter or longer chains of 2(2-hydroxyphenyl)2H-benzotriazole monomers. Shorter and more frequent photo-stabilizer chains attached to the polyolefin surfaces are more effective as photo-stabilizers than long and less frequent chains.

## **h. Reactions of 2(2-hydroxyphenyl)2H-benzotriazoles onto Reactive Polymers**

If the synthesis of the monomer suitable for radical polymerization initiated by AIBN is not desired, reaction on an already prepared polymer is a possibility. We used reactive polymers, especially methyl methacrylate/glycidyl methacrylate copolymers for this purpose. 2(2-Hydroxyphenyl)2H-benzotriazoles with aliphatic hydroxyl groups of available phenolic hydroxyl groups could be used to introduce the stabilizing groups into such polymers (42-45).

*Characterization of 2(2-Hydroxyphenyl)2H-benzotriazoles by K<sup>+</sup>IDS Mass Spectrometry:* Mass spectrometry using the potassium ionization of desorbed species (K<sup>+</sup>IDS) technique was an unusually fruitful method to characterize 2(2-hydroxyphenyl)2H-benzotriazole derivatives (54). This class of compounds has the proper molecular weight range from 200 Da up to 1200 Da and the proper volatility to maintain readily desirable concentrations in the mass spectrometer. 2

(2-Hydroxyphenyl)2H-benzotriazole compounds are stable under the conditions of measurements which allows the determination of their purity. The isotopic molecular weights have been determined and calculated with appropriate software programs to ascertain the correctness of the structures. We have analyzed over 120 2(2-hydroxyphenyl)2H-benzotriazoles during this work.

## **j. Photo-Chemistry and Photo-Physics of 2(2hydroxyphenyl) 2H-benzotriazole Monomers and Polymers**

Ever since K. Elbs described the first 2(2-hydroxyphenyl)2H-benzotriazoles, this class of compounds has had a special kind of attraction. 2(2-Hydroxyphenyl)2H-benzotriazoles are not only UV absorbers but also outstanding "UV stabilizers". They have made an increasing impact on polymer materials as the most effective "UV stabilizers" known today. Photo-physical studies recognized that the photo-activation of hydrogen-bonded states is the key to their effectiveness, and a mechanism to accommodate the photo-physical transition states has been presented (55-62).

2(2-Hydroxyphenyl)2H-benzotriazole derivatives form hydrogen-bonded structures; the long UV wavelength band of these derivatives (ca. 340 nm) is attributed to a planar form of the molecule, and the short UV wavelength band, which is often found at ca. 300 nm, is typical for 2(2-hydroxyphenyl)2H-benzotriazole derivatives which have no hydrogen-bonded structures or hydrogen-bonding capabilities.

The effect of electron donor or withdrawing groups was found to affect the position of the  $I_{\max}$  and the shape of the 340 nm band as it influences the electro density around the hydrogen-bonded part of the 2(2-hydroxyphenyl)2H-benzotriazole molecule.

Investigation on the effects of solvents on the UV spectra of 2(2-Hydroxyphenyl)2H-benzotriazoles showed that hydrogen bonding was more pronounced in nonpolar solvents, such as n-hexane, giving broader UV absorption peaks in more polar solvents, such as chloroform, which is represented in a decrease of the extinction

coefficient at  $\lambda_{\text{max}}$  of 340 nm. When 2(2-hydroxyphenyl)2H-benzotriazoles were incorporated into a polymer structure, the general characteristics of the UV spectrum were found to be determined by the "next neighbor" of the macromolecule *and not* by the solvent.

As mentioned before, the photo-physical behavior of 2(2-hydroxyphenyl)2H-benzotriazoles in the excited state depends on the intramolecular proton transfer which is affected by the polarity, but especially by the hydrogen bonding capability of the solvent. The absorption spectrum in a non-hydrogen bonding solvent, such as THF, shows the expected presence of two bands, the long wavelength band  $\lambda_{\text{max}} = 340$  nm and a shorter wavelength band at 300 nm.

When the proton-accepting capacity of the solvent was increased, the longer wavelength band decreased in intensity and *ethanol*, the long wavelength band, was almost completely eliminated.

The effects of polymer-bound ultraviolet stabilizers of the 2(2-hydroxyphenyl)2H-benzotriazole type have been used for photo-physics studies simplified by the copolymerization of 2(2-hydroxy-4-acryloxyphenyl)2H-benzotriazole with 2-naphthyl methacrylate (63-70). These copolymers show a substantial fluorescence emission at 560 nm. The fluorescence behavior was studied as a function of temperature. It was found that the activation energy is near -zero. It was also determined that the absorption at 320 nm, which is indicative of photolytic degradation, increased linearly as a function of irradiation time. No change was found in copolymers with 6.2 mol % 2(2-hydroxyl-acryloxyphenyl)2H-benzotriazole. Relatively little influence of the photodegradation was found when 2(2-hydroxy-5-methylphenyl)2H-benzotriazole was added in 6.7 mol % during the radiation experiment. This phenomenon has been explained by a migration of the photon energy to the acceptor where the emission is then dissipated in a non-radiative way. The proposed general photo-physical behavior of 2(hydroxyphenyl)2H-benzotriazoles was demonstrated.

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## F. Oriental Lacquers

*Urushi Research:* For centuries, actually millenia, oriental lacquer has been used to coat objects of high artistic and pleasing beauty. Oriental lacquer is produced from “urushi”, the sap of the lacquer tree *Toxicodendron vernicifluum*. The oleoresins of the sap consist of a mixture of 3-n-alkylsubstituted linear catechols of various degrees of unsaturation [7,8]. The chemical composition and identification of few components of urushiol were studied in several periods.

The first period was early in the 19th century by R. Maxima at Tohoku University in Sendai, Japan who had access to the sap of the lacquer tree because lacquer trees grow in the region around Sendai. In the 1950's, C.W. Dawson, at Columbia University in New York studied synthetic aspects and the exact identification of 3-alkyl and 3-n-alkenylcatechols. He was primarily interested in poison ivy; the chemistry of the components of the sap is similar to that of urushi. Two decades later, Professor Jun Kumanotani of the University of Tokyo with Yumin Du of Wuhan University, Wuhan, China became the primary investigator of the components of the sap of the lacquer tree. He introduced simple chromatographic techniques for the identification of the oleoresins of urushiol.

In the 1990's we reinvestigated the urushi problem and introduced combinations of modern instrumental techniques (1-12). Today we know much more about the

composition of urushi, and have established techniques and combinations of techniques that allowed us to isolate and characterize the oleoresins of urushi exactly and rapidly. Because of the chemical similarities, we now can analyze also the components of the sap of poison ivy and other *Anacardiaceae* species.

We have also developed polymerizable ultraviolet stabilizers of the 2(2-hydroxyphenyl) 2H-benzotriazole family that could be copolymerized (co-cured) with oriental lacquer and drying oils.

**Botany of the Family Anacardiaceae:** The *Anacardiaceae* is a moderately large family of about 80 genera and about 600 species. The plants of a few genera produce a sap that is suitable for being used as the basis of exquisite coating materials for art objects. To the *Anacardiaceae* family belongs the genus *Toxicodendron*, and the species *Toxicodendron vernicifluum*, the varnish or lacquer tree is the main source of oriental lacquer.

The genus *Toxicodendron*, grows in a temperate climate and has been the subject of regular investigations by botanists, but also by chemists and the medical profession [38]. In Asia, *Toxicodendron vernicifluum* trees grow in China, primarily in the Sichuan region, and in Japan. Similar species also grow in Vietnam, in Thailand and in Taiwan.

After ten years of growth, the stem of the lacquer tree is mature enough; it can be cut and a sap oozes out of the tree similar to that of the rubber tree. The difference between the sap of the lacquer trees and the rubber tree is that the rubber trees have *cis*-polyisoprene as the material of interest while urushiol consists of mixtures of substituted catechol derivatives.

A number of *Anacardiaceae* species produce a sap that causes contact dermatitis in susceptible humans. They include the cashew-nut tree, the varnish or lacquer tree and poison ivy, which belongs to the sumac family. Poison Ivy (*Toxicodendron radicans*)

grows in North America and East Asia, but not in Europe and Africa and is perhaps the best-known member of this family.

Dermatitis due to contact with poisonous *Anacardiaceae* is the source of misery for millions. It can be contracted by handling and ingestion of the sap. In the case of poison ivy, the offending oleoresins are present in virtually all plant parts with resin canals. The canals are not open to the surface and they must be injured in order to release the poisonous allergenic oleoresins.

The dermatological activity depends on the phenol (catechol) component of the sap [5,40]. Also the unsaturation of the aliphatic side chain contributes to the effectiveness of the compounds. The dermatitis causing activity requires that the aliphatic side chain be in *meta*-position to a phenolic group. A compound is formed between the urushiol components and a skin protein, which causes the immune reaction. Today no reliable antidote has been found to prevent *Toxicodendron*- caused dermatitis, only the effects can be treated.

**Chemistry of Urushiol and Drying Oils:** The oil soluble fraction of the sap of the lacquer tree (urushiol) is a mixture of catechol derivatives substituted in 3-position with unsaturated (trienes, dienes, monoenes) and some saturated hydrocarbon chains - C<sub>15</sub> and C<sub>17</sub> chain lengths. The quality of the Japanese lacquer depends to a great extent on the quantity of the triene component. The composition of the urushiol varies and depends on the individual botanic species of the *Toxicodendron vernicifluum* tree from which the urushiol has been obtained, the location, the growing conditions and on the season of harvesting.

A number of techniques have been used to analyze and characterize the components of urushiol. Initially it was based on chemical reactions. Now they include regular and capillary gas chromatography, supercritical fluid chromatography, high-pressure liquid chromatography and various techniques of high resolution NMR spectroscopy and two

techniques of mass spectrometry, especially potassium ionization of desorbed species ( $K^+IDS$ ) mass spectrometry.

A number of individual compounds were found in urushiol samples by capillary gas chromatography, but many were present in amounts of less than 2%. Two compounds were present in over 80% in a ratio of 6:2. Mass spectrometry and NMR spectroscopy indicated that the peak with the retention time of 11.2 minutes was the triene and the peak with the retention time of 12.2 minutes was the monoene.

A careful study was subsequently carried out by a combination of  $^1H$  and  $^{13}C$  NMR, and  $^1H$  COSY NMR spectroscopy. Individual compounds were isolated by preparative HPLC of urushiol mixtures and all the components and geometric isomers of the 3-n-alkylcatechols were isolated, identified and characterized (Figure 50).

The desirable 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl)catechol [ $M$ ] $K^+$ =353 (Figure 2) was present in the various samples of urushiol in amounts of 55-68 %, while 3-(8-*cis*-pentadecenyl)catechol [ $M$ ] $K^+$ =357 Da in between 15 and 25 %. 3-(8-*cis*-11-*cis*-pentadecadienyl)catechol [ $M$ ] $K^+$ =355 Da was there in less than 10%, while

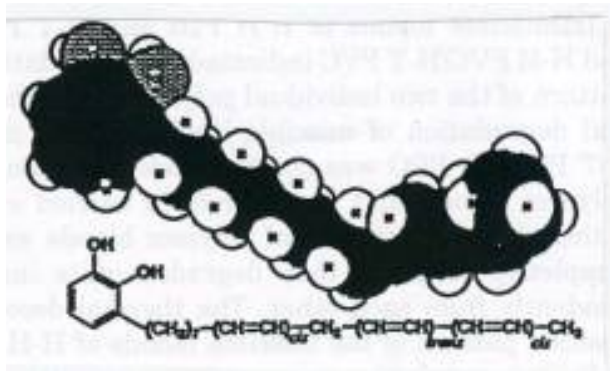


Figure 50: Urushiol: 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl)catechol

3-(8-*cis*-11-*trans*-pentadecadienyl)catechol and 3-(pentadecanyl)catechol [ $M$ ] $K^+$ = 359 Da was present in amounts of 2-4 % . All other components constitute less than 2 %, usually only trace amounts.

For the 3-pentadecenylcatechol, only one geometric isomer, the *cis*-compound has been isolated. Both geometric isomers of the dienes: 3-(8-*cis*-11-*cis*-pentadecadienyl)catechol and 3-(8-*cis*-11-*trans*-pentadecadienyl)catechol were found. Several geometric isomers of trienes  $[M]K^+ = 353$  Da, were also found in urushiol; the main component is 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl)catechol.

From the chemical point of view, important for the curing process of the oriental lacquer is the methylene group in 10-position. A methylene group in a-position to one or two additional double bonds is also needed just as in the carboxylic acid portions of the glycerides that are used as drying oils.

The compositions of the urushi compositions of poison ivy and the lacquer tree are quite similar. Significant in the difference is the presence of large amounts of the catechol of 3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl)catechol in the lacquer urushiol, which is needed for curing while poison ivy has the 3-catechol of 8-*cis*-11-*trans*-pentadecadiene as the main component, which does not cure efficiently.

Drying oils such as Tung and linoleic type drying oils, are glycerol esters of fatty acids and are vehicles for a considerable volume of surface coatings. Tung oil has as its main ingredient, in high percentage, eleostearic acid (9-*cis*-12-*trans*-14-*trans*-octadecatrienoic acid), linseed oil has linoleic acid 9-*cis*-12-*cis*-octadecadienoic acid and especially linolenic acid: 9-*cis*-12-*cis*-15-*cis*-octadecatrienoic acid as its main active components. The most important unsaturated acid, oleic acid, also has of a *cis*-double bond in the 9 position (9-*cis*-octadecenoic acid).

These fatty acids have similar structures to the aliphatic side chains in urushiol. The chain length of the linear hydrocarbon chains of these fatty acids is between 16 and 22 but the most important group has a chain length of 18 carbon atoms (stearic acid family). Linseed oil also consists of trienes, dienes and monoene carboxylic acids. Part of the molecular structure and the positions and stereochemistry of the double bonds

are similar to that of the trienes of the urushi.

The type of aliphatic side chains of some of the *Anacardiaceae* seem to be related to the fatty acids of natural fats. Natural fats are triglyceride esters of palmitic and stearic acids, some of their lower homologues and their unsaturated cousins. To the "stearic acid family" belong stearic acid (octadecanoic acid) but also oleic acid (9-*cis* octadecenoic acid), linoleic acid (9-*cis*-12-*cis* octadecadienoic acid) and linolenic acid (9-*cis*,12-*cis*-15-*cis*-octadecatrienoic acid) present in linseed oil but also the primary component of tung oil, eleostearic acid (9-*cis*-12-*trans*-14-*trans*-octadecatrienoic acid).

It appears that the alkyl side chains of the catechols of urushi could have been formed by decarboxylation of fatty acids and alkylation of phenols, resorcinols, catechols and salicylic acid (anacardic acid). The attachment of the aliphatic chain is always in *meta*-position to a phenolic group.

The aromatic rings of the catechols of the Thai lacquers, 3-n-(10-phenyldecanyl) catechols and 3-n-(12-dodecanyl)catechols, could also have been built starting with the carboxyl group of C<sub>16</sub> or C<sub>18</sub> carboxylic acids. Even the formation of decamethylenephenyl or the dodecamethylenephenyl side groups could be rationalized by assuming the addition of terminal methylene radical formed from the terminal methyl group by selective hydrogen abstraction to the C<sub>10</sub> of the C<sub>15</sub> side chain or the addition of a similar terminal radical to the C<sub>12</sub> double bond of the C<sub>17</sub> side chain.

***Preparation and Application of Urushiol:*** The sap of the lacquer tree, water-in oil emulsion; consists of the "oily" or urushiol fraction (about 65 % ) and an aqueous fraction (35 %). As has been mentioned, urushiol is a mixture of 3-substituted catechol derivatives with saturated and unsaturated aliphatic side chains. Nitrogen containing substances, glycoproteins, which are not water soluble but dispersed or dissolved in

urushiol are stabilizers for the water droplets of the native sap. Some gummy substances and mono-, oligo- and polysaccharides are in the aqueous portion of the sap. It also contains enzymes, most importantly, the copper-glycoprotein laccase which functions as dimerization catalyst for the 3-substituted catechol derivatives.

To prepare the lacquer from the natural sap, the sap is stirred in an open vessel at room temperature for about 1.5 hours, and then at a temperature increasing from 20°C to 45°C where it is kept for 2 to 4 hours in specially designed open vessels until the water content is reduced to 2-4 % in the **sugurume** process. The details of the process is a closely guarded secret and differs from manufacturer to manufacturer. This liquid, known as "raw lacquer", consists of urushiol and oligo-urushiol, dimers (about 5-10 %) from the action of laccase on the hydroxyl groups of the catechol portion of the 3- n-alkylcatechols. The raw urushiol is ready for application. Urushiol is cured by air oxidation; the effectiveness of curing depends very much on the triene components, and the amount and activity of laccase.

The temperature cycle must be carefully controlled to retain the activity of the enzymes. The sap is now clear, has become darker and has increased in viscosity. The components of the aqueous phase, which are initially suspended in the organic phase but on the preparation of the product for lacquer application, seem to play the ultimate role in the quality of the final product. Sometimes small amounts of iron salts or other chemicals are added as catalysts for the production of the oriental lacquer.

Curing of the lacquer is an enzymatic oxidation and the radical curing of the highly unsaturated systems initiated by the hydroperoxides that are formed on the 10-methylene groups between the double bonds. Painting is done in a multilayer process of many very thin layers. High quality products have as many as 30-40 layers. Painting and curing must be done in an environment of high humidity (65-80 %). Curing of the lacquer does not work well in a dry atmosphere. The detailed nature of the curing mechanism is not known. However, it is known that even after a month the curing is

not complete and some post curing still continues; the lacquered sample is still slightly soft even after one month! The process from beginning to end takes about 2 months.

For painting with oriental lacquer, a base coat is applied to the substrate, often cedar wood. It is frequently regular sap, without or with little processing.

A coat, of about 5-10 mm layers thick, is applied every one to two days. During the curing several steps occur simultaneously: water evaporates, polysaccharides are deposited from the water droplets and fine particles are then dispersed into urushiol. Urushi is attached to the glycoprotein and finally and most importantly urushi polymerizes. The drying of the lacquer at high humidity is initiated by the oxidation enzyme laccase and is affected by the diffusion rate of the oxygen.

*The Rattle Snake Model:* The most active component in oriental lacquers is **3-(8-*cis*-11-*trans*-13-*cis*-pentadecatrienyl)catechol**. After the oriental lacquer is applied the aliphatic triene structure polymerizes and ultimately results in a polymer, actually a cross-linked polymer with the desired properties of beauty and durability. Key to successful polymerizations is a relative humidity of at least 65% and a sufficiently warm temperature. To explain the requirement for successful lacquer applications, we propose what we call a rattle snake model, a nanostructure that is driven by the moisture to provide the surface and the highly unsaturated hydrocarbon tail that is needed for the polymerization (Figure 50).. The rattle snake consists of the head held in near horizontal position, the body and the rattle at the end. In active position, the rattle is also in a nearly horizontal position and moves almost continuously to display the activity of the snake.

The oriental lacquer, as prepared for painting application, is reduced from the original emulsion with 60 % water to about 4% water. This amounts to about one water molecule per urushiol molecule, which means that the urushiol is, in the average, a monohydrate. The application is done in a climate of high humidity (hydrophilic

conditions). The "head of the snake", the catechol portion of the urushiol molecule, is reaching for the moisture in the atmosphere. The two hydroxyl groups of the catechol are located in o-, and m-positions to the aliphatic chain. This "head", like the head of a rattlesnake is, slightly bent out of vertical position. In this near vertical position of the "body" of the urushi molecule, the seven methylene groups are aligned parallel to each other. The methylene groups are aligned as

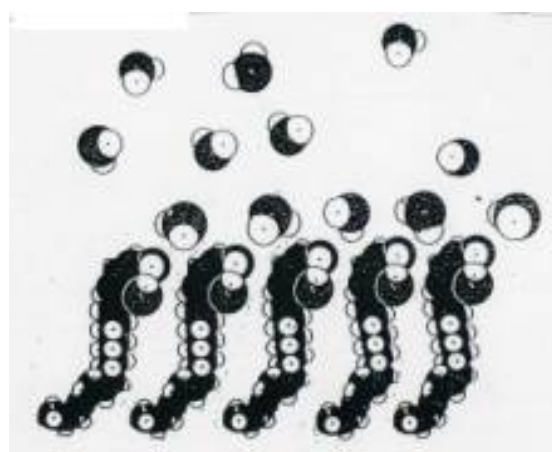


Figure 51: The Rattle Snake Model

the aliphatic part of soap molecules in detergents (carboxylate or sulfonate salts). The rattle, the polymerizable group of cis,trans,cis olefin configurations need to be in this arrangement for polymerization. This perfect arrangement allows for the polymerizable groups to line up in close proximity, which facilitates the polymerization and maintains the rate as the system becomes more viscous. At the same time the grouping remains flexible for the polymerization to proceed smoothly.

In this simplified model we have ignored the function of the dimerization enzyme laccase, (head to head) dimers caused by the action of laccase and the presence of small amounts of non-urushi components.

In summary, in this model for the polymerization of urushi, the molecules are likened to

the body of an active rattlesnake. The rattle is the polymerizing group, the seven flexible methylene groups hold the head in position, and the head, the catechol group, holds the molecule in its place by its desire to reach and grasp the high level of gaseous water in the atmosphere that is required for successful curing of the oriental lacquer.

**Curing:** The curing mechanism of the oriental lacquer consists of two parts 1) The laccase catalyzed dimerization of the catechol rings of the 3-n-alkylcatechols and 2) The oxidative curing of the unsaturated aliphatic side chains.

The laccase catalyzed curing is an oxidative dimerization involving the catechol rings and provides ultimately the crosslinker of the curing reaction. The urushiol consists of a mixture of 3-n-pentadecylcatechols: the saturated compound in small amounts, smaller amounts of the 3--(8-*cis*-pentadecenyl)catechol, 3-(8-*cis*-11-*cis*-pentadecadienyl)catechols and mostly the 3-n-(pentadecatrienyl)catechols. Oxidative dimerization of the catechol mixtures gives dimers of a molecular weight [M] of 626 to 636 or [M] $K^+$  of 665 to 673. The most important dimer is formed by dimerization of two molecules of the most abundant catechols, 3-n-(pentadecatriene)catechols, [M] = 626,. The dimer from the triene and the diene may also play a role as crosslinker. The formation of the dimer and the role of the dimer is specific for the 3-n-alkylcatechols.

The type of process used for the preparation of urushi (we have mentioned only the common **surugome** process) and the activity of the enzyme laccase also plays a role in the amount of dimers and other condensation products formed during the preparation of the lacquer.

The next step of the oxidative curing reaction involves the structure of the unsaturated aliphatic side chain is also common in drying oils and, with some modifications, for the curing of butadiene based rubbers. The mechanism of the curing consists of a number of interconnected steps involving: radical reactions, radical additions of radical

termination.

It should be pointed out that these reactions proceed in continuously changing environments of viscosity. At the initial application, the lacquer is in a fluid environment. As the curing proceeds, the viscosity of the lacquer increases rapidly, which makes the reactive sites less and less available and the individual processes become increasingly diffusion controlled. At the same time the diffusion of oxygen for the oxidative curing to the reaction sites also decreases. It has been mentioned that it takes almost 2 months until the lacquer is judged cured.

The curing of Oriental lacquers seems to proceed according to traditional schemes of oxidative polyene polymerizations that have been established for polydiene curing ; 1) The creation of the first radical; 2) The formation of oxy radicals: 3) Addition of low molecular weight and polymer radicals to double bonds. 4) Termination of the radical process by radical recombination.

The initial formation of radicals consists of the abstraction of an undefined radical from the activated methylene group in the 10-position of the urushiol components. This radical can do the following: a) Add oxygen to form a peroxy radical or b.) Recombine with a radical already existing.

Should interaction with oxygen be the path, molecular oxygen can be added to give a peroxy radical, which will abstract hydrogen from an appropriate carbon hydrogen bond, and lead to a hydroperoxide. Hydroperoxides can dissociate directly to give a (polymer)oxygen radicals and hydroxyl radicals. This dissociation may occur directly (for example by photo induction) or by induction. Carbon radical or oxygen radical can and will add to double bonds, especially sterically available and/or activated double bonds to form new radicals. Ultimately, the polymer radicals will terminate by recombination.

Oriental lacquer is used almost entirely for objects for indoor use. In part it is the high

cost that limits the use of oriental lacquer for decorative objects. In part it is based on the fact that further reactions continue in the solid state. After the curing is “complete” many reactive groups are still available for further curing.

Especially under the influence of the outdoor environment, and solar radiation, the oriental lacquer undergoes photochemical crosslinking reactions, which increase its crosslink density and increase stress on the film. The result is the formation of blisters and cracks.

We have developed polymerizable ultraviolet stabilizers that can be copolymerized with oriental lacquers and drying oils and for cured oriental lacquer that seem to increase the durability of the coating by a factor of three. They are linolenic or linoleic esters of 2(2-hydroxy-*tert.* butyl(-5(3'-hydroxypropyl)phenyl)2H-benzotriazole.

*Oriental Lacquer Ware:* Oriental lacquer as the coating material produces exquisite pieces of lacquer ware.. The number of layers determines the quality of the final product. Specially prepared urushi samples are used for the preparation of high quality Japanese lacquer ware. The lacquer used for individual applications contains several ingredients in addition to the urushiol base depending on what special effects and what coloring is desired.

Several types of coloring pigments have been used to pigment oriental lacquer ware. For the yellow color, *orpiment*, for the red *vermilion* color *cinnabar* or *hematite*, a ferric oxide pigment and for black *metacinnabar*, black iron pigments and carbon black as well as Indian ink were used. Heavy pigmentation is needed because processed raw urushi used for painting has a deep bluish/black to black color.

As the final layer, a clear raw lacquer coat is applied. The final product of the oriental lacquer is a crosslinked polymer; it is resistant to water, alcohol and oils.

For centuries, actually millennia, oriental lacquer has been used to coat objects in a highly artistic and pleasing manner. The results have been exquisite artifacts and useful objects of long lasting beauty. Wooden boxes and other articles coated with oriental lacquer in various techniques are a central theme of the art in the orient and represent beauty and permanence.

A long time ago, well before the Christian era, the technique of producing boxes with oriental lacquer coating was well developed. We know of an almost perfectly preserved box coated with oriental lacquer from the Qin dynasty, about 200 B.C. Oriental lacquer wares have been continuously improved in China and, especially during the Yuan period (14th century), many beautiful objects were produced. The lacquered boxes and containers were of black and vermilion colors, and were elaborately carved which demonstrated the taste of that time.

Oriental lacquer art was originally developed in China and several articles from the 2nd century B.C. have been found, the oriental lacquer technology was brought to Japan in the 6th century A.D. Different tastes of lacquer techniques developed in Japan, as the Japanese culture became independent and different from the original roots in China. The art form to produce Japanese lacquer products has gone through several periods of development; it was greatly affected by the religious and ideological foundation of its time. The initial art form of Japan, in the Nara and following periods, the lacquering techniques used the traditional Chinese style.

Japanese lacquer trays from the 14th and 15th century show the impact of the simplicity of *Zen Buddhism*, which resulted in the simplification of the design, which is called the ***negaru*** style. It is a simple vermilion and black painting without decoration. The beauty of the objects: trays, containers and boxes relies on the shape of the original wooden object.

In the *Muromachi period* of Japan (16th century), another version of designing and

producing lacquered objects was developed. It used more elaborate techniques, which included the use of gold and silver flakes, mother of pearl and shell for elegant designs. In the interior of the temple Kodaiji, in Kyoto, built in the early 1600's the ***makie*** technique, which uses silver flakes in black lacquer, on a larger scale was first used.

In the Edo period of Japan of the late 18th and early 19th century further advances were made in Japanese lacquer ware. Sophisticated decorations with silver and later more and more gold flakes (*hiramakie*) are incorporated in the last few layers of lacquer for boxes, writing equipment and desks, trays, and even tables of lacquer ware.

In the Meiji period, at the end of the 19th century, Japanese lacquer products became very fashionable worldwide and the European market demanded considerable amounts of Japanese lacquer ware. A new art form and modifications of the traditional way of preparing Japanese lacquer ware was developed to satisfy the European market.

Objects coated with Japanese lacquer have not decreased in desirability and in value. High quality Japanese lacquer ware of high artistic value can now be obtained in traditional but also in novel and modern designs and styles (Figure 52).





Figure 52: Oriental Lacquer Boxes

Lacquer ware originating from Okinawa, Korea and China has used a considerable amount of mother of pearl or shells as inlay materials for decoration. These latter techniques have also produced many beautiful objects

**Way to Oriental Lacquer Research:** Over much of my career in polymer science I interacted extensively with the Orient, primarily with polymer science in Japan. I have been in Japan 29 times, lived there nearly 2 1/2 years when various periods are added together and had 20 Japanese Postdoctoral Research Associates in my laboratories in the U.S. More details are presented in the recent article [42] [Journ. Polym. Sci., Part A: Polym. Chem. Ed. 38, 2293 (2000)].

During this period I became interested also in the Art and the theater of Japan (Kabuki and Noh). Since I was mostly located in Kyoto, the old capital and the cultural center of Japan, I was exposed to the many scrolls and screens, in temples and other places, became fascinated with the block prints of the 19th century Japan (Hokusai, Hiroshige and Shigenobu) but most importantly with Japanese Lacquer ware and the interior and the inner *sancta* of temples.

When I moved to New York in 1982, I became a member of the Metropolitan Opera and of the Metropolitan Museum where I became acquainted with people from the Metropolitan Museum in New York responsible with the restoration of Old Masters. These old oil paintings have a final transparent coating, which has to be removed and reapplied from time to time after a few decades because of aging and deterioration. New lighting technology required some new thinking for possible incorporation of UV

stabilizers in the coatings and I was heavily involved in the development of polymer bound UV stabilizers. Other changes in restoration techniques required improvements in the backing of paintings. As a thesis advisor at the Polytechnic University in Brooklyn, I conducted a joint master's thesis between the University and the Museum.

By 1987, we had founded and created the Pacific Polymer Federation and planned for the first conference in Maui, Hawaii (PPC-1), of which I was chairman. A one-day session "Polymer Science and the Arts". was included (with the hope it would become a permanent institution). It was organized with Raoul Hoffman and Hartwig Hoecker, with some input by Seizo Okamura and Riichiro Chujo. It was originally planned as *restoration* of Art objects by synthetic polymers. For PPC-2 two years later in Otsu, Japan, the *creation* of Art using synthetic polymers was added as a new and important aspect of the contribution of Polymer Science to the field of Arts.

After PPC-1 I decided to become more actively involved in the subject of Polymer Science and the Arts and selected Oriental Lacquers as the subject. This selection was influenced by the fact that the main authority in Japan on Oriental Lacquers, my friend Kumanotani of the University of Tokyo, had just retired and we had developed and perfected in our research group several techniques that were ideally suited to be applied for the complete and rapid identification of all components of samples of urushi, the active component of Oriental Lacquer. In my next trip to Japan I had been appointed to a special professorship at the Kyoto Institute of Technology (KIT) where Takeo Araki, Dean of Technology and Shinzo Kohjiya, were my hosts.

On a Saturday I said I would like to see how oriental lacquer was produced, distributed, sold and used. For many years I had known the Kyoto Handicraft Center as a source of many items of Japan, gifts, pearls, Art objects, but where English is spoken. When we went there and asked how to find out about oriental lacquer, we were advised to visit the *Zohiko Urushi Art company* on *Raisen Dori* in Kyoto. This company and store were known for their exquisite lacquer ware. From there, we were directed to a small

company in the heart of old Kyoto. There Araki and I met Mr. Shigero Tsutsumi, the President of the *Tsutsumi Asakichi Urushi Company* of Kyoto. After a relatively long period of negotiating and explaining the purpose of our visit, we obtained Mr. Tsutsumi's trust, and he explained in detail the growing, harvesting, preparing of the various kinds of lacquers and the final applications. We purchased three typical samples, received them in sealed tubes and thereafter we were ready to start our work.

Since it was impossible to work on a problem that involves Japanese culture without a Japanese counter part we convinced Professor Koichi Hatada of Osaka University to join us. He was invaluable because his group was highly competent in two-dimensional NMR and several separation techniques that were needed to separate the components of urushi. William J. Simonsick Jr of DuPont contributed mass spectrometry, especially  $K^+$ IDS mass spectrometry of the mixtures and after separation, of individual components. In Brooklyn Jan Bartus carried out other analyses, synthesis and polymerization experiments, as well as curing and aging studies.

The work would not have been possible without the input of a competent botanist. Before starting the work, I decided to contact the New York Botanical Garden in the Bronx. I was directed to a certain John D. Mitchell who, I was told, could show me in the herbarium the species of *Toxicodendron vernicifluum*. Not only did he show me the species, collected some time ago in Sichuan, China, but it turned out that he was one of the world's experts on the botanic family of *Anacardiaceae*, and especially on the genus *Toxicodendron*. Without his help, cooperation and his guidance through the botany of these plant species this work would not have been possible.

In the Fall of 1996 when I was a Monbusho Professor at KIT in Kyoto I reported our work that had been published in 12 articles before an audience of experts that came from as far away as Tokyo.

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## G. Chiral Nucleation and Chiral Polymerization

Crystallization involves the agglomeration of molecules from solution or the melt into solids having highly organized structures. Some of the most elegant crystals are produced by nature as "minerals" and a number of these are valued as "precious stones."

Crystallization has been used for a long time for the isolation and purification of both organic and inorganic compounds. Crystallization of solids has even been used successfully for the separation of racemates of crystalline solids of organic compounds to enrich them or even obtain enantiomerically pure compounds. The technique has greatly benefited the pharmaceutical industry and enabled it to provide pure enantiomeric drugs. Crystallization is often initiated by the addition of "seed-crystals" or other nucleating agents.

Quartz (silicon dioxide) is one of the most common minerals. It has an asymmetric, helical  $9_2$  lattice structure. Work by Biot in 1812, demonstrated that quartz crystals can rotate the plane of polarized light. With this discovery the notion of "optical activity" was born.

As discussed in an earlier chapter I had asked Jan Bartus to develop a reliable technique to measure the optical rotation of solid samples. We settled on sodium chlorate as a test case because its crystallization behavior had fascinated scientists for about 150 years. Sodium chlorate crystallizes in dextro- or levo-rotatory crystals (Figure 53). They can be found simultaneously during the crystallization (1).

The problem of the chiral crystallization of sodium chlorate has been investigated and

reinvestigated, but not much progress had been reported. The phenomena remained a puzzle. Over all these years small contributions were made toward the understanding of the problem. Some groups counted the number of dextro- and levo-rotatory crystals and compared them from experiment to experiment, others measured the weight relationship of the dextro- and levo-rotatory crystals in each batch. The time consuming step was that the optical rotation of each individual crystal had to be individually measured. Some experts could recognize a sight difference in the crystal habits. Later someone noticed a bluish hue for the dextro- and a yellowish hue for the levorotatory crystals. It was also proposed, that this way of distinguishing the enantiomeric crystals could be used reliably and also for small crystals. We questioned that this approach was valid. For years, even decades, the crystallization of sodium chlorate



Figure 53: Sodium Chlorate Crystals

but also of sodium bromate has been studied with increasing curiosity. The crystal structure of the salts was determined, large crystals were grown and statistical studies were made in order to evaluate the puzzle: "What causes the formation of left handed or right handed crystals and under what circumstances ?". Many possible causes for the formation of either one or the other of the chiral crystals were taken into consideration-

*Statistical Quiescent Crystallization:* We decided to undertake our own investigation and study the chiral sodium chlorate crystallization in detail. We started first with the "statistical crystallization" under quiescent conditions. As it was done the past, we grew platelets in dimensions of 2 cm x 2 cm x 1/2 cm from a nearly saturated solution of

sodium chlorate. Dextro- and levo-rotatory platelets were found in these crystallizations. The crystals were isorefractive and had the same rotation in all three directions.

We carried out the crystallization by placing the nearly saturated aqueous solution in a Petri dish and covered the top with a piece of filter paper. This set-up was left at room temperature completely quiescent. It resulted in a slow evaporation of water but the filter paper cover prevented any particulate matters from the atmosphere from entering the solution and possibly act as nucleating agents. Over a period of 3 days to one week large crystals had been formed. They were placed in a polarimeter and their optical rotation was measured. Some crystals had a (+) and some had a (-) optical rotation. Each crystal was measured individually.

*Statistical Crystallization under Agitation:* When we entered the competition to solve the crystallization problem, we had a simple analytical technique on hand that distinguished our work from previous investigations. We could measure directly and simply, the optical rotation of the enantiomeric sodium chlorate crystals that had deposited as small crystals.

We decided to undertake these crystallization experiments under "tumbling conditions". We constructed a machine that allowed us to agitate (rotate) the saturated sodium chlorate solutions, to control the rate of temperature decrease, rate of rotation and the type of nucleation. It worked well and allowed us to study the chiral crystallization of inorganic salts. We have carried out a large number of crystallization experiments of sodium chlorate without any outside influence other than tumbling as the agitating motion.

Soon after we started our investigations, an article appeared in Science describing that optically active sodium chlorate crystals had been obtained by rotating the solution during crystallization. The authors had undoubtedly, during the rotation, broken up the

developing nuclei and caused nucleation throughout the system. The authors even speculated that the direction of rotation influenced the sign of the rotation of the final product. The investigators did not have the technique to measure optical rotation and they only described the type of "hue" as the optical activity of the powder.

Our basic experiment was as follows: Into a 7 mL test tube was placed *purified* sodium chlorate and water in a 3:2 ratio. After capping the tube with a silicone rubber septum, the solution was heated to 85°C in our apparatus. The tubes were rotated at 70 rotations per minute while being cooled at 1.2°C per minute. In most cases, small crystals began to appear at or below 58°C and sometimes as low as 35°C. Our results were as follows: Of 29 separate experiments, 15 provided levo- and 14 dextrorotatory crystals. Over 3/4 of the experiments gave optically pure crystalline powders while 17% were more than 80% optically pure. The remaining experiments provided solids that were essentially racemic. Crystals with the highest optical purity were obtained when the crystallizations began between 55°C and 60°C. In those experiments where crystal formation began near 40°C and below, chiroptical purities were low. In a few experiments where crystals had not formed at 35°C, the tubes were manually shaken to induce rapid crystallization which gave racemates by random nucleation. Identical results were obtained when our tubes were rotated in clockwise or counterclockwise fashion. This crystallization behavior is not limited to the statistical crystallization of sodium chlorate but can also be observed for sodium bromate (1).

About half of the crystallization experiments produced levorotatory, the other, dextrorotatory sodium chlorate crystal. The overwhelming proportion of the crystals was chirally pure, either purely levo- or purely dextrorotatory. In some crystallization experiments, the temperature of the first observation of any crystals was very low, indicating a very high degree of supersaturation. In these cases, when crystallization finally occurred, lower degrees of chiral purity of the sodium chlorate crystals were observed. Our explanation takes into account this behavior.

We interpret our findings in the following way. The agitation or tumbling action within our tubes generates a chiral "seed" of sodium chlorate having one handedness or the other. The actual mechanism by which this seed is generated is unknown. However, our data do suggest that there exists an equal chance that a given seed will be "right-handed" or "left-handed." No chiral bias is apparent. Further agitation may break *this seed* into a large number of secondary chiral seeds which then go on to rapidly nucleate the solution in chiral fashion. When the sodium chlorate solutions are above 50°C, this process has little competition and crystalline solids having high chiroptical purities are produced as the solutions slowly cool. For those experiments where crystallization was delayed until below 50°C, the solutions become increasingly supersaturated. Now, there is a greater tendency for "normal" chiral crystallization to occur and competition with the original seeding process ensues. Depending on the exact dy-namics of each system, solids having low chiroptical purities will generally result. Finally, if the sodium chlorate solutions cool to a point where they are completely supersaturated without being nucleated, a simple agitation event will result in the rapid formation of a nearly racemic mixture of seeds. Here, the normally observed chiral crystallization process will not dominate and optically inactive samples will be obtained.

When we started our work on sodium chlorate crystallization we had used an old bottle of sodium chlorate for our experiments. We measured the crystals as powder which showed a near zero rotation. Sometimes later, we had to order a new bottle. Before we used the sodium chlorate from the new bottle, we measured the optical rotation of the content. To our great surprise, the value of the optical rotation of the sample was nearly that of a powder obtained from a pure large sodium chlorate crystal. We concluded, that the manufacturer had used agitation in the final crystallization of the new sodium chlorate batch and had produced the chiral salt. In the old sample random nucleation must have occurred and dextro- and dextro-rotatory nuclei of both antipodes had been produced prior to the crystallization.

It is important to note that a spontaneous resolution of this kind of dissymmetric inorganic crystals from achiral solutions of ions could provide insight into the origins of bimolecular chirality on Earth. The origins of bimolecular handedness, including such problems as chiral synthesis, chiral fields, parity non-conservation, and chiral symmetry breaking have all been in peoples minds.

*Chiral Nucleation:* Only recently some thought has been developed that suggests that the preference of the formation of one enantiomer of sodium chlorate over the other is caused by the breaking-up of the primary nuclei. The primary nuclei are formed "by chance" by spontaneous formation of the first nuclei of sodium chlorate crystals but even the very early associates, the nucleating nuclei are chiral. This process, it was insinuated, might become the dominant factor for further crystal growth by secondary nucleation. Chiral symmetry breaking during sodium chlorate

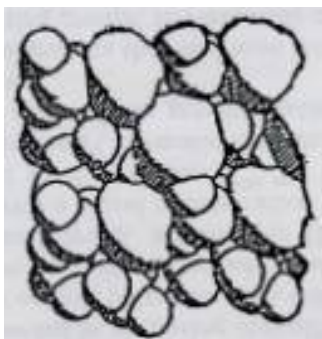


Figure 54: Chiral Sodium Chlorate Structure

crystallization on agitation which we have observed, *in the absence of any added chiral nucleating agent* allowed me to come to the obvious conclusion. We should be able to nucleate a saturated solution with a shaved powder from pure dextro- or dextro-sodium chlorate crystals (1) (Figure 54). This experiment could be carried out simply in an Erlenmeyer flask. The first experiment was a huge success. Bartus measured the optical rotation of the crystal powders and found that the values were as good as the best samples that we had been obtained from large sodium chlorate single crystal. Sodium chlorate and sodium bromate, are intriguing examples because they are achiral in (aqueous) solution. They are dissociated into ions but crystallize very

specifically and perfectly as either levo- or as dextrorotatory crystals. Once the crystal is nucleated and starts growing, the entire crystal, that is formed, is chiral, there is no reversal of the handedness, nor is there a formation of mixed crystals. There is a good reason why chiral crystallization is so specific. Sodium ions are small cations and chlorate or bromate anions are large anions. They fit in a chiral crystal only in a very specific way, in a chiral way!

In addition, levorotatory sodium bromate crystals, which have the same crystal structure as dextrorotatory sodium chlorate crystals, when used to chiral nucleating agents for a supersaturated sodium chlorate solution, gave chirally pure dextrorotatory sodium chlorate crystals. Analogous results were obtained when dextrorotatory sodium bromate crystals were used for the chiral nucleation of aqueous sodium chlorate solutions gave levorotatory sodium chlorate crystals. Levorotatory sodium chlorate crystals gave dextrorotatory sodium bromate crystals and dextrorotatory sodium chlorate crystals produced levorotatory sodium bromate crystals.

Finally, instead of lowering the temperature of a nearly saturated aqueous solution to obtain a supersaturated solution of either sodium chlorate or sodium bromate to carry out crystallizations, we used water miscible solvents to reduce the solubility of the salts and cause chiral nucleation of sodium chlorate and sodium bromate solutions. Both methanol and ethanol proved to be suitable "precipitation" solvents and facilitated the crystallization of purely enantiomeric salts. Acetone was too much of a "non-solvent" and caused the crystallization of chirally impure salts apparently by chiral and achiral nucleation.

*Chiral Crystallization and Chiral Polymerization:* I have drawn parallels between chiral crystallization and stereospecific polymerization in an effort to show that there is a common thread linking these two seemingly disparate fields (2,3). Chiral crystallization of inorganic salts and the stereospecific polymerization of specific monomers to give helical structures can both furnish chiral entities at a molecular

level. However, in our macroscopic world, we isolate these crystals and helices as racemic mixtures.

We have seen similar examples where steric bulk determines structures. Not in crystallization but in polymerization. After all a crystal, an ionic crystal, like sodium chloride or sodium chlorate is a three dimensional polymer which is held together in the crystalline state by ionic forces. Chloral polymerizes to polymer in a stereospecific and conformational specific way (4), the ultimate structure of the polymer is clearly determined by the relative size of two parts of the molecule. The small polymerizable carbonyl group and the large trichloromethyl group determined that the resulting polymer was both stereospecific and conformationally specific. The polymer was a tight rigid helix. When initiated with a chiral anionic initiator, the polymer chain is chiral. In both cases, chiral crystallization and chiral polymerization, the discrepancy of the sizes of the small sodium cation in the crystallization in sodium chlorate as compared to the great size of the chlorate anion. allows chiral preferences. In the polymerization of chloral, the trichloromethyl group is overwhelming in size by the small carbonyl group, the group capable of polymerization..

*Chiral Polymer Crystallization ?*: We have demonstrated that crystallization induced by chiral nuclei gave pure chiral sodium chlorate. As I said before, it should be possible to use chiral nuclei to induce crystallization of isotactic polymers (especially with a bulky side group) to crystallize as single helices (5). Before I retired from active research, I asked my last co-worker to work on the chiral crystallization of isotactic poly (n-heptaldehyde). I considered this system to be the most promising. I thought that the tendency to side chain crystallization might help the attempted chiral crystallization. With the small effort that was left prior to retirement it turned out to be unsuccessful and I had to abandon this initiative.

Incidentally, every polymer that can crystallize in a helical conformation should be subject, if nucleated properly, to chiral crystallization. The principle is that

crystallization can start with a homogeneous mixture of a potential nucleating agent and polymer, allow the nucleating agent to form chiral nuclei first which then induces the chiral crystallization of the polymer as chiral helices.

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## H. Isotopes in Polymer Chemistry

At this final section of the scientific part of this treatise I would like to share with you my interest in my last contribution to polymer chemistry, The Final Step Toward True Uniformity in Macromolecules, Isotopically-pure uniform polymers:

Over the years I had many coworkers and I have cooperated with a number of research groups here and abroad. In the last 20 years I worked closely with the group of Koichi Hatada in Osaka. I also cooperated with Gary D. Jaycox, a close friend, now is at the Central Research and Development Department at DuPont in Wilmington and with William J. Simonsick Jr. at Marshall Labs. As I was teaching the key courses in

polymer chemistry in the PSE Department at UMass I became interested in the various approaches of explaining molecular weight and molecular weight distribution of polymers. We started from the most probable molecular weight distribution  $M_w/M_n$  of 2, to the "living polymerization" which approaches  $M_w/M_n$  of 1.

In the early 1980's Koichi Hatada made a major step toward Uniformity by isolating and characterizing "uniform polymers." The uniform polymer cannot be made directly but has to be isolated by special techniques from a mixture of nearly uniform polymers, from samples of "living polymers". Hatada has demonstrated this case decisively. He took a poly(methyl methacrylate) with a  $M_w/M_n$  of 1.06 and subjected it rigorously to HPLC. He found that this so-called highly "monomolecular" polymer, also called "living polymer" still consisted of about 120 macromolecular species of similar molecular weight.

For some time I have been cooperating with Bill Simonsick on  $K^+$ IDS mass spectrometry. He recorded and characterized for us UV stabilizers we had made for DuPont. He measured the molecular weight by  $K^+$ IDS, but as an extra, he calculated also the isotope molecular weight. Our cooperation intensified when he helped me analyzing the oligomers of chloral (and bromal). The latter was particularly intriguing and the calculations interesting. Chlorine and bromine have two isotopes at about the same amounts which makes the calculated spectrum more interesting.

One day I said to Bill: I wonder how many isotopic species are in macromolecules ? To my knowledge, nobody had been interested in this question. Hatada's work had shown that uniform polymers could be isolated and work (on a tiny scale) could be done with them. I asked Bill: How many isotopes would a polychloral 500-mer have ? This question was reasonable because we had estimated (by end group analysis) at one

time that polychloral under favorable conditions can have a DP of 500. Bill came up with a number of 7,500.

Now we know that the number of theoretical isotopes of polychloral of a DP of 500 is about 10 to the power of 1141. The number of the isotopes in the monomer, 192 has to be taken to the power of the degree of polymerization. It goes without saying that many molecular weights are present in the same molecular weight. Still, the possibility of the individual entities is staggering.

Imagine nucleic acids, and the number of isotope species. The number is calculated by taking the number of the isotopes (fortunately phosphorous has only one isotope) in the monomer unit to the power of the molecular weight that in most cases is in the billions.

*Isotopes in Polymer Chemistry:* Carbon, hydrogen, nitrogen, oxygen, and sulfur - the fundamental building blocks of organic matter have two or more stable isotopic forms differing in atomic mass. The terrestrial abundance of the higher mass isotopes for each of these atoms are relatively small, but the diversity has a notable impact on a variety of scientific disciplines. For example, the nuclei of  $^{13}\text{C}$  and  $^{15}\text{N}$  provide the basis for NMR techniques that are now widely used.

The presence of higher mass isotopes and their corresponding isotopic distributions within larger macromolecular systems have received little attention (1). Because polymers are high molecular weight constructs formed from repetitive monomer sequences, even relatively simple materials like polypropylene and poly(methyl methacrylate) can possess remarkable levels of diversity or heterogeneity at the atomic or isotopic level.

Using a series of computer-aided calculations that allow for mass spectral simulations,

we found that uniform" polymer species possess remarkable levels of mass heterogeneity that are dependent on both chain size and elemental composition. For many macromolecules with commercially relevant chain lengths, this natural variation in molecular weight can easily exceed the mass equivalent of one or more monomer repeat units that the comprise the polymer backbone (2-5).

Polypropylene is well suited for use as an example here. Each  $C_3H_6$  repeat unit along the polymer chain will naturally contain two stable isotopes of carbon and two stable isotopes of hydrogen. In this case, a total of 512 ( $2^3 \times 2^6$ ) isotopically distinct species can be calculated to exist for each propylene monomer repeat unit. As individual repeat units are coupled together to give dimers, trimers and ultimately larger polymer chains, the number of isotopically distinct species that are *theoretically possible will* grow in exponential fashion. For a relatively short polypropylene 50-mer (excluding end groups),  $512^{50}$  ( $2.91 \times 10^{135}$ ) different isotopic combinations are possible, which, collectively, will span a mass range that is over 450 Da wide! Of course, the vast majority of these species will have extremely low probabilities of formation and at some level of analysis they can be realistically excluded from further consideration. Many of the more abundant species residing in this theoretically derived envelope will have identical masses and will thus be indistinguishable from one another in a simulated mass spectrum for this polymer construct.

Poly(methyl methacrylate), another important commodity polymer, can also be subjected to this form of simplified mathematical analysis. With a more complex repeat unit of  $C_5H_8O_2$ , a poly(methyl methacrylate) 50-mer will have a theoretical mass envelope over 850 Da wide that is populated by well over  $2.40 \times 10^{241}$  isotopically unique entities! As for the polypropylene example above, the vast majority of these species can be safely ignored in any real world consideration because they have extremely low probabilities of formation.

Default parameters for this program were selected to capture over 99.95 percent of the mass peak abundance in this distribution and to purposely block the inclusion of molecular species constructed from the least probable isotopic combinations residing at the high and low regions or "wings" of the mass envelope.

Simulated mass spectra for the 500-mers of polypropylene and polychloral have been calculated. The mass envelope for the polychloral 500-mer is characterized by greater degree of complexity than that observed for polypropylene or for poly(methyl methacrylate). This behavior is specifically linked to the unique isotopic diversity of the chlorine atom. Two naturally occurring isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , are randomly distributed throughout this hypothetical linear 500-mer in an approximate three to one ratio.

The number of possible isotopes in a polymer can be calculated by the molecular weight of the monomer unit to the power of the DP. Our favored polymer polychloral has the formula  $\text{C}_2\text{HOCl}_3$  and the monomer unit has 192 isotopic species. A 50-mer could have 192 to the power of 50, which means  $1.14 \times 10^{114}$  isotopic species, a 100-mer  $2.14 \times 10^{228}$  and a 500-mer  $4.43 \times 10^{1141}$  (Figure 55). Not all MW are equally represented and ultimately there is a peak of the most probable isotopic molecular weights. This "peak" can be focused by using a computer program. It can tell you the "concentration" of isotopic molecular weights, depending on the sensitivity. We have used this program at a 1: 1,000,000 setting and at a more reasonable 1:2,000 setting.

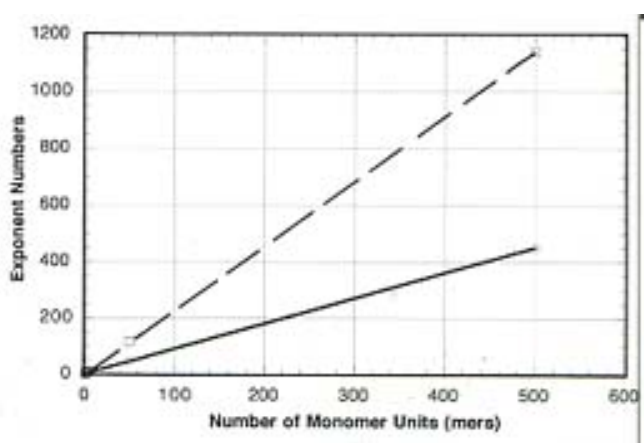


Figure 55: Number of Isotope Species as a Function of Monomer Unite (mers) for

Polychloral. a.) for all isotopes considered, number of Isotopes per Chloral Monomer unit is 192; b.) for only important isotopes, number of monomer units is 8.

But first to the basics: The unit molecular weight of the lightest isotope molecular weight of  $^{12}\text{C}_2^{1}\text{H}^{16}\text{O}^{35}\text{Cl}_3$  is 145.909. When this MW is used as the basis of higher DP's of polychloral, the 100-mer has a MW of 14,590.93 and the 500-mer of 72,954.64 Da.

The structure of the heaviest chloral monomer unit is  $^{13}\text{C}_2^2\text{H}^{18}\text{O}^{37}\text{Cl}_3$  with a calculated MW of 157.020 Da. For the 100-mer, the MW of is 15701.98 Da and for the 500-mer (Figure 56) it is 78,509.91 Da. It should be remembered that the MW of our normal "terrestrial" chloral monomer unit is 147.447 Da. The MW of the "terrestrial" polychloral is 14,744.7 Da for the 100-mer and for the 500-mer, it is 73,723.5.

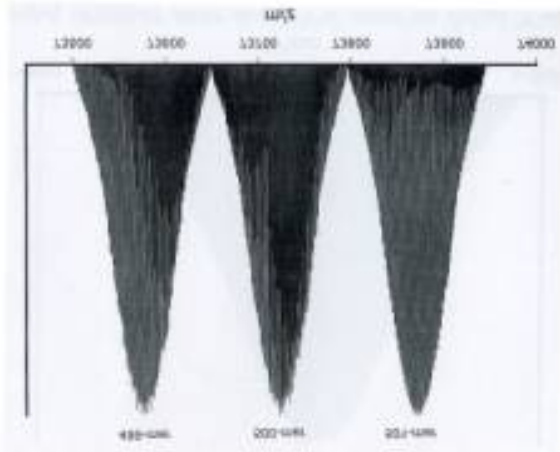


Figure 56: Isotopically Pure Uniform Polymers: Simulated Mass Spectra Of 500-mer of Polychloral

Now, we go to some more delicate and detailed distinctions. We are considering the "overlap" of the MW's I mentioned the MW of the "low" and "high" MW monomers, those that had the lowest and highest combination of isotopes in the monomer structures. For the 100-mer the difference is 1,111.05 Da. For the 500-mer it is 5,555.27 Da. In both cases there is an "overlap with an overlap of +/-7-8%. In other words Isotopic molecules with a MW 7 to 8% for the 100-mer or 7 to 8 Da and 36 to 38 Da for the 500-mer could fall within the envelop of the polychloral 100-mer or 500-mer.

One more comment. The position of the "peak" of the most probable isotopic molecular weights, depends on the width of the space between the "all" low molecular isotopic structures and the "all" high isotopic structures. It also depends on the percentage of the isotopic species. Hydrogen has only a 0.015% of deuterium, carbon of 1.1 % of  $^{13}\text{C}$ . Chlorine on the other hand has 75.8% of  $^{35}\text{Cl}$  at 75.8 and 24.2% of  $^{37}\text{Cl}$ . This means that the "peak" position monomers (and polymers) depend very much on the percentage of the minor isomers.

Let us compare these "peak" positions they are from the low side: 13.84% for polychloral, 27.40% for polybromal, 0.47% for PMMA and 0.44% for PP.

The introduction of bromine atoms into the polyaldehyde chain has a similar diversifying effect. A simulated mass spectrum for the 500-mer of polybromal shows nearly 3,300 distinct species.

The degree of mass variability present within a macromolecular construct depends upon two different factors: (1) Length of the polymer chain and (2) Polymer chain's elemental composition. As the degree of polymerization (DP) increases, the overall isotopic complexity of the polymer construct can be expected to grow in an exponential manner. For a fixed degree of polymerization, polymer structures enriched with chlorine or bromine atoms will possess higher levels of isotopic diversity when compared to their more simple polyolefin counterparts like polyethylene and polypropylene. The presence of oxygen will have a similar diversifying effect.

For every macromolecule, a unique degree of polymerization can be reached where the spread of the mass peak envelope will ultimately exceed the mass of an individual repeat unit residing along the polymer chain. At this critical chain length, a sufficient level of mass heterogeneity will be present so as to effectively blur the distinction between uniform polymer species fitted with  $N$  and  $N+1$  repeat units. Beyond this limit,

mass measurements can no longer be employed to definitively assign DP values to individual polymer chains. If theoretical mass distributions containing all isotopically distinct species are considered.

Less probable isotopic combinations reside at the edges or "wings" of the mass distribution envelopes. Our results depend upon the fraction of the mass envelopes actually considered and any comparisons made with our data will tend to be meaningful only in a relative sense. For this particular exercise, individual parameters were run at two different sensitivity settings, either capturing peaks with abundances greater than 0.05 percent (the default setting) or at the lowest possible detection threshold of 0.0001 percent. This critical chain size occurs earliest for polymers of chloral and bromal that contain their heavier halogen isotopes in relatively high natural abundances. A computer-aided simulation depicting peak envelope overlap for the 499-, 500- and 501-mers of polychloral have been established. Mass peaks falling within the overlap regions of these plots cannot be definitively assigned to a specific polychloral species having one unique chain length.

The past four decades have witnessed the development of new synthetic methodologies that allow access to ever more uniform macromolecular structures. Living polymerization techniques first developed for polystyrene now routinely provide for a variety of polymers with molecular weight distributions approaching unity. With the proper choice of initiator and polymerization conditions, a high degree of control over a macromolecule's sequence distribution, regiochemistry, stereochemistry and conformational behavior can often be realized. However, even at this level of refinement, the polymerization techniques employed do not furnish polymer products that are truly monodisperse. As reviewed by Hatada, a number of approaches have been devised in recent years to synthesize and isolate so called "uniform" polymers that are endowed with single, well-defined chain lengths. In many cases, these efforts involve the tedious fractionation of oligomeric or polymeric species that have been prepared by well-controlled polymerization processes. Not surprisingly, materials of

this kind often exhibit novel properties that are unlike those observed for their more non-uniform counterparts.

We can now put forth the notion that an added level of uniformity can be applied to both synthetically derived and naturally occurring macromolecules - namely that linked to *an absence of heterogeneity or diversity at the isotopic level*.

At this point, there are several questions that one may reasonably ask. How, for example, might the chemical, physical or biological properties of isotopically pure, uniform macromolecules differ from those of their more atomically diverse or more "natural" counterparts? Would the behavior of these isotopically uniform constructs differ to an extent that we would notice? Does the final level of polymer uniformity discussed here have any practical significance?

New tools developed over the past decade that increasingly allowed for the precise manipulation and study of individual (macro)molecular species, including relatively complex structures like enzymes and DNA. The small behavioral differences that are likely to arise from unique isotope compositions will not be averaged out by larger randomized populations of the same polymer. It is interesting to note that many natural products can already be differentiated by their specific isotopic signatures.

Nature has provided us with a remarkable pallet of atomic building blocks. Isotopes of the same element provide for additional levels of diversity. It has used these building blocks, to build large molecules, like DNA. Its unit molecular weight is approximately 500 Da, not considering the isotopes of hydrogen, carbon, nitrogen and oxygen. The phosphorous atom has only one isotope. But imagine the difference in DP's, which is 500 for polychloral and about 10,000 for commercial polyethylene. It is in the billions for nucleic acids. With these enormous molecular weights, and the length of life on earth, perhaps 2 billion years one important question arises: How much if any has the terrestrial composition of the 5 isotopes giving us life changed in the millions of years.

If it did even slightly, did it influence the development of life as we know it and if so, how much?

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## VI. Publications

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### Introduction

Scientists may present their work orally, (in meetings or other gatherings), in poster form or as printed articles. Such permanent publications, printed articles, are now more and more prepared and distributed in electronic form. I always believed in the printed word, it has permanence and can be quoted. In order to produce this printed word there has to be someone to publish the article, the publisher. Most articles in our profession are published as articles in journals and magazines, fewer directly in book form. In fact the sequence of publication begins usually with an oral presentation, followed by a journal article. Several articles are then combined, reorganized, and appear in review articles and books. The best, most popular and fashionable results end up in textbooks.

The publisher of a scientific Journal relies on the editor, who receives the manuscripts reviews them himself or has them reviewed by experts in the field, makes final corrections and submits the manuscripts to the Journal for printing. Finally the Journal Editor returns the article to the author in proof form. The author reads the proof of the manuscript with pride, makes his final corrections, if necessary, and forwards the "corrected proof " to the publishing editor for printing.

All scientists begin as authors; they publish their scientific results in the ways mentioned above. Some of them become editors of journals or book editions. In many ways they become involved in the publishing process and influence the printed word. .

My involvement with "publications" started in the late 40's with the Monatshefte. I became active in the Journal of Macromolecular Science when it was in the planning stage and when it was first published in 1967. Through my friends at Brooklyn Poly I became familiar with the Journal of Polymer Science, played a role in the creation of the Journal, "Macromolecules" and the Japanese Polymer Journal. When I was the treasurer of the ACS Polymer Division I had to pay close attention to the publication of the "Polymer Preprints" of the Division. Throughout those years, I never had my "own" Journal, where I could make policy decisions and direct the fate of the Journal. In 1985 I became the Editor of Progress in Polymer Science. Under my leadership my Editorial team took Progress in Polymer Science to first place in impact factor ranking of 75 polymer Journals.

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## A. The Monatshefte fuer Chemie

For a number of years toward the end of, and after the Second World War, The Monatshefte fuer Chemie had as its Editor-in-Chief, Professor Spaeth. He had dominated Organic Chemistry in Austria and part of Europe, and was the Head of the Institute of Organic Chemistry, Rektor of the University of Vienna and President of the Austrian Academy of Sciences. His death in 1946 propelled Docent Galinovsky into the Editorship of the Monatshefte. The Monatshefte, a Springer Verlag Journal, had a good reader-ship and subscriber-ship because it was sponsored by the Austrian Academy of Sciences. Each article of the Journal had to be approved by (the appropriate committee of) the Academy.

I began my graduate work in October 1947 with Galinovsky as my advisor. As I mentioned earlier I had been assigned a steroid problem. For various reasons I needed to have at my disposal 3a- and 3b- sterin alcohols. I developed within a few months the chromatographic separation of 6 pairs of these alcohols and could isolate the pure 3a- and 3b- compounds. I did not know nor could I believe that this was a remarkable

achievement. It was finished in May 1948. Galinovsky checked personally every melting point was satisfied and very enthusiastic; he said: "We must publish your results immediately", because it will be interesting for many people and we cannot afford losing priority. - are you ready?

I was completely naive and did not know how to go about preparing a manuscript for publication. Galinovsky said that we did not have much time because the meeting of the Academy was in 2 days on June 24, 1948, and the manuscript had to be submitted. For the Academy meeting, however only a list of titles and authors had to be submitted but not the complete manuscript. Of course the Editor had to have the papers in hand.

In was June 22, 1948, when Galinovsky sat at the typewriter and said: now we have to decide on the title of the manuscript. He decided on the title and sequence of authors: Galinovsky and Vogl. Next he took the "official" approval stamp and set it exactly on the day June 22 and stamped "submitted". Having done this he sat down and smiled. "Now," he said, "We have to write the paper."

The manuscript (without manuscript, only the title) was approved by the Academy on June 24 and was sent to the Editor for the usual publication proceedings. The paper appeared in Volume 79(3/4), 1948 on page 325 of the Monatshefte.

Although my subject interests changed over the years and I had to publish in polymer related Journals, I remained faithful to the Monatshefte and published more than 25 papers in the Journal, the first in 1948 and the last in 2000. That means I had published in 7 decades, from the 1940's to the 2000's.

One experience with the Monatshefte takes me back again to the first few years with Galinovsky. In 1948 I had been appointed Instructor at the University Institute and had an official standing. One day, I believe it was in 1949, Galinovsky said. That he was taking a few weeks vacation. People at that time did not take a real vacation they just stayed home. Galinovsky had a nice home in Rodaun where he lived and stayed mostly in the

summer. He also had two rooms in the Institute, where he lived with his wife. She was his first graduate student.

Galinovsky said: "Take care of the Monatshefte. Stamp every incoming paper properly, make sure all the pages are there and let me know - I will come once in awhile". During the summer, very few papers were received. Papers were typed sometimes with ancient typewriters (electric typewriters existed but were not used much in academia) with a number of carbon copies on onion paper. Some papers were handwritten, had to be submitted hand written twice because there was no mechanism of duplicating manuscripts.

One manuscript was particularly impressive for me (I accepted it immediately without any question). It was written by Professor Skrabal, of Graz, a theoretician and kineticist, and subject wise, way above my competence. Curiously, it was handwritten in a beautiful handwriting and full of brown fingerprints, which reeked of tobacco and made me realize how difficult the times were for smokers. Skrabal smoked his cigarettes down to the last half of an inch! For the last 2 decades I served on the Editorial Board of the Monatshefte and am still serving as the American Editor.

I was involved in the early development of a number of polymer Journals as early as the 60's.

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## **B. Macromolecules**

Some of the earlier stories might have the sense of legends but I will still mention them. In the 50's polymer science in the US was in the hands of 3 people: Marvel, Mark and Flory.

From the publishing point of view, Mark had created (with Maurits Dekker and Proskauer) Interscience Publishers and the Journal of Polymer Science. Marvel was a leader in ACS

affairs, had been its President and was an avid nationalist who seldom went to international meetings. Mark had created a school of thinking (I became a part of it) on the basis of Internationalism in Polymer Science. After Mark had created the Journal of Polymer Science he became involved in other activities and handed the Editorship of the Journal over to Charles Overberger, the head of the Chemistry Department at Brooklyn Poly. Overberger was then in his mid 30's He had been a post doc of Marvel and had become interested in ACS matters. In 1967 he became President of the ACS.

From the mid 50's Marvel wanted an ACS Polymer Journal. Overberger, according to legend, as the Editor of the Journal of Polymer Science, a publication of Interscience Inc., a private publishing company, was not interested in supporting the creation of a competitive ACS publication. Even though he was a Marvel student, he privately opposed this movement. However under Marvel's leadership the pressure mounted and by 1963 investigations were undertaken by the ACS for the creation of a Polymer Journal. Speed (as he was called among friends) was able to organize a committee at ACS. Under the leadership of the committee chairman Blaine McKusick appointed George Belnap, a senior staff member at ACS, to look for a possible name for the Journal, should the ACS publication committee approve it?

Blaine was a Director of organic research at the Central Research Department of DuPont in Wilmington. He asked me to discuss the possibility of starting a new ACS Polymer Journal with Belnap. We were to come up with possible names for this Journal. I was still a young man in my 30's and was flattered. I told Belnap that Macromolecules might be a good name for the proposed Journal. I pointed out that, with this name, if the Journal flourished it could be divided into sections such as Chemistry, Physics, and Biopolymers etc. I still have this letter. To my surprise this name was accepted and the new ACS Polymer Journal was named Macromolecules. "Macromolecules" is now the most widely used primary Polymer Journal in the world.

Through Marvel's influence Stretch Winslow, the Manager of Polymer Chemistry Research at Bell Labs was appointed the first Editor of the Journal. Stretch accepted and

remained for almost 25 years in this position. Stretch appointed me to his first Editorial Board and I served until 1976. The Journal was first published in 1967.

A few years ago, ACS decided to have a separate Journal entitled Biomacromolecules, exactly what I predicted almost 40 year ago. Ann Christine Albertsson of the Royal Institute of Technology, Stockholm, one of my postdoctoral Research Colleagues, became the Editor and the Journal has been very successful ever since!

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## **C. Journal of Polymer Science**

For many years I have been associated with the Journal of Polymer Chemistry, which was created by Herman Mark in 1945. In 1960 I needed to have our newest discoveries on the polymerization of higher aldehydes published as soon as possible because the competition, Furukawa and Natta, had also been working on the subject. Mark, remembering my Viennese background, had the article published within 6 weeks. Needless to say I was most grateful to Mark and the Journal. For 30 years now, I have been serving on the Editorial Board on the Chemistry Edition of the Journal of Polymer Science. Many of my articles were published in the Journal, the Polymer Chemistry Edition. In 2000, with the persuasion of the present Editor, I published summaries of a number of my scientific interests and research activities as 'High-Lights'.

The Journal of Polymer Science had as its Editors friends of mine: From Mark to Overberger, Pearce and Salamone. The newer generation arrived in the 80's, with my former student Tirrell as The Editor and now Virgil Percec also a student of mine. Virgil has been closely related to me from the time he was a student of my friend Simionescu in Iasi, Romania. In the last 15 years the Journal has been modernized and additional Editors were added, in light of the ever-increasing complexity of scientific publishing.

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## D. Polymer Journal (Japan)

When I was at Kyoto University in Japan for a semester in 1968 I was invited to many events of the polymer world in Japan. My family and I were very quickly "accepted". The Society of Polymer Science was still a young organization and the scepter had been passed from the first President, Sakurada, to Sobue, who also had done some work on aldehyde polymerization. One day one of the Japanese Professors, Seizo Okamura, of Kyoto University, the Editor designate, still in his mid 50's came to see me at my residence, at Konoe Hall, near the University, where we were living. He knew that I was somewhat involved in publishing and was also influencing policies of the ACS Division Polymer Chemistry. The Society of Polymer Science, Japan had been publishing **Kobunshi Kagaku** in Japanese and was considering publishing a Journal in English on their own. He asked me what I thought about this proposal. I contemplated but did not think that this would be a good idea. To have authors in English was very problematic and to have the Editors, which had to be Japanese, was also a problem. Very few Japanese scientists had been abroad and spent a year abroad at that time. The quality and fluency of English in Japan, in "our" community was not very high. I had also mentioned that in the last few years polymer related Journals had been created and would be competitive. But ultimately Okamura convinced me that it would be a Journal in English with mostly Japanese contributors, who wanted to be read in English. He was right: The Journal, the **Polymer Journal (Japan)** is now over 30 years old and doing well. The journal did not have an explosive growth but has served the intended purpose.

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## E. Books

Although I wrote many articles, and learned how to prepare for the writing of patents, I never was a book writer. Maybe I started my more extensive writing late in life. I edited a booklet "Aldehyde Polymerization" which also came out as hard copy. It was based on an ACS Symposium, which I organized in 1967. I kept editing booklets and issues but I never sat down to write a textbook.

I always complained that the books available in Polymer Science are either too specific too broad or too long. I always taught from my own notes and on the blackboard with my own soft chalk. I used "Ravve" as my primary source, with some of "Lenz" or "Odiان" as reading materials. The primary requisites for doing well in my examinations knew my lectures well.

There was and there is still today a need for a "readable" Textbook on Polymer Chemistry. Ravve was too detailed and outdated on chemistry, Lenz was uneven and questionable, Odiان was too wide in scope and became more so as one after the other editions appeared. The contents of my lectures were mixed by combining chemistry, physical chemistry and physics and even some fabrication. Odiان revised and up-dated his book frequently and ultimately, it became too long.

I had been thinking of writing a book "Introduction to Polymer Chemistry" strictly limiting the subject to chemistry. The idea was to concentrate on polymer chemistry, the organic chemistry of high polymers. Other subjects of polymer science should be treated in a minimal way. Books on polymer chemistry that are published today are too long and include many subjects that are not necessary. We envisioned that the envisioned should not exceed 300 pages. I did not want to write the book alone and invited Dave Tirrell to join me. It was during the time that Dave had finished his thesis and had become an Assistant Professor at Carnegie-Mellon University. The agreement was that the book would be based on the organic chemistry as it was laid down in my lecture "Introduction of Polymer Chemistry." Dave and I had agreed that I was to prepare and provide the figures and drawings and the first rough draft and Dave was to finish the book. We signed a contract with Wiley in 1978.

Before we could begin the book several circumstances developed preventing us from really getting started. Dave had to worry about teaching, building of a research group, grants, local politics and all the prospects of a brilliant academic career. I became involved with organizing the IUPAC Symposium on Macromolecules in 1982. In 1983 I

moved to Brooklyn and Dave took my position in Amherst. Other pressures took over and we never wrote the book. Interestingly enough, there is still no book of this kind available -- times have changed and a book of this kind may not be needed any longer. In 2000, Wiley reminded me that the commitment agreed in a contract was still on their books. I told him that was nice, but we ultimately concluded that we did not wish to write the book.

About 8 years ago I became involved in another edited book. My friend, Koichi Hatada, wanted that we write and edited book. We gave it the title ***Macromolecular Design of Polymeric Materials***. Hatada wanted to write the book with his Associate Professor Tatsuki Kitayama. He convinced me to join them as co-author, and write a chapter, a request I could not refuse. Hatada and I designed the outline and subjects that we wanted to cover in the book. I was to contact all my friends that could contribute chapters to the book, persuaded them to write and follow up. Once the manuscript arrived in Hatada/Kitayama's office, they would deal with the authors and the publisher Marcel Dekker. The cooperation between Hatada, Kitayama and myself worked extremely well and the book was published in 1997.

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## F. The Journal of Macromolecular Science, Chemistry

It was in the spring of 1965 that I attended for the first time the West Coast Gordon Research Conference in Santa Barbara. That year Fred Bailey was the Chairman and had asked me to deliver a talk on my developing work on the polymerization of chloral.

One afternoon some of us were strolling on the beach. I met one of the conferees, George Ham who said: "I would like to talk with you".. I had known George from the famous Brooklyn Poly Saturday morning seminars. I remembered him giving one of the Seminars. I also knew him from his position at the J.T. Baker Company, where he was Research Manager or Research Director. He had actually been talking with me about a possible interest in a supervisory position at J.T. Baker. We had found out that it was not suitable for me.

Now back to the Gordon Conference and the beach in Santa Barbara. George told me he had been appointed by Marcel Dekker as the Editor of the newly established Journal of Macromolecular Science. He asked me to join the Editorial Board and possibly act as the Assistant Editor. As a young 33 year old, Marcel Dekker the oldest son of Maurits Dekker, had founded Marcel Dekker Inc. in 1963.

I told Ham that I would like to think it over. After awhile I decided to accept the position on the Editorial Board, but not that of an Assistant Editor. I believed it too risky to show another commitment to my employer DuPont at that time. I still functioned as an Assistant Editor without the official title. For about 5 years I handled the refereeing of about one third of the papers that were submitted to the Journal.

I still remember vividly a number of papers that were submitted to the Journal in the late 60's. It had to do with the solubility of noble gases in solutions. With the help of Professor Nemeth we brought the manuscripts into a publishable form.

During this period I also organized my first Symposium at an ACS meeting, the Winter ACS meeting held in Phoenix, AZ on January 20 1966. The Symposium was called *Symposium on Polymerization of Aldehydes and Structure of Polyaldehydes*. The contents of the Symposium were published in the Journal of Macromolecular Science/ Chemistry Volume A1, Nr. 2 (1967) under "Aldehyde Polymerization" and were also produced as a hard copy.

We are now at the 36th Volume of publication of the Journal of Macromolecular Science. George Ham had early recognized the importance of having an occasional "Special Issue" in the Journal devoted to a current subject. He and subsequent Editors have continued this custom with considerable success.

In 1972 I published an edited book with Marcel Dekker Inc. entitled "Polymerization of Heterocyclics" with Junji Furukawa as the co-editor it was based on a Symposium held

during the IUPAC meeting in Boston. Sandy Beberman designed the cover.

My appointment at the University of Massachusetts required more time and attention at the University. I still served on the Editorial Board of the Journal of Macromolecular Science/Chemistry; saw George every year at the Polymer Gordon Conference in New London or at ACS meetings. The Journal prospered and became the best "money making" Journal of the Dekker organization.

On a personal basis, I became better acquainted with Marcel and his father Maurits Dekker. I still remember the beautiful anniversary celebration of Marcel Dekker Inc. at the Plaza Hotel in New York.

One day in 1980 I received a phone call from Marcel Dekker, in which he reminded me of our long-standing relationship and told me that he had a problem with the Journal of Macromolecular Science/Chemistry. George Ham our Editor, had for several years personal, and professional problems. He now had also some health problems. It appeared that he had to be replaced as Editor. I told Marcel I would find a replacement, I myself was not interested.

I had started at that time as regular consultant for DuPont and was for about three years in regular contact with my old friends at DuPont. By chance, my old friend Karl Frensdorff, a former Editor of "Rubber Technology" was retiring. I asked him if he would be interested taking the as Editorship for the Journal of Macromolecular Science/Chemistry of Marcel Dekker Inc. Marcel called him and they agreed that Frensdorff would take over as Editor as soon as possible.

For seven years Karl was the Editor of the Journal. He completely reorganized the Journal, computerized the day-to-day operation and modernized its operation. During these days we had a few special; issues and the Journal continued to grow. I came to Wilmington 3 to 4 times a year and we coordinated the operation with the Dekker organization. I had then taken the position of holder of the Mark Chair in Brooklyn and

was on a close personal basis with Marcel Dekker, visited them frequently and everything worked well. Karl had developed his operation as Editor excellently and his office was working well. He was very satisfied with his achievements and so was Marcel. Still Karl was ready to retire after 6 years as Editor.

Again Marcel again asked me to identify and find a successor. Karl had found the limitation of his operation was the secretarial help that was available at the price that Dekker was willing to pay.

I now turned to my first post doctoral Associate. Russell Gaudiana He had risen to Director of Chemical Research at Polaroid Corporation. What was most important, he had a wife that had been a technical secretary at Amherst College when Russell was a post doc with me. Knowing that Karl's limitations as Editor were based on his inability to find a personal and dedicated secretary/assistant that he could afford, I decided to propose as the new Editor, husband/wife team that would efficiently take care of the needs of the Journal.

In 1988 Marcel Dekker appointed Russell Gaudiana as the new Editor. He has been in this position ever since, now for 15 years. Lyn Gaudiana, also known under the name of Lyn Roberts, became the Managing Editor. She is responsible for most of the day-by-day operations of the Journal.

Even now, I still keep an eye on the **Journal of Macromolecular Science/Chemistry** as Special Advisor. When Frensdorff became the Editor I became the Senior Advisor (with Kennedy). More recently I became more involved as the Special Advisor. I feel that my decision to have Russell and Lyn Gaudiana appointed was the right one. The day-to-day operation has worked perfectly. Once in a while I have organized a special issue. Some were based on the proceedings of the US-Japan Symposia on Polymer Synthesis, some on Mark Symposia. We also had one issue on the Symposium honoring Bengt Ranby on his 75th birthday.

I have enjoyed working for the Dekker organization for 40 years. Marcel was more or less my generation and we had a good business and personal relationship. My admiration for his father Maurits ultimately resulted in my proposal for a special issue for his 90th birthday that was bound in hard copies. Marcel agreed to be a co-guest editor for this issue.

While I was in Brooklyn I stopped regularly at Dekker's office, Marcel and I had regularly lunches together, and Jane and I went to the Season's parties at the Dekker organization and enjoyed the interaction with all the people that we knew and worked together. We were almost friendlier with the old Maurits and his wife Roe. Jane and I went several times to see old Maurits and his wife Roe for lunch or dinner at his home in Greenwich. Maurits was very European and knew the publishing business of his time extremely well and taught me many fine points in publishing.

As Marcel's interest in the organization faded, the younger generation, Marcel's sons Russell and Andy have taken over. We expect them to lead the organization Marcel Dekker Inc. into the electronic age.

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## G. Polymer News

I mentioned before that professional politics played an important role at the Gordon Research Conference on Polymers. Not only science but also business and personal relationships became more important. Almost all the Editors of important Polymer Journals met at the Gordon Conferences. In the 60's Stretch Winslow, the Editor of Macromolecules and a dominant factor in the Polymer Division was a regular. Many participants of the conference were either from Brooklyn Poly, had done their graduate work at Poly or were associated with Brooklyn Poly and I became closely related to this group. Several Poly faculty members attended the GRC meetings and good friends with Interscience-Wiley people were regulars.

*The Journal Polymer News* (a Gordon and Breech publication) was first published in 1975 with Edmund Immergut (originally from Vienna) as the Editor and Gerald S. Kirshenbaum (Jerry) as the Associate Editor. Both Ed and Jerry were graduates of Brooklyn Poly. After a few years "Ed" went with another publisher and Jerry became Editor and asked me to write an article on Aldehyde Polymerization, which I gladly did. [Otto Vogl, Twenty Years of Aldehyde Polymerization, *Polymer News*, 5(4), 150 (1979)]. Jerry had an interest in my views on this subject because he worked for Celanese and had become the Research Manager for Celcon, the Celanese variety of polyformaldehyde.

In the middle of the 1970's my interest in International Polymer Science intensified. I had started to travel abroad and became interested in the locations where I had become involved. This curiosity started 3 series of subjects that I wrote for *Polymer News* and Jerry gladly published (see references). It served for me as a diary, for Jerry new places of interest and for some of the co-authors a satisfaction of recognition. I traveled to places that were not very well known, attended important conferences that had some scientific giants in Poland, Hungary, East Germany, Romania and Czechoslovakia, but not very widely known abroad, because many could not travel for political or financial reasons. Today they have only financial limitations. I started with a.) Centers of Polymer Research in 1978; b.) Conference reports in 1982 and c.) Personalities in Polymer Science in 1994. It was very important that I wrote these articles where feasible with a "local" scientist who prepared the raw data and checked the accuracy of my writing. For the "Personalities." The individual "personality" checked personally the accuracy of my writing before the manuscript was submitted to the Editor, Jerry Kirshenbaum, for publication.

For special occasions Jerry gave permission to republish selected Conference Reports in *Progress in Polymer Science* and the *Journal of Macromolecular Science- Chemistry*.

*Centers of Polymer Research:* I began these articles with *Polymer Science* in the GDR. I had been there previously I wanted to find out how the scientific polymer field worked in

this East German system. I had to write this article alone since my colleagues in the GDR were reluctant to co-author an article that was to be published in the US. After an extensive article that was supported and co-authored by all the important polymer scientists in the GDR, we obtained a proper account of Polymer science in the GDR.

Next came 2 articles from Poland, Lodz and Kattowice. After Poland came Japan with an article on Kyoto, and later editions on Kyoto University, the Kyoto Institute of Technology, two on Tokyo, the central area and the suburban area and 2 articles about Osaka, the Nagoya area, the South and West of Japan, Hokkaido, Northeastern Japan, the Hokkuriku District, and the Remaining Universities of Japan. Finally, In 2001, Osaka University celebrated its 70th Anniversary. One of the main points was: A Focus of Polymer Science.

Regarding the Scandinavian countries I wrote articles on Polymer Science and Technology in Universities in Sweden, the Royal Institute of Technology: Department of Polymer Technology in Stockholm and Polymer Science in Finland.

I then turned to Europe with 2 articles about: Slovakia: the Polymer Institute of the Slovak Academy of Sciences, Bratislava, the Universities and Research Institutes, and the Polymer Institute of the Slovak Academy of Sciences in Bratislava.

In 1981 I was in China and organized 3 articles for Academy Institutes, in the Southern Part of the People's Republic of China (South of the Yangtze); one article specifically for the: "Shanghai Area".

I wrote 2 articles on Academy Institutes in the Northern Part of the People's Republic of China (North of the Yangtze), one on "Beijing", and one on "Changchun."

We also wrote articles on Polymer Science in the Czech Republic, Institute of Macromolecular Chemistry, Prague, and the: Universities in the Czech Socialist Republic.

We must not forget the article on Polymer Science in Romania, the "Petru Poni" Institute of Macromolecular Chemistry, and Iasi, Romania.

We next moved to Hungary. Three articles described the Institutes of the Hungarian Academy of Science, the Universities in Hungary, and the Industrial Research Institutes and their Factories.

With Natta's shadow in the background I wrote an article on Polymer Science in Milan - ITALY with some of his former coworkers,

In three articles we described Polymer Science in Austria: the Facilities in Styria: Graz and Leoben, the Universities in Vienna and in Linz, Innsbruck and other Research Institutes in Austria including Industry.

In four articles, Polymer Science in Australia was covered: Sydney and Canberra, Brisbane and Queensland, CSIRO and Other Government Institutions, and Universities in Victoria and Southern Australia.

Dang Van Luyen provided us with Polymer Science in Vietnam, and Zvonimir Janovic and others with Polymer Science in Croatia.

*Conference Articles:* The Symposium on "Functional Polymers" was held in China. In Kunming, Yunnan. The proceedings were inaccessible but I was the opening speaker with Professor Kiichi Takemoto of Osaka University, Japan, the second speaker. China had opened 2 years earlier to the West and this was probably one of the first international meetings in China. Everyone, men and women alike wore Mao Jackets with the standard bluish - gray color at that time. One of the young scientists, Mr. Li, was trying to work for me in Amherst. Mr. Li. had found some beige cloth and had had a Mao jacket made of the fabric. When the official picture was taken he was the only "light spot" of the Chinese delegation (we were only 3 foreigners. On my suggestion Takemoto and I decided to write this meeting as an article for Polymer News He (We) wrote a Japanese version for

Kobunshi Kagaku, the official Journal of SPSJ.

Later in the year I attended the US workshop on Photodegradation in Stockholm, Sweden. This was a small meeting and Ranby, the co-chairman and member of the Royal Swedish Academy obtained for the foreign participants tickets for the presentation of that years Nobel Prize and (in a side room) an invitation for the Nobel Ball. Naturally I felt obligated and to show gratitude I wrote an article describing the conference.

1981 and 82 were busy years for me. In 1981 I was the chairman of the Gordon Research Conference on Polymers, and, in 1982, the Co-Chairman of the 34th IUPAC Congress on Macromolecules with 2100 participants in Amherst MA. And in 1983 I left Amherst for Brooklyn.

I continued to write these articles for Polymer News. They became an important record for me. When I now sometimes sit in my easy chair, read and daydream I am amazed what has happened 10 and 20 years ago.

I regularly attended several series of conferences where I was usually a main speaker, an organizer or was active in some other important function. They were known as the Cationic Symposia until the Borovets meeting in 1993. From that year on they were called Ionic Conferences. I had started the U.S.-Japan Seminars on Polymer Synthesis, which were held every 3 years. From 1989 on, the Pacific Polymer Conferences were held every 2 years, we held 2 U.S.-Romanian Seminars on Polymer Science, the Bratislava Conferences, and several conferences in Stockholm and Euro-American Conferences in England were also held during this time period.

I have always used co-authors for these manuscripts, because I wanted to be sure the proceedings were correct, subjective but unbiased. This was enough work, but I did not bother with Sessions and Symposia at ACS meetings to which I was invited.

Here are the accounts of these meetings. In the last few years, selected articles were

republished in Progress in Polymer Science making them available to a broader readership.

Symposium on "Functional Polymers". Kunming. Yunnan (P.R.C) 1981

U.S.-Swedish Workshop on "Photodegradation and Photostabilization of Polymers", Stockholm 1981

IUPAC 6th International Symposium on Cationic Polymerization and Related Processes, Ghent 1983

Second S.R. Romania-U.S.A. Seminar on Polymer Science, Bucharest 1983

Second U.S.-Sweden Workshop on Photochemistry of Polymers, Pasadena CA 1984

Specialty Polymers -Present and Future, - An International Conference Celebrating the 25th Anniversary of the Journal "Polymer" Birmingham, September 18-20, 1984

IUPAC Polymer Chemistry Meeting honoring George Smet's on his retirement, Leuven, Belgium, 1984

Advances in Synthetic Polymer Chemistry: New Polymer Types and New Directions, The Sixth Carl S. Marvel Symposium, Tucson, 1985  
Makromolekular Kolloquium Freiburg, 1985

5th International Congress Aplichem "85 International Chemistry Fair", Incheba, 1985, in Bratislava

US-Japan Symposium. Kyoto, Japan, 1985

Polymer Science: Trends, Opportunities, Promises, and Plaza Hotel, New York, NY, 1985

IUPAC 7th International Symposium on Cationic Polymerization and Related Processes, Jena 1986

Synthesis of Polymers and Polymer Liquid Crystals: A Euchem Conference in Lahti, Finland, 1986

First Polymer Discussions of Dresden in Gaussig: Polymer Blends, 1986

"Macromolecules 86": An International Conference on Functional Polymers and Biopolymers, Oxford 1986

31st International Congress of Pure and Applied Chemistry, Sofia, Bulgaria, 1987

U.S.-Japan Seminar: "Synthesis, Properties and Reactions of Specialty Polymers", Napa Valley, 1987

IUPAC 32nd International Congress on Macromolecules "MACRO 88", Kyoto, Japan 1988

Organic and Polymeric Nonlinear Optical Materials, Virginia Beach 1988

9th International Symposium on Cationic Polymerization and Related Ionic Processes, Strasbourg,

France, 1989

Second Euro-American Conference in Oxford on "Functional Polymers and Copolymers", Oxford 1989

First Pacific Polymer Conference, Lahaina, Maui, 1989

Japan-U.S. Seminar on Polymer Synthesis, Tokyo, 1990

The 33rd IUPAC Congress, Budapest, August 17-22, 1991

IUPAC Conference on New Polymers, Saegusa's retirement, Kyoto, Japan, 1991

10th International Symposium on Cationic Polymerization and Related Processes, Balatonfured 1991

The Second Pacific Polymer Conference, Otsu, Shiga, Japan, 1991

Professor Kratky on his 90th Birthday, 1992

IUPAC Symposium on Ring-Opening Polymerization '92, Warsaw, Poland, July 7-11, 1992

XIth Herman Mark Symposium Advances in Polymer Degradation, Mark Symposium, Vienna 1992

Polymer Science and Technology for the 21st Century, New York, NY 1992

9th Bratislava Conference on Modification of Thermoplastic Polymers, Stara Lesna, 1993

XIth Symposium on Cationic Polymerization and Related Ionic Processes, Borovets, Bulgaria, 1993

Sixth U.S.-Japan Seminar on Macromolecular Design for Advanced Materials, Santa Rosa, Sonoma Valley CA, 1993

Third Pacific Polymer Conference, Gold Coast - Australia, 1993

Croatian Symposium of Chemistry and Macromolecular Chemistry Zagreb 1995

International Symposium on Macromolecular Architecture, Ranby's 75th Birthday, Stockholm 1995

International Symposium on Ionic Polymerization, The First Ionic Symposium, Istanbul, Turkey, 1995

Fourth Pacific Polymer conference Koloa, Hawaii, 1995

Japan-US Seminar: Macromolecular Architecture and Engineering, Sendai, 1996

ICRIS '96: Controlled Organization and Molecular Dynamics of Polymers, Uji, and Kyoto, Japan, 1996

International Symposium on Ionic Polymerization IP'97, Paris 1997

International Symposium on Macromolecular Architecture, Paris 1997

12th Bratislava Conference on Polymers: Modified Polyolefins for Advanced Polymeric Materials, Bratislava 1997

5th Pacific Polymer Conference, Kyongju, Korea, 1997

17th International Herman F. Mark Symposium: Polypropylene - a Material of the Future, Vienna 1998

Sixth Pacific Polymer Conference, PPC-6 Guangzhou, China, 1999

INSTITUTSDAGEN At the Royal Institute of Technology, Stockholm, Sweden, May 3, 2000

POLY MILLENNIAL 2000 HILTON WAIKOLOA VILLAGES, HAWAII December 9-13, 2000

SPSJ 50th Annual Meeting, Osaka, Japan, May 23-25, 2001

Macromolecules in the 21st Century: An International Symposium on Polymer Science and Technology on the occasion Otto Vogl's 75th Birthday, Vienna, Austria 2002

18th Bratislava Meeting on Modified Polymers in Stara Lesna, October 6-9, 2003

**Personalities in Polymer Science:** In the last two sections I explained my interest in the activities and interactions in Polymer Science.

At the end of the 1980's I became interested in the personalities of successful scientists and how they influenced and determined the progress in polymer science and engineering. As many things in life the writing about Personalities in Polymer Science" started accidentally. One day, my friend and former post doc Ioan Negulescu called me and pointed out, that Professor Simionescu would be 70 years old soon. He wished to write an article honoring his birthday and wanted to know if I would be willing to help him and provide guidance for such an article. The article was for the Journal of Macromolecular Science. Ioan and I wrote another article for Simionescu's birthday for the Romanian Polymer Journal.

In 1992-93, shortly after Herman F. Mark died, I had to write several versions of his obituaries including the formal one for the Austrian Academy of Sciences. Then in 1993 a tragedy struck. My friend Tibor Kelen died in an automobile accident and I wrote his life story as an obituary. I found out that these writings could be used not only for obituaries but also to honor the extraordinary personalities during their lifetime.

In quick succession followed personality articles on Tudos, Ranby, Saegusa, Philip and my Austrian friend Janeschitz-Kriegl. The style of writing and the length made further writing interesting and easy.

I reached to the wives of my friends to help me write these articles, and Plash, Schurz, Galli, Corradini, Bamford, Peace and Emits were written.

As a gesture of appreciation I wrote the life stories of all the Presidents of the Society of Polymer Science Japan: Shu Kambara, Iwakura, Furukawa, Tsuruta, Takayanagi, Miya, Imanishi and Higashimura.

I did not forget my other Japanese friends and giants in their fields starting with Murahashi, Horio and Fukui. Further Onogi, Kawai, Tadokoro, Inagaki Okawara, and Yamazaki.

The Chinese "giants" included: Qian Renyuan, Yu Tongying and Feng Xinde, and He Binglin.

I have included a substantial number of European Personalities in Polymer Science: Bengt Ranby, Karl Kratzl, Burghard Philip, Dieter Freitag, Sir Geoffrey Allan, Ian Ward, Peter Plesch, Otto Kratky, Marian Kryszewski, Zbigniew Jedlinski, Milan Lazar, J. Johan Lindberg, Henri Benoit, Ephraim Katchalski-Katzir, Oskar Friedrich Olaj, Dietrich Braun. Pierre Sigwalt, and Bahattin M. Baysal.

In addition to the life of the ACS President Eli M. Pearce I also wrote the life stories of my American friends Richard S. Stein, Burton Carl Anderson, and Vivian Stannett.

After an extensive article that was supported and co-authored by all the important polymer scientists in the GDR, we obtained a proper account of Polymer science in the GDR.

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## H. Progress in Polymer Science

One day in 1985 I received a phone call from my friend Vivian Stannett. He asked if I **would** be interested in the Editorship of the Journal "Progress in Polymer Science." My immediate response was: NO. Still I was intrigued by the possibility -- and asked what it involved and what I would have to do. The answer was nothing -- "it runs by itself". I was suspicious and asked to have some time to think about it.

On investigating in detail that the Journal, "Progress in Polymer Science" (PPS), I found that PPS was published by Pergamon Press in Oxford, UK as an International Review Journal. In 1985, PPS was publishing Volume 11; the Editors were Vivian Stannett and Aubrey Jenkins. The frequency of publication had slowed and the Editors were preparing to publish a double issue 1/2 of 161 pages to fulfill the obligation for the subscribers: 4 issues per volume. I found out the reality of this mysterious publication strategy. No further publication was planned because no manuscripts were on hand. In other words, the Journal had collapsed and had ceased to exist.

I felt I had two options: a.) To start a new Journal, or b.) To revamp the Journal entirely. This required that I distanced myself completely from the past style of operation and let it be known that we were entering a new period for PPS. While I was still contemplating how to handle the situation, I received a phone call from Amin Mayur of Pergamon Press who was responsible for PPS. He offered me officially the position of Editor of PPS. I discussed with him the options above and he begged me to revamp and save the Journal. The reason for this was that Pergamon did not wish to go through the process of closing one review Journal and opening a new one. Pergamon was prepared to accept my suggestions, which I thought, were necessary to resuscitate the Journal.

For Pergamon it was also practical. I had established myself in Brooklyn; I was traveling extensively traveling both to the Orient and to Europe, especially Eastern Europe. I was in the midst of putting the Pacific Polymer Federation together and I had major industrial

consulting responsibilities. This had an enormous advantage. I knew many people, not only the senior scientists, but also the younger generation, especially in Japan.

I told Mayur that I would be ready for the first Volume of my Journal, Number 13 by 1988.

I had to set up the operation of the Journal and appoint an Associate Editor, and Editorial Board and various policies.

I selected L. Stephen Corley as my first Associate Editor. When Steve was part of my research group, he was responsible for "publications." My subsequent "publication managers" were Gary D. Jaycox, Liping Hu and Andres Sustic. I need to explain this position. As my research grew rapidly in the mid 70's, I identified certain responsibilities and assigned a student for this responsibility. The situation was similar to a cabinet position in government. The publication manager was particularly important because we were publishing 20-25 papers per year. This person needed to keep track of each paper; from the time it was finalized and submitted for publication until the paper was printed.

I should point out that this was before computers and everything had to be done by hand and typewriter. At the time I took the job with Pergamon we still sent the manuscript for final typing to Elizabeth Cary in Wisconsin, who had worked for Dekker Inc. for their "book finalizations". Corley turned out to be an ideal Associate Editor, conscientious, dedicated and reliable both in terms of accuracy in editing and also in following deadlines.

I also invited Jane C. Vogl (Mrs. O. Vogl) of the ACS Division of Polymer Chemistry to become my Assistant Editor. She was the Business Office Manager, and knew many scientists, old and young from all over the world. She did not have an official position in the beginning but assisted with considerable skill in setting up the Journal. When I did not have time to go to see Steve in Houston, she would go and oversee the operation in Houston.

The next item that had to be addressed immediately was the composition of the Editorial

Board. In the initial stage, while Progress in Polymer Science was published by Pergamon, I wrote the invitation letters and also the termination letters. When Elsevier took over we found it convenient to change this policy and the publishing Editor wrote these letters based on my recommendations. The termination letters became especially difficult because they touched on personal feelings, which we concluded, should be avoided.

Over the years we changed the Editorial Board Members as is customary with most Journals. The most devoted and cooperative members remained for a longer time on the Editorial Board. Officially we considered a 2-year period for membership on the Board as the minimum, but we have kept the most devoted members for 18 years.

M. Auer (Finland), R. Epton (United Kingdom), K. Hatada (Japan), S. Inoue (Japan), Z. Janovic (Croatia), G. Kossmehl (Germany), J.E. McGrath (USA), J. Moacanin (USA), L. Monnerie (France), St. Penczek (Poland), B. Philipp (Germany), P. Pino (Italy), M. Raetzsch (Germany), A. Romanov (Czechoslovakia), J. C. Salamone (USA), K. Takemoto (Japan), F. Tudos (Hungary), M. Wismer (USA), T.Y. Yu (China).

In the beginning I relied a great deal on Koichi Hatada. He and his Assistant Professor Kitayama helped me design the new cover page for the Journal, which had to be ready for the first issue of 1988. It represented in two-dimensional form a helical structure with connecting P's representing "polymer" or Progress in Polymer Science. The symbol was orange on blue background with white print.

A major policy decision for PPS was to publish articles by invitation. This did not mean that it was by invitation only. We were very open to "uninvited papers", but they were usually carefully refereed and few were actually published. Article solicitation was a difficult task but I also gave the editorial team and me the opportunity to select subjects, which we thought timely, novel, and of interest to the readership.

In the beginning we liked senior scientists as authors for our review articles: those whom

I knew well and I could persuade to write articles. We also requested that each article be at least 50 pages long, **not including** figures and references. This prevented the contributors from reviewing only a collection of a few of papers in their subject of competence. We were determined to present reviews of the entire subjects, with all the ramifications and interrelationships. By and large this policy was successful and the review articles published by PPS became key references of the subjects - and the authors the authorities on the subjects.

We were aiming for scientists, about 40-45 year of age as our primary authors. They had achieved their scientific maturity and competence. Our invitations were particularly important for our young authors from Europe and from Japan. By inviting young scientists in Japan, we have helped a number of them to be promoted and reach full professorship.

We liked to target young Japanese professors who were very anxious to write review articles for our Journal. They suggested subjects of novelty and interest in their field of expertise. Most came from the second and third generation of scientific academicians who had spent some time abroad and had improved their competence in English. For some it was very difficult to think and write in English and the Associate Editor devoted much of his time helping the authors on expressions and grammar.

Initially we published 4 issues per volume per year. I had to twist the arms of a number of my friends and authors to provide the articles on time. What we had to do was far from the promises that had been made when I accepted the Editorship of the Journal PPS.

**It must be remembered that the time from the solicitation of the paper to the time of its receipt often took 2 to 2 1/2 years.** By the fall of 1986 Jane and I were ready to visit Pergamon Press in Oxford located in Maxwell House. Mayur Amin welcomed us warmly and showed us around. The new publishing director Peter Shepherd, the Managing Director, had just arrived. He sat in his new office surrounded by numerous stacks of books, completely helpless there was no furniture in the room -- we all had to laugh.

We worked well with the two colleagues at Pergamon. Reestablishing the Journal not easy. Money to support our efforts had to be found from other Pergamon budgets. The number of subscriptions for the Journal had substantially diminished, and had to be built up again!

I should point out again that this was still the time before computers were in everyday use and typewriters were common equipment in an office. Overseas telephone calls were extremely expensive and could only be used in emergencies. There was no e-mail. I do not know how we did it but it worked and by the first of January 1988 the first issue of Number 13 was distributed to the old subscribers.

The trivial day-by-day operations were handled by Jane with my secretary in Brooklyn. We could not afford a separate secretary and Pergamon would not provide me with more than the absolutely essential amount money. We loved our job AND PERGAMON KNEW IT. I had as my objective to take the Journal to the top in my lifetime. When we began, it was not even ranked.

As papers arrived in 1987 and 1988 we decided expand from the 4 issues per year in 1988 to 6 issues in 1989. We could indeed handle it because we had 833 pages in 1988 and 997 in 1989. Journal publishers do not like to have 4,8, or 10 issues, they prefer 6 (bimonthly) or 12 issues (monthly).

The way it worked was as follows: Members of the Editorial Board or friends and I would identify potential authors, Jane would write the personal letter of invitation and I signed them personally. We would receive either a **yes** answer or a **no** answer; the most common case was when the invitee did not bother answering at all. Those were the contacts that had to be "followed up." This process received our continued attention. About 40% of these people ultimately provided a manuscript, sometimes in 2 years!! About 25% of the answers were positive.

We were now ready for the contract. As in book publications, Pergamon issued a formal

contract to the author. This process, trivial as it was, was a source of continued irritation. The publisher used inefficient secretarial assistance; the secretaries **were frequently replaced**. Every time a change occurred, the next person was not trained by the publisher and we as editors had to help them - on our time - in handling the Journal correctly.

In the beginning of our activities as an editorial team, it was fairly simple because the number of papers and pages produced were relatively few. As the Journal increased in size and scope, closer and closer attention had to be paid to **the** details.

We did not keep records of the details of our proceedings and Pergamon did not keep them either. Such records would have documented the "struggle" in these early years. Steve Corley received the manuscripts, **checked them over** for the proper format, corrected them and if necessary had them refereed. It should be remembered that I had made the decision to invite the authors **and this** meant **that** they were already selected. My decision to invite an author to write and submit **a** review article in PPS was the key for the selection process. If a serious problem arose, I also checked the manuscript. The manuscript was then brought into the proper format for publication in Progress in Polymer Science by the Associate Editor.

Steve had the authority to send **the approved manuscripts** to Pergamon. Steve and I were continuously in contact **if** there were any questions. In the beginning it was a question of providing Pergamon with publishable papers as soon as possible. This was not too difficult because in the beginning we relied on well-known friends as the contributors and there was no question of the quality and even the style of the manuscripts. Since PPS was a British Journal, at Pergamon, the manuscripts were translated into **the "British version" of** English and the **standard** PPS format

As time went on there was a question of the style and subject for publication. I always wanted papers of different subjects in one issue. Our Editorial Board Member, Manfred Raetzsch had stated it very clearly. I like to have one article in one issue that I like to read from cover to cover. On one of Jane's visits to Corley in Houston, she found that Steve

had compiled the manuscripts in piles according the subject matter and he waited for the last manuscripts of some of the areas before putting an issue together. Of course we diplomatically (which was not easy) talked Steve out of this modified policy and the flood of publishable papers was not interrupted any longer.

After 1991 we finally formalized what had existed since the beginning of our Journal. We made Jane C Vogl officially the Assistant editor and her name was displayed prominently on the front cover.

In 1991 Michael Mabe replaced Amin Mayur. Michael was and is a very pleasant person and **was** also easy to work with. He was a graduate of Oxford University and knew all the ins and outs of the town and of publishing. By now Progress in Polymer Science was composed of 22 papers a year **spanning** 1100 **printed** pages. Our publication strategy was working well. We had lengthy and well-written articles with timely subjects. The operation of the publication of PPS on the whole had increased significantly. The. Computer age had also reached us and we worked from an Apple II E computer. This made life much easier and we only had to change the name and address of the recipient of the letter and could write the standard letters individually with my personal signature. I always believed and still do that a personal or a personalized letter has to be signed by **its** writer.

Every 2 years I would contact about 120 scientists; the positive response would be about 25%. Then necessary information on the manuscript and the proceedings of the publication in PPS was forwarded to the author by Pergamon Press' Editorial Manager Michael Mabe. Mabe's Assistant would "**log**" the information **into** the Pergamon system with the request to have a contract prepared. Among the many details it said that the author would receive \$ 12.50 per printed page and 50 reprints. This was **then** sent to the author for his signature. Do not ask me how often Jill Hewlett and later Anne Smith who handled this part of the operation complained that the authors did not bother returning the signed contract to Pergamon and very rarely on time. The actual contract was **actually** prepared by another department **at** Pergamon.

For Jane and me, the "NO" answers were **not a** problem, but what about those colleagues who did not answer, or answer in a reasonable time? This was when **our** telephone was activated. The overseas calls were at a tolerable rate and we could afford to contact the people by phone. **In this way**, I could perhaps squeeze another 15-20% of positive answers from the initially contacted people.

Now came the next hurdle: The delivery of the manuscripts: **Most scientists have far more to do than just** writing papers.. This was another reason why we did not rely on the "big guns". To have a paper written by important people was and is difficult. On the other hand, the old principle of "getting things done" is also true for writing review papers. "Go to the busiest person and you will have whatever you need done in time". They have the knowledge, the experience, and they have been there and they know they might need a similar favor from you!!!

In the contract it stated that the manuscript was to be delivered to L.S. Corley within 9 months of signing. Few authors complied as expected. That meant that I had to do the convincing, twisting arms and even some mild begging. We needed **about** 4 papers per month per issue. 1992 came along and the page numbers had increased by another 10%. I was consulting with Shell on their ethylene/CO alternating copolymer. **This** had not been arranged by Corley but by Eric George.

**It was at this time that** Steve Corley told me he would like to retire from the responsibilities of Associate Editor. He liked the job but he was going to be married and **he felt that** his responsibilities were shifting. After a short search I contacted Gary D. Jaycox and asked if he would be interested in this position. He was delighted and accepted. Gary was the successor of Corley as my publication manager at the University of Massachusetts in the early 80's. He had **just finished a two-year post-doctoral position** at Columbia University and had started to work for DuPont. With the consent of DuPont, I had Gary appointed to Associate Editor of Progress of Polymer Science. He shared the position with Steve for the year 1993.

In 1994 Elsevier bought Pergamon Press and we found ourselves with a new owner. The relationship still worked well, Michael Mabe was still our contact man - now at Elsevier. But it was **also** clear that new personnel would be brought in from Amsterdam, the home base of Elsevier. There were other changes **to come** as well; some of them were beneficial.

I met Michael Mabe in 1996 in Akron at the IUPAC Symposium on Macromolecules. He introduced me to Henri van Dorssen, who soon took over Michael's position. Henri was Dutch and lived with his English wife and two children in Oxford. I **initially** had great reluctance **for this** major change. **Fortunately, in** this case our new association with Henri van Dorssen turned quickly into a close relationship **concerning** the Journal -- **and** personally as well. The next 5 years were the most productive and rewarding period during my stewardship of PPS.

Henri and I decided on a new cover design for Progress in Polymer Science. We went from 6 to 8 issues per year and even guided the Journal to 10 issues per year in 1999 with a change into the European Format in 1998. The same year I assumed the position of Editor-in-Chief and Gary Jaycox became Technical Editor.

Henri and I became good friends and he always stayed in our home whenever he came Massachusetts. We had our jokes about soccer in Holland and Italy and exchanged news of our families

The same year, in 1998, Elsevier had decided to change to a larger format for the Journal, which gave it an increased page size, an increase of about 25%. At the same time, the **print style** of the Journal was also altered. The cover page remained the same, and the paper quality also remained the same. For years I had pressured Pergamon to use a better quality **of** paper for the Journal without success. Years later, with Elsevier, we went to art quality papers within 2 years. I was surprised and happy at the turn of events. Outside influences probably forced this decision at Elsevier. At the same time the price of the annual subscription went up from 0.50 \$ per page to **1.11** \$/page. At the

same time, the remuneration for the Editors did not change.

When I was still at DuPont I was selected to attend a 2-week technical writing course. It was held at DuPont and attended by middle management personnel. The instructor was Robert S. Burger. Burger had been an essayist for the St. Louis Post. He gave his course in a number of major companies and colleges. It was called the "Burger Course on Effective Writing". Later Bob Burger published a book entitled *How to Write - So People can understand you*. When in Brooklyn, I bought for each student a copy before he started to write his thesis.

The Burger book describes among other things - focusing. He emphasized that first sentence in a paragraph should be the most important sentence. The key paragraph at the beginning of the chapter should be most important, as should be the key word at the beginning of the sentence at the beginning of the paragraph. Of course this is not always practical or desirable.

Gary Jaycox has extended this principle to the construction of the Volume and Issues of PPS. Editorials should begin the first issue of the new Volume with accomplishments and next year's objectives first issue of the Journal. Gary was an excellent writer and wrote the Editorials with little help from me, except for policies. The first issue was a "heavy" issue and consisted of what we judged to be the best and most important paper that we had on hand. Another reason for favoring the first issue of the new Volume was, that a few extra copies of issue #1 were printed by Elsevier for publicity purposes . . .

From 1992 on, the publishers became very aware of **the Journal's** ranking and paid attention to **a** new system that had been developed: the impact factor index. It is fundamentally based on how many quotations are **given to** papers that are published in the last two years. As an example: The number of citations of articles **in** Progress in Polymer Science in 2002 **was** based on articles published in 2000 and 2001.

The Journal flourished under our joint leadership of Henri van Dorssen at Elsevier in

Oxford and the Editorial team, in Amherst. Henri and I met regularly, in Kyongju, Korea in 1997, in Guangzhou, China in 1999 and in the US, a number of times. Jane was very much involved in the operation of the Journal in Amherst. She and I went to Oxford for the celebration of the Elsevier Journal "Polymer" honoring Ian Ward and Ron Eby for their retirement as Editors. We had regular meetings of the Editorial Board of Progress in Polymer Science whenever it was possible and feasible. The Journal was progressing and in full swing.

In 1998, when I reached the age of 71, I proposed a retirement scheme covering a 4-year period to Henri. He agreed, but suggested being careful and to be sure that I had everything in writing. In my final contract I was to retire as Editor-in-Chief at the end of 2002 and on Henri Van Dorssen's advice I would then become the Honorary Editor-in-Chief for Life, a position that I accepted.

In my proposal of a transition period I recommended that Robert R. Matheson and Krystof Matyjaszewski be appointed as Editors in 1998 and ultimately take over as the Editors of PPS in 2003. The fundamental idea was that during the first two years they would learn how the Journal functioned. The practical aspect was that I would continue for the next two years **with** the solicitation of manuscripts and the follow up correspondence. The two new editors would start to contribute lists of potential contributors by the end of their first two-year period. This scheme almost succeeded. Kris Matyjaszewski started the first serious solicitation campaign in May 2000 and the papers began to arrive in the middle of 2001. Until the end of 2002, 90% of the papers that were submitted had been commissioned by Gary and me.

By the middle of 2001 Gary Jaycox expressed his intention to me that he wished to retire as Technical Editor of the Journal. My 4 year retirement scheme was about to end we decided that the editorial office should be moved to the Carnegie-Mellon University. Guy Berry, a colleague of Matyjaszewski at Carnegie-Mellon, was delighted to take over the entire responsibilities for processing the incoming manuscripts for publication. Berry began as Editor and is now Co-Editor-in-Chief of Progress in Polymer Science.

At the time I was ready to hand over my responsibilities as Editor-in-Chief to my successors, a significant change took place at Elsevier. Henri van Dorssen, the partner in our success with PPS, was given other responsibilities within Elsevier and was replaced by Rumen Duhlev. Rumen, of Bulgarian birth and up bringing, had a Ph.D. in inorganic chemistry and was a competent scientist. He is an enthusiastic Opera fan and an avid traveler. We have cooperated well during the 3 years since 2000, when Rumen took over.

During the Symposium "Macromolecules in the 21st Century" in Vienna, I held my last Editorial Board meeting on October 8, 2003. Jane and I handed over our responsibilities to Ruman Duhlev, the Senior Publication Editor of Elsevier Science Ltd, and to Kris Matyjaszewski the new senior Editor after 17 years at the helm of Progress in Polymer Science.

A new challenge came about when rankings of Journals became quantitatively handled: The Impact factor, newly introduced in 1992, became an important factor in describing the success of a Journal. Universities, and other organizations declared that if the scientist were to publish in one of the "desired" Journals, he would have a better chance of promotion or advancement. The subject and the actual invention became unimportant, as long as a "highly regarded" Journal, like Science or the Journal of the American Chemical Society provided the stamp of approval.

Initially about 40 Journals were ranked in the Polymer Science category. The number of Journals increased steadily over the next 10 years and 76 Journals were ranked in 2003.

To our surprise, the Journal Progress of Polymer Science that started from no ranking in 1986 but had a ranking of # 3 in the category of Polymer Journals in 1993. We could not understand it but **we** were happy. We had a ranking of 2.00 as compared to 2.86 of our next higher-ranking competitor "Macromolecules". In 1999, we had surpassed Macromolecules by 3,62 to 3.54. Our battle for the top position continued and we still

remained ahead.

But was it fair to say that we were ahead of Macromolecules? Macromolecules has many more papers and the quotation of papers in Macromolecules by other author publishing in Macromolecules is also somewhat of a "clubman ship." It still is fair and correct. On the other hand Progress in Polymer Science is a review Journal and review articles are preferentially quoted.

At the end I would like to present briefly the progress that we have achieved in the 17 Years, 1985-2002, that I was the Editor of PPS and responsible for the publication of Progress in Polymer Science. I have divided our progress story into a few categories a.) Number of papers and pages, b.) Price of annual subscriptions, c.) Number of issues per year, d.) Price per page, e.) Ranking and Impact factor

*Number of papers and pages:* For Volume 13 (1988), 7 papers in 401 pages, Volume 14 (1989) 16 papers in 833 pages, Volume 15 (1990) 22 papers in 997 pages, Volume 16 (1991), 22 papers in 1074 pages, Volume 17(1992), 23 papers in 1205 pages. For the next Volume (18) the same cover-page was retained but the new format was larger by 25% Volume 18(1993), 27 papers in 1195 pages, Volume 19(1994), 34 papers in 1152 pages, Volume 20(1995), 34 papers in 1199 pages.

For the next volume, Volume (21) we kept the same format, but with a new cover design: Volume 21(1996), 25 papers in 1233 pages, Volume 22(1997), 34 papers in 1720 pages.

For Volume 23 the format changed to a more European format which meant that the pages were 16 % larger: Volume 23(1998), 37 papers in 1553 pages, Volume 24(1999), 38 papers in 1528 pages, Volume 25(2000), 33 papers in 1555 pages, Volume 26(2001), 42 papers in 2156 pages, and Volume 27(2002), 45 papers in 2382 pages.

For Volume 28(2003), the first year of the new Editorship the same format and cover design were maintained but double column was introduced. Progress of Polymer Science

in 2003 published 1754 pages with 40 papers.

Now a few more interesting statistics regarding the price of the annual subscriptions of PPS: The annual subscription price for Progress in Polymer Science when I took over for Volume 11(1985) and 12(?) was \$ 110, also for Volume 13 (1988).

The price of the annual subscription of Volume 14 (1989) was \$ 294, for 15 (1990), \$ 372. For these years the pricing was based in DM. Currency fluctuation caused uncertainties in pricing abroad. Volume 16 and 17 were priced in Pound Sterling, but I have recalculated it into \$. Volume 16 (1991) was \$ 458 and Volume 17(1992) \$ 515. After the take-over by Elsevier the initial official currency of the annual subscription rate for Progress in Polymer Science was in Dutch Guilders. From Volume 15(1990) to Volume 21(1996) the quotes were for prepayment.

With Volume 18(1993) a new Journal size was introduced, the cover design remained the same but a new format, larger by 25% area was introduced and the subscription rate rose to \$ 600. The rate for Volume 19(1994) was \$ 649, for Volume 20(1995) \$ 788.

With Volume 21(1996) a new cover design was introduced with the same size and the subscription rate increased to \$ 1127. For 22(1997) it remained the same at \$ 1127.

Volume 23(1998) brought a new format change to bring the size and better relationship to the European format and the format of other Elsevier publications. This is the format and size of Progress in Polymer Science as it is today. The subscription rate was \$ 1396. The subscription rate per Volume of Progress in Polymer Science for Volume 24(1999) was \$ 1630, for Volume 25(2000) \$ 1752, for Volume 26(2001) \$ 1992, and for Volume 27 (2002) \$ 1992.

For 2003 with a new editorial team and 12 issues per year the subscription rate for Volume 28(2003) is \$ 2290.

*Number of issues:* Progress of Polymer Science was produced for Volume 13(1988) in 4 issues, from Volume 14(1989 to 21(1996) in 6 issues, Volumes 22(1997) and 23(1998) in 8 issues and 24(1999) to 27(2002) in 10 issues. Beginning in 2003 with Volume 28, the Journal is **now** being published in 12 issues. Monthly publications demonstrate the regularity of any Journal publications and are very important for most publishers.

A very significant and important characteristic in publishing is the price that the publisher charges per page. It probably shows more than anything else the profitability that the publisher demands for their publication. It also is a danger signal when the price per page increases rapidly. For these problems the Editors are never consulted. The publisher never tells the Editor, at least at Elsevier, about their business objectives **s** and attained profitability.

*Price per page:* 30 year's ago I was involved in **the** pricing of publications. The ACS Division of the Polymer Chemistry produced the so-called Polymer Preprints. **During my** years as the Treasurer of the ACS Polymer Division I had to keep a close watch on how much the Editor was spending. Our goal was to keep the price per page to about 0.38-0.40 c/page.

I also checked the same procedure for Progress of Polymer Science Volume 13 (1988) cost 0.58 c/page, Volume 14 (1989), 0.35 c/page, Volume 15 (1990), 0.37 c/page, Volume 16(1991), 0.42 c/page, Volume 17(1992), 0.43 c/page, and Volume 18(1993), 0.50 c/page.

Elsevier took over with Volume 19(1994) and the price per page started slowly and steadily to climb and the price per page was 0.56 c/page, for Volume 20(1995), 0.66 c/page, Volume 21(1996), 0.91 c/page, and Volume 22(1997), 0.66 c/page.

With the new European format and a significant improvement of the paper and printing quality we saw a sharp increase in the annual page cost. For Volume 23(1998) it was 0.90 c/page, for Volume 24(1999), \$ 1.07/page, for Volume 25(2000), \$ 1.11/page, for

Volume 26(2001), 0.92 c/page, for Volume 27(2002), 0.84 c/page and for the new Volume 28(2003), with a double column it will be \$ 1.30 per page because of the sharp decrease of the number of pages produced by the new team.

*Ranking and Impact factor:* For three years we had been declaring to the world correctly that we were the number one of Polymer Journals published on a regular basis. We had been a few points, even 0.001 points ahead of Macromolecules for three years.

The decisive breakthrough came just last year. Our impact factor rose to 7.27 over Macromolecules of 3.73, a doubling of the index rating in one year.

The impact factor that is published in 2003 reports the number of individual citations in the Journal in 2002. The citation recorded in 2002 considers only articles published in the years of 2000 and 2001 in the Journal.

Complicated - perhaps, but if a Journal attains a dominant position, like the first place in the ranking of the Journal among 76 Polymer Journals, it is time to enjoy this accomplishments. How long it will last is the problem of my successors.

*The new Editorial Board:* The most recent Editorial Board (until the end of 2002) is shown below. The initial number of characters per page in 1988 increased from about 3300 to 4300 per page in 2002, an increase of 30%. The cold war had ended and the consideration and requirements for board members had changed.

A.C. Albertsson (Sweden), D. Freitag (Germany), S.K. Fu (China), G. A. George (Australia), N. Hadjichristidis (Greece), K. Hatada (Japan), G.D. Jaycox (USA), T. Kitayama (Japan), S.C. Kim (Korea), G.S. Kirshenbaum (USA), S. Kobayashi (Japan), B. Lotz (France), R.R. Matheson (USA), L. Matisova-Rychla (Slovak Republic), O. Nuyken (Germany), St. Penczek (Poland), V. Percec (USA), J.C. Salamone (USA), D.A. Tirrell (USA), J.P. Vairon (France), F.S. Wang (China), Y. Yagci (Turkey), B. Yamada (Japan).

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## VII. Teaching

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  - [E. At the Université Louis Pasteur in Strasbourg, France](#)
  - [F. In Japan](#)
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Teaching on the Elementary, Middle, High School and College levels provides the student with the basic and increasingly sophisticated skills. At the graduate level the reliance of the student directly on the teacher becomes less important because the teacher has become the advisor rather than the classroom lecturer. In the sciences, it is essential that the student increasingly forms his own ideas and becomes independent with the guidance of the advisor.

I have described my own experience as a student in Chapter I. I also mentioned in Chapter II some of my experiences as an Instructor at the University of Vienna. For over 50 years I have taught: as an Instructor at the University of Vienna, as Professor at the University of Massachusetts, as Herman F. Mark Professor at Polytechnic in Brooklyn and in various Universities around the world. If teaching is communication of knowledge, I will also point at the hundreds of lectures I gave here and around the world over the last 40 years. I will try to mention those experiences that I think are relevant to understand my career.

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### A. As Instructor in Vienna

My Ph.D. thesis with Galinovsky as advisor. I was the first of a new generation of graduate students and was anxious to obtain a position as an Instructor at the

University. I was convinced that if an opening of an Instructor position became available, I had a good chance of obtaining it. No appointments were made until a new Director of the Institute was appointed. This interregnum lasted from May 1946 to the fall of 1948. Finally Professor Friedrich Wessely became the new Director. He had new ideas much different from Spaeth's. He tried to modernize organic chemistry at the University but could never reach Spaeth's competence, authority and personality.

Wessely came to see me in July of 1948. There were two openings as Instructors in the II. Chemical Institute, one in Galinovsky's laboratory of inorganic quantitative analysis and one in the organic chemistry laboratory. The appointments were made for the beginning of the Fall Semester, on October 1, 1948. Wessely immediately took Tuppy (previously with Spaeth and Galinovsky as thesis advisors), and appointed him to the organic chemistry laboratory as Instructor. He also assigned him to work in his own expanding research group.

The Laboratory of Inorganic Quantitative Analysis: of quantitative analysis had three Instructor positions. It was controlled by Galinovsky and he had the primary choice for the selection of the candidate, if an opening for a new Instructor occurred. When one opening became available, Galinovsky proposed me for the position and Wessely accepted it.

Instructors at the University were required to have a PhD degree, but Galinovsky bent the rules a little bit and I ended up as an Instructor at the age 20 years and in the second year of my dissertation. I admired Galinovsky for this coup, was grateful and devoted to him ever after.

The Instructor position was a non-tenure track position, and the appointment was for two years, not too different from the Assistant Professor positions in this country. It could be renewed two or three times. The position could not be permanent without having a doctoral degree.

What did teaching as an Instructor mean with Galinovsky's guidance? He had the 3 Instructors; they had to supervise a laboratory of 56 students. The students had to be supervised and tutored to perform about 40 experiments planned for one semester. The laboratory was open from 8-6 and the students could come and go as they wished.

The "successful" students worked from morning to evening, barely taking time to go to a lecture. In principle, as I did, the student could finish this laboratory assignment in one semester. Most students took two. Each of the tests, had to be approved by the Instructor and stamped as "accepted" When I joined the team of Instructor as junior Instructor, we had also two Senior Instructors, Goldberger and Kainz.

The real exams were given by Galinovsky for his laboratory. Other laboratories also had "directors", like the laboratories of qualitative analysis and the Organic chemistry laboratory. Teaching as an Instructor was time consuming both technically and psychologically. The students after the war were a peculiar mix. Some were the "normal" students and started their University studies at the age of 18 after receiving their high school degrees. Many students had been in the war and had returned after years of hardship or having been POW's for several years. This was very complicated for me as I was several years younger than some of the returnees.

I still remember individual students. Gerhard Holzer was 28 years old when he started as a freshman. He had been in the war and a POW for years before coming back to study at the University. Another student was the daughter of a famous German language Professor of our University and had been a good friend of Spaeth, and many others. Goldberger, Kainz, and I took everything one day at the time.

To be allowed to start the laboratory course, each student had to take an oral exam with Galinovsky. Only Docents could give "accepted" examinations. That meant you

had to be a docent to be allowed to lecture and give official exams. We could only give minor examinations and laboratory quizzes. Every examination was conducted orally.

To complete the lab of quantitative analysis required the gravimetric analysis of individual inorganic ions, of two minerals and one alloy (with a tricky separation, such as antimony/ tin). For the minerals the analyses usually required the quantitative separation of potassium/ sodium or calcium/magnesium. If the student was very recalcitrant he obtained a silicate, which required a special fusion reaction before the actual analysis.

Two years after Wessely had become the director of the Institute, Galinovsky (including me) was reassigned to the laboratory of inorganic qualitative analysis. The laboratory course of qualitative analysis was actually the first course in the sequence of laboratory courses, if one wanted to study Chemistry at the University of Vienna. Goldberger had left his University position to join an industrial company. Kainz, with his interests in analytical chemistry had joined the newly appointed Associate Professor of Analytical Chemistry, Hecht, as his right hand man.

I should mention the structure of the two Chemical Institutes. The I. Chemical Institute had as its Director the Professor of Physical Chemistry and an Associate Professor of Inorganic Chemistry. The II. Chemical Institute had as its Director the Professor of Organic Chemistry with an Associate Professor of Analytical Chemistry.

In our new assignment, now on the first floor of the Institute, I worked with Eiter, who was a lecturer. He had already achieved his promotion to docent or lecturers and was independent from Galinovsky. Another Instructor had been appointed for the laboratory of Inorganic qualitative analysis, Heribert Michl. The three of us became an effective team. Oddly enough, Karl Eiter always wore leather Knickerbockers pants and Michl was always overweight.

Galinovsky still gave all the beginners' exams and the final exams for each of the 56 students. The exams were oral. To my knowledge there was never any question of the fairness of these exams. Some people failed (as in the quantitative laboratory) they came back until they passed. Three attempts were allowed. In my judgment a good system, but it required a skilled examiner.

In the qualitative laboratory, in 1950, the students were more "regular" type students. The returnees from the war had progressed to the more advanced laboratories. Pharmacy students also had to take the laboratory course of qualitative inorganic analysis. They produced a different clientele for the lab, because many pharmacy students were women.

For the three of us it was exciting to see young people enter their first semester of University study and follow their progress. I mentioned in chapter II one of the problems we encountered, had to solve and solved it in an exciting manner - the safety explosive.

After the Spring Semester 1953 I left for America with a leave of absence from the University of Vienna for two years. I returned only to wait for my visa to depart permanently for the US.

One funny situation happened after I returned from the US, married and with a first preference quota visa for the U.S. in my pocket. I had to wait for the actual issuance of the visa. I was assigned a laboratory office in the II. Chemical Institute on the second floor. This was the "empire" of a certain Docent Matthias Pailer. Totally incapable of understanding the situation, he expected me to work for him. Pailer later became a Professor of Pharmaceutical Chemistry at the University of Vienna.

I received my US visa on October 15, 1955 for my permanent immigration to the U.S. A. I resigned my position at the University of Vienna and my wife and I sailed for the

United States on November 3, 1955. On my resignation, I received a sarcastic reply from Professor Wessely, the head of the II Chemical Institute who was known for his cynical comments. He wrote in his letter accepting my resignation: "I hope you found what you wanted." As it turned out, I had.

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## **B. At the University of Massachusetts**

From the time I left Vienna in 1955 until my appointment in 1968 in Japan I did not formally teach. I gave scientific lectures during my industrial career at DuPont. I stayed in Japan for a semester and taught at Kyoto University and Osaka University. During the last few years I was with DuPont, I was active in the ACS Division of Polymer Chemistry and had started to become active in publishing.

The possibility of commercializing polychloral was for DuPont no longer a high priority item. There were serious deficiencies with the product and the process of making commercial products from polychloral. Attempts for commercial production was no longer justified and research could not be pursued.

After I returned from Japan I very soon received two inquiries for a University position. The first was as an Associate Professor at the University of Connecticut, which was of no interest to me.

At the ACS Fall meeting 1969 Professor Porter, the newly appointed Head of the Polymer Program at the University of Massachusetts asked for my advice. He wanted me to identify a scientist and/or Professor who could take over the responsibilities for the organic chemistry part of the program. I mentioned a few names but he finally asked me if I would be interested - and I asked him why he had not asked me in the first place.

Indeed, I was interested and after some negotiations I went to the University of Massachusetts for an interview. Soon we agreed on details and I received an offer from Porter on behalf of the Polymer Program at the University. In our negotiations, Porter said there were three essential points for the appointment. Position, salary and tenure - permanence of the position and I could select two. I told him I would accept the position as Full Professor with the desired salary. I understood that he (as a representative of the University) wished to be sure that I would handle the classroom teaching successfully. In my acceptance letter I stated these points. I agreed that the tenure decision would be made after one year. Actually the tenure application was made one year after I joined the Polymer Program and tenure was obtained at the end of my second year at the University of Massachusetts.

Meanwhile at DuPont, I went to see the director of CRD, Ted Cairns, and told him that I had an offer from the University of Massachusetts. He was an academically oriented industrial leader and very sympathetic to persons having academic ambitions. He advised me to accept the position immediately otherwise it might be offered to someone else. He commented that if people are beginning a new organization you should start as the organization is in the process of being built. I mentioned that in a year I would be eligible for a pension from DuPont. He said the amount of the pension would be as much annually as I could receive giving a single lecture. He was right and I was very thankful.

Around that time quite a few people from industry left for academia: Muefterties a Director of CRD and father of boron hydrides cage chemistry went to Cornell University, Bill Phillips, Director of Biochemistry of CRD, an NMR expert who was responsible for the building of the first superconducting magnet for NMR instruments and Bill Statton, a Manager of Textile Fibers of DuPont went to the University of Utah, Henry Hall, CRD left for the University of Arizona, Joseph P. Kennedy from Exxon joined the University of Akron and several other industrial scientists went to academia and became full professors.

I neglected to mention: The University of Massachusetts in Amherst was in the process of building a Graduate Research Center, a 17 Floor Tower for Chemistry, Biochemistry, Mathematics, and the newly created Computer Science Department -- and us - PSE. When I visited before accepting, this tower had reached the 9th floor. There was a labor strike and nobody knew when the work was to continue. So - I asked: Which are the floors for PSE and was told they were 7 and 8. This gave me courage and I accepted my position at UMass. 1973 we moved into our new offices.

My appointment at the University of Massachusetts began officially with the beginning of the Fall Semester 1970 but I was encouraged to come as soon as feasible. We went house hunting, found a place in Amherst, in the "Echo Hill" section of town that was partially built and planned to move in early June.

The Head of the Polymer Program, Roger Porter, had arranged for some summer salary for me and I arrived at the University officially on June 10, 1970.

The Polymer Program consisted of 4 Professors. Roger Porter, Frazer Price, Frank Karasz and me. Roger Porter had come from Chevron, Price and Karasz from General Electric and I from DuPont. There had been an Assistant Professor, named Carmichael in the Program but he left before I came.

I should mention one important event that occurred while I was still in Wilmington. Professor St. Pierre was a Seminar speaker of the Delaware Section. He had been a Manager at GE and had just joined McGill University in Montreal. I confided in him and asked for his advice and his opinion about Industry and academia. He encouraged me to go immediately to academia and said there is no substitution for a good position in a leading University. I followed his advice and have been grateful to him for his convincing argument.

The Polymer Program at the University of Massachusetts had been baptized as the "Polymer Science and Engineering Program". This was an excellent name. The Program had started functioning in 1967. Earlier, Professor Stein of Chemistry had written a proposal to the University to create a polymer program at the University and Porter was hired to bring it to fruition - Stein, a Chemistry Professor was not a Member of the core program or later of the Department. Several Professors interested in Polymer Science became Affiliates of the Program: James Chien and Richard Stein from Chemistry, Stanley Middleman and Robert Lawrence and Robert W. Lenz from Chemical Engineering.

At first, the program had no laboratory or office space and existed in borrowed quarters. When I arrived I moved into a small office in Draper Hall, which was also occupied by Bill Prest one of Porter's graduate students. In the fall the 4 Professors of PSE moved into a wooden building left over from a World War II extension, called Draper Annex.

Shortly after I arrived Porter told me that we (members of the Polymer Program) would be teaching a summer course of 20 credit hours. "Be prepared in 2 weeks you have to start teaching the organic part of the course".

As the summer course came to an end I had to prepare for PSE 501, a 3 credit hour course and perhaps the most important course in PSE. It was entitled "Introduction to Polymer Chemistry" and was taught in 2 parts; I gave the "organic" part and Karasz or Porter the physico-chemistry part. When it was inconvenient for one of the lecturers, we started with the physico-chemistry part. In our department we gave the 3-hour courses in 2 sessions of 1 1/2 hours.

In the beginning, we gave the classroom lectures, especially the introductory course, in the evenings. We tried to attract people from industry, especially from the neighboring Monsanto Company, to take our courses and eventually join PSE as official graduate students. This course was the basic course for the first year graduate students that had

come from various Universities and Colleges and was the course, which molded them into PSE students.

In the Spring I taught the course PSE 760 "Organic Chemistry of Synthetic Polymers". This was the main course in Polymer Chemistry and provided the students with the knowledge in chemistry they needed for the full understanding of polymer chemistry.

I always presented the lectures as "chalk talks", always from memory with an occasional checking of the notes. Chalk talks have the tendency to force the students to copy from the black board what is being presented. I never believed in giving students brief information and instructing them to "work it out". This is now a common procedure. I always relied on my notes based on my experience in polymer chemistry. As background reading I used the book of Ravve. I never met Ravve personally but found this book the most useful for my courses. It was mainly chemistry, with very few sections of physico-chemistry. It was not perfect. Some chapters were extensive, others scanty. Since Professor Lenz was in our University's Chemical Engineering Department, I used some parts of his book for the preparation of my notes.

Over the years, books on polymer science had been written but I did not find any that was clear and short enough to have textbook quality. I always believed in the sequence of "listening to the lecture, copying from the blackboard, transcribing the notes and studying; I always believed in acquiring knowledge by repetition. This is the way little children learn how to speak ---- or people learn efficiently a foreign language.

A laboratory course in polymer chemistry was badly needed. Frazer Price had created the course in polymer physico-chemistry, the year I arrived. To create the laboratory course in polymer chemistry (synthesis) was complicated because PSE did not have any space. Finally we negotiated with Chemistry to have the use of one of their laboratories suitable for 13 experiments (one per week for each student). We had to pay rent, which was illegal, but we found a solution. We paid for "instrument repairs"

that were needed in the Chemistry Department: \$ 1,500 per semester. The course became PSE 503 and was given in the fall semester of the new students arrival, I had a Laboratory assistant, David Lipp, assigned who was one of my graduate students. We prepared a booklet describing all the experiments, including some chemistry, relevant for the experiments. We also provided in this booklet detailed safety instructions. The booklet was updated every year (as long as I was in charge of the laboratory). Unfortunately, several experiments that I would have liked to include in the program of the laboratory course were not possible.

We were limited in time for the laboratory course because we had to finish the experiments in one day. Some of the experiments were Polyester Synthesis, the Nylon Rope Trick, Polyurethanes, Oxidative Coupling, Emulsion Polymerization, Suspension Polymerization and my favored Experiment, Determination of the Ceiling Temperature. The experiment also had to be tailored to students who did not have much experience in chemistry, especially experimental chemistry.

Each student, after he had performed an experiment, was examined by an oral quiz. As I mentioned before I had a lot of experience in oral quizzes from my years at the University of Vienna. These quizzes were actually personal tutoring sessions. Many students sat or stood around and listened to the quizzes. Since many students never had personal interactions with a major Professor that must have been a grueling experience for the first months. I heard some rumbling how unusual these quizzes were but after a month the students were used to it. I spent 6 hours each Friday in the PSE 503 laboratory and loved it. I also had an opportunity to meet the students in person and not on the corridor or in seminars. In the end the students were happy that they had been prepared well for the qualifying cumulative exams.

PSE 501, PSE 502, and PSE 503 were the "basic" courses that we needed in our education scheme of the department. Two other required courses were given in the Spring Semester "Organic Chemistry of High Polymers", my main course, and

"Physico- Chemistry of Polymers", the course given by Karasz or Stein. Another important course was "Rheology" given by Porter or Middleman.

I taught special courses in the Spring Semester every 2 years. One of my favorites was "Degradation, Stabilization of Synthetic Polymers"; another was "Applied Spectroscopy of Synthetic Polymers". This was more of a seminar course, because I prepared, with an individual student, a selected topic and we discussed it in the course with full participation of the other students.

As the research groups of each individual Professor at PSE became larger in size and I as well as other had more than 12 coworkers, we started to give more and more extensive course like instructions in the research groups.

I had a weekly seminar open to everybody in the department on "What's going on in polymer chemistry?" Each student had to read one or more assigned Journals and had to discuss what he had found. I also conducted a regular monthly seminar of "Who is who in Polymer Chemistry"? In addition we had all the regular PSE seminar and speakers that I invited personally. I believed that this combination served the needs for graduate students and postdoctoral fellows to call it an "education in Polymer Science at UMass."

In addition we had in my research group our weekly and later, as my group became larger, biweekly discussions of the students research and research accomplishments.

*The PSE Department:* Before I joined PSE the fledgling faculty had established a teaching program. It consisted of core lectures, a Cumulative Examination system and a Graduate Program Director. Porter was responsible for everything. As soon as I arrived (for the class beginning 1971) he appointed me as the Graduate Program Director. I held this position for 5 years and our student body increased during that period from 32 to 62. It was demanding time-wise and my family helped me during

these years sorting and preparing papers for me to study and make the necessary decisions for admission to PSE. I should emphasize that the PSE program was a graduate program.

In 1973, the PSE Program applied for Department status and was approved by the University and we became a Department. We still remained a graduate department, probably the only one in the country. I do not wish to discuss the problems that were involved.

One of the main objectives of PSE was to attract students to the department, and provide Professors and funding to support students. We were able to pay for them, first from department funds. After one year, the individual faculty member had to provide the funds to support their students. Our faculty members had excellent reputations and students liked to come to PSE and to Amherst.

The cumulative examinations were effective and brought the best out of the students and the knowledge of the students increased. I still remember when I was still Graduate Program Director, the incoming class had an average rating of 1385 (out of possible 1600) for the GRE scores, almost unbelievable for a new department. This class had 2 students who later became Professors, and one became Dean (Vice President) of Science at Caltech.

When I came to UMass the "Cume" (cumulative examination) system had been established. The exam was given on the second Saturday of every even numbered month, summer period not excluded. It consisted of 6 questions. 4 had to be answered. Two questions were of the synthetic type, 2 of physico-chemistry/physics and 2 of engineering. At each cumulative examination, we passed about 60% of the students. Each student had to pass 5 exams and 10 attempts were allowed. A few students did not complete these cumulative exams successfully and ended up with a Masters Degree. Cumes were supposed to show that life as a student consisted of acquiring of

knowledge and handling the day-by-day functions - a very important combination for professional life.

Other obligations for the Ph.D. student of PSE required the successful passing of 2 different and independent Research Proposals and a language examination. The student could select from German, French, and Russian. The student was obligated to translate about 10-15 pages of an article in one of these language selected by me. I administered these exams myself. My knowledge in these languages were sufficient, and if needed I asked for outside advice.

Since this section is only concerned with my teaching, and what was required in PSE, at the University of Massachusetts, I will not go into departmental politics. After PSE became a department in 1973 with 4 faculty members, the student body increased rapidly, and PSE was able to hire more faculty members. First Isaac Sanchez joined PSE then Farris (from the Civil Engineering Department), Shaw Lin Hsu came from the Allied Company, and to replace Frazer Price, who had unexpectedly died, with Ned Thomas.

A successful career as a Professor in a major university requires teaching and capable graduate students that can produce the scientific results that demonstrate, imaginative and future-oriented research.

Our vigorous recruiting efforts for PSE brought to Amherst exceptional students. Among them were Tirrell, Deits, Southern, Corley, Yoon, Misra, Russell, and many others. By 1975 we had 62 graduate students and accepted about 15 new ones per year for their graduate work. PSE was and remained a Graduate Department. It (and the Computer Science Department) were the envy of other University Departments.

The incoming students were divided among the core faculty. As new students came in to PSE they could chose their advisor, as long as the advisor was able to pay for the

support for the students. PSE did not only consist of the "core" faculty but also of Professors that were affiliated with other departments, had polymer interests and were consequently associated with PSE (Stein, Lenz, Chien, Middleman and Lawrence). The simple requirement was: This faculty member in return for some service to PSE, could take an "incoming" PSE student as advisor to work in their research group. The Professor had to provide the funds for the student's subsistence. The students had to go through the PSE requirements and obtained their Ph.D. from the PSE department

For some years I had an advantage. I was not only the Graduate Program Director of PSE, but I was teaching the Introductory course PSE 501 and the organic laboratory course, .PSE 503. Students who were interested in polymer chemistry and polymer synthesis were exposed to me in their first Semester. . For a number of years I was able to have excellent incoming students. The limit was funding. The department funded 2 students for the first year and the Advisor had to pay after that. If a Professor could attract more than 2 students, he had to provide the funds for the students even for the first year. Sometimes an individual Professor could attract a student because of the work he was doing, and could not provide the funds later; this was a problem and made us think of the possibilities of obtaining "block-funding" for the department - At this period we had funding from the Materials Research Laboratory, later it was CUMIRP in addition to MRL.

With the various funding possibilities I had at one time 12-15 graduate students and 10 post docs in my group. The real problem was then and still is to have careful balance: a.) New and exciting ideas that can be funded, b.) Amount of funding that is available from a funded proposal. c.) Co-worker who are interested and willing to work on the funded project and produce at the rate that the progress of the project required for continued funding. Sounds easy, but try getting your coworkers to fulfill all the requirements.

I had some excellent students and postdoctoral co-workers who produced exceptional

results. They formed a tightly knit group and I am still in contact with many of them.

We worked on a number of different projects. It was my idea and objective to select subjects, different subjects for all students and post docs according to their capabilities. By working in different areas, the members of the group learned first hand that many problems existed. I expected them to be exposed to various problems and appreciate the subtleties of the individual and sometimes difficult problems. I did not want to work on the details of problems that could become obsolete.

The list of subjects of our accomplishments include: Head to Head Polymers. Alternating Co-Polyamides, Polyamide Desalination Membranes, unusual High temperature Polymers, Functional Polymers Polymerizable and Polymeric UV Stabilizers, and some work on Polymeric Drugs.

When I knew that I was leaving the University of Massachusetts to go to the Polytechnic University in Brooklyn, I tried to have my students complete their work toward their Ph.D. To some I offered the opportunity of coming with me to Polytechnic University. Others I allowed to finish in Amherst under the "local" primary supervision of some of my colleagues.

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## C. At the Polytechnic University

In January 1982 I received a phone call from the Provost of Brooklyn Polytechnic University in Brooklyn who told me that Polytechnic had created an endowed chair named after Herman Mark. Polytechnic wished to fill this position and the Provost asked me if I were interested. I said I would think it over and discuss it with my family. After some time I called him and said: **No**. I had to go abroad for a month in April, I had a great deal of responsibilities as Vice Chairman of the upcoming IUPAC Symposium in Amherst, was over-committed and not interested in changing my position. Shortly

thereafter he called me again and asked me to visit in Brooklyn Poly with my wife before going to Europe and discuss the position with him personally. The atmosphere had changed favorably and it looked as if the proposal was serious and could lead to an offer.

The Mark Chair was an endowed chair. The idea of creating an endowment for a Chair in Polymer Science at Brooklyn Poly in the name of Herman Mark (as an endowed chair) was initiated at the 80th birthday of Herman Mark. By 1980, adequate funds were appropriated and the search committee could begin to look for candidates. Some funds from the endowment had been used for a three months visiting Professorship for Professor Ephraim Katchalski-Katzir after he finished his term as President of Israel.

In addition to the Mark Chair the Provost offered me the Chair of the Chemistry Department and the directorship of the Polymer Research Institute at Polytechnic Institute at Polytechnic or both, which I declined.

The Mark Chair was a position of Research Professor but I was encouraged to teach, I was to receive a 60% increase over my Massachusetts salary and most importantly, I would report directly to the Provost, not to a Department Head or the Dean of Science (that meant I was a "de facto" dean). Again I told them that I would consider it and give my decision after the IUPAC meeting.

I went to the personnel director at UMass and discussed my options. He pointed out that I would be 55 years old in the coming November and that as a Professor of the University of Massachusetts I would have the option of retiring from the University. He said, I did not have to "resign"; I could simply "retire" if I would complete the Fall Semester at the University. In the fall of 1982 I accepted the offer of the Mark Chair of Polytechnic University and retired from the University of Massachusetts as an Emeritus Professor.

During the time I negotiated with Polytechnic, the ACS Division of Polymer Chemistry created the position of a Business Office Manager, and had asked my wife Jane to assume this position. The business office was to be located at Polytechnic University in the complex of the Mark Chair office.

In January 1983 my wife and I moved to Brooklyn Heights into a parlor floor apartment overlooking lower Manhattan and the Brooklyn Bridge. The PSE Department of the University of Massachusetts allowed me to take most of my equipment with me to Brooklyn. I moved into the newly renovated office and laboratory complex on the 6th floor of the Jacobs Building of Polytechnic University, as it was now called, in Brooklyn.

I started to teach in the spring after I had arrived and presented a course combined from my introductory course and my former main course that I taught in Amherst. It was a three credit hour course. Unlike most courses that were given in the evening, I gave my course in the late morning. I have always been a "morning man" and preferred my important work to be done in the morning. The course had to be taught slower than in Amherst, because we had more foreign students, graduate students that came from various back grounds and schooling. Some students came from the Chemistry Department and others from the Chemical Engineering Department. Although I was independent from the Chemistry Department I was a member of the Polymer Research Institute.

When I arrived in Brooklyn, Professor Mark was 88 years old and came into the University every day, when he was in town, I visited him in his office on the 7th floor of the Jacobs building at least once a week. He liked to chat with me in Viennese dialect. After all we were both born in Austria and had received our Ph.D. from the II. Chemical Institute of the University of Vienna - although 29 years apart.

The Mark Chair was not only the first endowed Chair in Polymer Science in this country, but it also demanded a great deal of time attending functions representing

"Brooklyn Poly" as it was still called by many. Brooklyn Poly was the cradle of Polymer Science in the U.S. and had its glamour period shortly after the war.

After almost two years living in Brooklyn, my wife and I moved from Brooklyn to the suburbs of New Rochelle in Westchester County which required commuting for one to one and a half hours by car or by public transportation, Metro North and the New York subway.

Polytechnic University consists of the downtown campus on Jay Street in Brooklyn, the Long Island Campus in Farmingdale, and also a North Campus in Scarsdale, Westchester County. This North Campus activity was created to provide a teaching mechanism away from the Brooklyn Campus and in West Chester County. It was primarily for people who worked in Industry and wished to acquire a master's degree based on 30 hours of course work.

I was asked to lecture on this North Campus and provide the courses for the polymer science curriculum. I taught "Polymer Chemistry" and a course on "Selected Polymer Subjects" for several years. I usually had 15 to 25 students in my class. The students worked during the day and took the 3 credit hour courses in two evening sessions a week. This course was easy for me to teach, the students were knowledgeable and anxious to obtain their degree. In addition I had come from industry to teach at the University and understood their problems, having families and working for a master's degree. When having a B average, the companies would reimburse the students for their tuition.

When we had a smaller class and there was a need for it I gave the evening lecture in our living room in New Rochelle, which was fun and provided a more personal atmosphere. The students tried to finish their course work in 2 1/2 years with 6 credit hour (2 courses) per semester. In some cases, students wished to finish their course work in 2 semesters. I provided a program that allowed a student to obtain graduate

credit hours, if they were willing to write a review article based on my suggestion, but of their choosing. My last graduate student, John Crawford wrote an excellent review article on the very popular subject of UV stabilizers. He selected the title "Polymerizable and Polymer-Bound 2(2-Hydroxyphenyl)2H-benzotriazole Stabilizers".

I gave my last course at the North Campus in the Spring of 1995.

As I mentioned earlier my research group had very good laboratory facilities at Poly. Each student had his own hood and there was ample space for our instruments. The graduate students and postdoctoral associates that came to work with me in Brooklyn were highly motivated and devoted to their subjects and our organization. We were a closely knit family, often had our lunch together in our central room, which had books, Journals, some files and the Xerox machine. There was a little kitchen with a small refrigerator and a coffee machine. We had also a side room with a computer for post-docs if they wished to use it. It was planned for use by those visiting scientists who came to spend some time in my organization. The office for Polymer Division business office and later the business office of the Pacific Polymer Federation with Jane Vogl in charge was also located in this complex. My secretary also had her separate office. We had a number of visiting Professors: Ann Christine Albertsson from Stockholm, Albert Zilkha from Jerusalem, Ferenc Tudos from Budapest, Pippel from Dresden and Freitag from Jena. Post-docs came from Imperial College, Slovakia, Japan and China, we also had once a student from Austria for the summer.

The students that I had at Polytechnic University were the most productive and devoted co-workers you can imagine and now, after many years and I am still in close contact with them. My coworkers produced some of our best work, which included polymerizable and polymer-bound UV stabilizers, the genesis of chloral polymerization, the first chiral pentatomic molecule. H-H PVC blends, spacers in macromolecular structures, reactions on polymers and urushi the component of oriental lacquers.

In the fall of 1995 I retired again, this time from Polytechnic University and became the Herman F. Mark Professor Emeritus. My wife and I moved to Amherst and I assumed my position as emeritus professor at the PSE Department of the University of Massachusetts.

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## **D. At the Royal Institute of Technology, Stockholm, Sweden**

In the 1960's, Polymer Science had made substantial progress in Sweden. Some companies had divisions that were using polymers in a number of ways. This is not surprising since macromolecules like cellulose and wood are natural polymers that were and are harvested and utilized extensively in Sweden and Scandinavia. When I first went to Sweden in September of 1971 the Department of Wood Technology at the Royal Institute of Technology was well established and was well recognized. Cellulose and polysaccharide research was in full swing at the University of Stockholm under the leadership of Professor Lindberg.

In 1961, the Department of Polymer Technology was established at the Royal Institute of Technology with the appointment of Bengt Ranby as Professor. Ranby, born in Stockholm, was educated at the University of Uppsala, and had his postdoctoral experience at Brooklyn Poly. He had become a Professor at Syracuse University, which had a Chemistry Department with a strong cellulose (and pulp and fiber) component. After a few years he moved to the Sun Oil Company in Markus Hook near Wilmington and joined in their efforts on polyolefin research.

As mentioned, Ranby gladly joined the Royal Institute of Technology with the objective of establishing a Department of Polymer Technology with some interaction with the Department of Wood and Cellulose Technology.

I knew Ranby from many encounters at international meetings. After I joined the

University of Massachusetts, he visited here and proposed that I come to Stockholm and present a 3-credit course in 6 weeks. In the Swedish University system, course credits were given in units of 7 hours. Consequently I prepared my lectures for a 4-unit course. The course was similar to my course in Amherst, "Introduction to Polymer Chemistry", a little bit extended. I gave it in two-hour sessions over a 6 weeks period. My wife and my daughter were with me and we had a nice apartment on Karlsbergvägen. Not only did I serve RIT but my family and I also learned much about the history, culture and social life of Sweden.

The students told me that the course was a success and their star student and leader, Ann Christine Albertsson presented me with a glass vase; Sweden was and is well known for its glass, wood and cellulose products. I was not the first lecturer to present this type of course; Professor John Stille had done that before. The course was subsequently given by well-known people from other places in the world.

I played another role at RIT. Ranby wanted and needed his own building for the Department of Polymer Technology. He had been negotiating with the University and told me that my visit presented an opportunity to visit the President (Rektor) of the University. He introduced me as the course lecturer but also as the Treasurer of the ACS Polymer Division and upcoming chairman elect of this, the largest polymer organization in the US. I gladly cooperated. If it did some good, I do not know, but the building was built shortly thereafter.

I kept in close contact with the Swedish polymer community but my interaction intensified by two events. First Ranby together with Stretch Winslow, organized a US-Sweden workshop on Photochemistry in Stockholm in 1981 based on my models of the Seminars in Japan and Romania. Secondly, Ann Christine indicated that she would like to spend a year in Amherst as a postdoctoral Research Associate, which she did. Two years later she also spent one semester with me in Brooklyn. In the late 1980's she became the Executive Manager of the Department of Polymer Technology and for

the last 15 years she has been the head of the Department.

It is perhaps of interest that I also mention also my other involvement with the science community in Sweden. In 1985 I was a Member of the Committee (with Barry Trost as the Chairman) of the Swedish NSF to oversee the programs on "Organic Synthesis and Biochemistry" that were funded by the Swedish government. In 1988 I headed a committee on "Polymer Science". In 1993 I was elected a Foreign Member of the Royal Swedish Academy of Sciences, the organization that hosts the Nobel Prizes for Chemistry, Physics and Economy.

I was also involved in the First Sweden US seminar on Photchemistry in Stockholm in 1981 and the second US-Sweden Seminar in Pasadena, CA in 1984 In 1995 I organized and co-chaired with Ann Christine Albertsson in Stockholm the Symposium honoring Bengt Ranby on his 75th birthday. In 2000 I spoke at the Seminar for his 80th birthday in Stockholm.

Bengt and I had a lasting friendship till the end of his life.

My friend Hatada became Vice President of Osaka University and was interested in a cooperation agreement between Osaka University and some other English speaking University. I advised him to consider Sweden as a possibility rather than the US or UK. I went to RIT and discussed this proposition with the Dean of Science who was very interested. It took some time to finalize the proposal between RIT and the University of Osaka. In May 2001, on the occasion of the 70th anniversary of the modern Osaka University, I met with the (now) new Dean of Science at RIT, Professor Andres Hulst in Osaka for the signing ceremony of the Osaka University - RIT agreement of cooperation.

When I looked back on my records, I found that was in Sweden at least 15 times. I gave 4 more short "one-unit" courses at RIT in recent years. The interest had shifted

from my first teaching basic polymer chemistry to "present-day active areas in polymer science".

I gave the last course in 1998 entitled "Polymers for the 21st Century." It included Polyolefins: Synthesis, Catalysis, Structures and Economy, Dendrimers, New Polymerization and Polymer Stabilization Techniques, Polymer Crystallization and other subjects. About 40 students and other interested people attended not only from RIT but also from other Institutions of Stockholm and nearby Institutions, for example from Uppsala

During my frequent visits to Stockholm, I also visited and lectured at the other important Universities in Sweden, the University of Stockholm, Göteborg, Lund and Uppsala. On my last visit, I was invited to join a doctoral examination committee of the University of Uppsala.

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## **E. At the Université Louis Pasteur in Strasbourg, France**

My year of sabbatical leave came up in the fall of 1975. A faculty member at the University of Massachusetts was permitted to take a year of sabbatical leave after every 5 years of service to the University. The faculty member had a choice of one year at half salary or one half year at full salary. My wife and I chose to take a sabbatical leave for one year at half salary. Our intention to go abroad required a considerable amount of planning.

First of all, we had to secure a place where we were welcome, and second, a place that supported our stay, at least in part. My wife and I decided to try to go to Strasbourg. We talked with Professor Benoit who at that time was the director of the Institute of Macromolecular Chemistry (CNRS) and Professor at the University of Strasbourg. Because of the uncertainties in life we also accepted Professor Manecke's

proposal to apply for a Humboldt Prize for me to be used to stay at the Free University of Berlin.

Professor Benoit's proposal was successful, and I became a Professeur Associé at the University of Strasbourg. I was honored and accepted it with pleasure.

However going abroad for a whole year presented other problems. I was responsible for a young and growing research group that needed supervision. I approached Professor Gyula Hardy, the director of the Institute of Industrial Chemical Research of the Hungarian Academy of Sciences and invited him to take my place for the Fall Semester of 1975, and Professor Saegusa of Kyoto University to replace me in the Spring Semester of 1976. They were to overlook and supervise the scientific operation of the group and the lecture responsibilities for the department. I handed over the day-by-day operation of my research group to David Tirrell, a graduate student who had come from MIT. Even though Dave was only in his second year as graduate student, he developed quickly into the leader of the group. This arrangement worked and worked well.

I also had to deal with the family needs. My daughter was enthusiastic. She wanted to finish of Amherst High School and took extra correspondence courses authorized by the Education Department of the State of Massachusetts, including two 4-hour courses in the summer. She was ready to graduate when we left for Strasbourg. She actually graduated in January of 1976, 15 1/2 years old. She (as a senior) had also taken French at Amherst College, to prepare for our year in Strasbourg. We had no plans to let our daughter go to the University because of her age. Instead she attended the last class (terminal) at the Lycée, Place Bordeaux in Strasbourg. The French Lycée had 13 grades, one more than we have in our high schools and is terminated by a Baccalaureate degree. Yvonne did not have to work for grades, so she could take courses that were not available at the Amherst High School, certainly not in French. Most importantly, the teaching was in French!

Very critical for the family, was to find a "temporary home" for our dog, a black Labrador retriever. By chance my wife spoke with Mrs. Lenz. The youngest daughter of Professor Lenz loved our dog. So- our dog lived with the Lenz's for one year and the Lenz's did not have to acquire a dog permanently!

We rented our house to the 2 Proffers who were replacing me at the university, to Professor Hardy in the fall and Professor Saegusa in the spring at no cost, other than the utility expenses.

At the end of August we were ready to leave for France. We had booked a round trip to Europe on the Stefan Batory, a Polish ship that sailed from Montreal. It was the only ship that took cars at that time for a transatlantic voyage. We consequently drove to Montreal, embarked with our red Opel and we landed in Rotterdam several days later. Soon we arrived at the CNRS on rue Boussingault in Strasbourg. Fortunately, we had the use of the comfortable apartment of the former director in the Institute, Professor Sadiron's apartment. It had not been occupied by the present director had been used for distinguished visiting professors for several years.

My appointment and teaching responsibilities were that of a Professor of the University. My primary function was with the CNRS Institute.

On the first possible occasion, Benoit and I went into the rue de Goethe where part of the University administration was located, to start the confirmation of my appointment. Soon the appointment document arrived signed (with the official signature stamp of the President of France, Valery Giscard-d'Estaing) and my salary was approved.

The next step was my teaching assignment. We decided that I would present two 3 credit hour courses, one in the Fall Semester entitled "Degradation, Stabilisation et Viéissement des Polymères" (Degradation, Stabilization and Aging of Polymers) and

the second in the Spring Semester: "Synthèse Techniques des Polymères Commerciaux" (Technical Synthesis of Commercial Polymers). While I had my office and functioned at the CNRS Institute on 6 rue Boussingault with Professor Henri Benoit as the director, my teaching responsibilities were at the "Institut des Haut Polymères", with Professor Wippler as the director, a University Institute, on 4 rue Boussingault.

I held a meeting with the students who wished to take my course; I arrived with a copy of my notes. I had already given the course twice in Amherst and was ready to begin. We had about 25 students and I suggested that we decide whether to teach in English in French. The students overwhelmingly concluded that my French was much superior to their English.

This slightly complicated the situation, because I had only a few days to "rethink" my course into French! There was no question; it had to be done from English notes in fluent French. I had 6 years of French in high school and a one-year extension course at the Sorbonne branch in Vienna after the war.

The real problems were the correct technical names of general polymer related expressions. I knew that "to catalyze" was "amorçer" meaning "to sting" - like a bee. But to find the proper expression for "tensile strength" or "injection molding" was a different story. I asked my daughter, after all she went to the Lycée everyday and was much more fluent than I; she tried but without success. I tried in the CNRS Institute, also with little success. Nobody "knew" all these 'exotic' expressions, because they were organic chemists or physico-chemists. There was no "technical English-French dictionary in the Institute - and I had not much time. I was teaching 1 1/2 hour on Monday morning and Friday 1 1/2 hours in the afternoon.

At the end of the Semester I gave a written final exam graded these devoted students graciously. My wife invited the whole group for an elaborate party in our apartment and

we were ready for Christmas and the Spring Semester.

When I was not teaching or preparing my talks, I wrote papers of some of the work that we had done in Amherst. Since I was using my time at the Strasbourg CNRS Institute, I used the Institutes address for the publications. I also produced two joint papers with Benoit. His coworkers used their measurement techniques to measure my samples of head to head polystyrene, which I had brought with me. I had not much time left for traveling. My wife and my daughter traveled extensively with our red Opel through the Alsace and the neighboring countryside. The cultural life in France and the beauty of the countryside that they experienced was an unforgettable experience for them.

For the Spring Semester, my French was now established as the language of my teaching. My fluency in the delivery of the lectures had substantially improved and I was ready for the spring course. You might ask, why this title "Technical Synthesis of Commercial Polymers"? There was a good reason. Wippler had created a course on technical polymers, as an excuse to invite his friends from industry to give a lecture at the Institute. It was a string of presentations of such subjects as fiber spinning blending or some other technical processes **on** already formed polymers.

Nobody in the two Institutes had enough competence and knowledge about chemistry and technology to teach a course in technical monomer synthesis of monomers and their polymerization. I had been teaching most of the monomer synthesis in my two courses in Amherst, "Intro" and "Chemistry of High Polymers" and adapted it to the polymers that had already been mentioned in these various lectures/seminars. It was much easier than the fall course. The course was well received, the examination was successful and the finale was again a party in our apartment.

I had a few more interesting experiences that are somewhat related to my teaching activities in Strasbourg. One research advisor of the CNRS Institute, Jean Marchal, a Directeur de Recherche, had a graduate student from Hong Kong, a Mr. Chang.

Marchal had been his advisor for some time, but he had never bothered to have a Ph. D. committee appointed. The time of the final examination approached. He quickly had the committee appointed, consisting of Professor Banderet from the University of Mulhouse, also a Professeur Associé, who was associated with the Institute des Hautes Polymères, next door and my office. Chang was to receive the doctorate from the University. Marchal was not qualified to be an advisor for University functions, because he was not a member of the University, only Banderet and I were. Marchal could chair the examining committee, Fortunate for all of us; Banderet had the appointment of Professeur Associé. Fortunate for me was that his appointment predated mine by two weeks. Otherwise I would have had to say to Chang. "Au nom du President de la Republic Francaise.." In the name of the president of France I declare you a doctor of science --- but Banderet awarded the degree.

I took two trips to Paris on behalf of the CNRS Institute. The first time I went with Benoit for the celebration of the 60th birthday of Champetier who was probably the most influential Polymer Chemist in France at that time. I became acquainted with his successor Lucien Monnerie, worked together with him for awhile and published a couple of papers.

The second trip was trickier. Benoit asked me to go to Paris and represent him and the Institute. He had something urgent to attend to. I suspected that he did not feel like going but an Institute representative had to be there. It turned out to be a meeting of the directors of the CNRS Institute with DR. Cantacuzene the President of CNRS presiding. I did not and could not say much; I just had to be there.

Having fulfilled my obligations, my wife, Yvonne and I left Strasbourg at the end of April in our red Opel with Yvonne's 6-speed bicycle (acquired in the home country of the Tour de France) tied on top of our red Opel for Berlin. I still consider myself a Francophile with my ties to Strasbourg - and the Benoit's two of the best friends of my family. Our time Strasbourg was for me an important step forward in my career.

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## F. In Japan

My first contact with Japan's polymer chemistry came at about 1960, when Professor Furukawa visited DuPont with his Associate Professor Saegusa. It was a delicate situation. We were direct competitors on the polymerization of higher aliphatic aldehydes. We, at DuPont had abandoned further efforts because we could not see a commercial product that could be developed. Still we were listening to scientific groups that were still continuing in this field. A few years later Professor Tani, Osaka University also visited the Experimental Station. He showed us a rolled sheet of polyacetaldehyde made by polymerizing acetaldehyde with aluminum alkyls. This was similar to the description of acetaldehyde polymerization by Vandenberg.

In 1965, I attended the IUPAC Symposium on Macromolecules in Prague. At the banquet table I was seated with Professor Seizo Okamura of Kyoto University and Professor and Mrs. Natta of Milan, who had just received the Nobel Prize in Chemistry for his invention of isotactic polypropylene.

Okamura said, "Why don't you come for a semester to Japan as an "Industrial" Professor to the Department of Polymer Chemistry I thought this would be wonderful, I was just 37 years old. I was trying to follow up Okamura's suggestion discreetly, but without success. Okamura had lost interest of this proposal. When I went to the IUPAC meeting in Kyoto/Tokyo, Japan in 1966, I was invited by Furukawa to his house for tea, an unusual honor in Japan at this time.

I explained to Furukawa my experience with Okamura and he was surprised. He said: "In 1968 I will be the Chairman of the Department of Synthetic Chemistry and if you wish, I will invite you to come to Japan, to Kyoto University and to my department as an industrial Professor from abroad. With this verbal invitation I went to the Director of DuPont's Central Research Department Ted Cairns. Ted was a true scientist, member

of the U.S. National Academy of Sciences and interested in the development of young chemists. He was also interested in improving the international reputation of the Department especially in the orient. At that time Japan was a new territory for DuPont. All the international contacts were with Europe. Cairns said, you can go for 3 months at full salary and I will provide you with \$ 2000 dollars for additional expenses.

With this confirmation in hand I asked Furukawa to extend a formal invitation, and I became an Adjunct Professor of Kyoto University in the Department of Synthetic Chemistry.

### **a. At Kyoto University**

The plans were all made and my family was ready for our journey to Japan. We had to fly via Anchorage and arrived in Tokyo, Haneda Airport. Narita Air Port, the now huge international Airport of Tokyo was in the process of being built, did not exist at that time. We stayed overnight at the Marunouchi Hotel in Tokyo, the Hotel I stayed when I was the first time in Japan, 2 years earlier. It was quite exiting for my wife and the children, Yvonne, age 8 and Eric, age 10, the first time in the Orient. The room cost Y 2,600 a night and the exchange rate was 360 Y for one dollar. Next we took the Super Express Shinkansen train to Kyoto. I still remember it as if it were yesterday. Nearly 20 people met us at Kyoto station. As the train pulled in slowly and we exited from the train, they all bowed and greeted us respectfully and warmly: The Furukawa family, the Saegusa family and several others from the department were there. They took us by taxi to Konoe Hall, the guesthouse for senior University visitors. We moved into the apartment on the first floor and had Professor John Ferry and his wife Barbara from the University of Wisconsin, Madison, Wisconsin, as our neighbors.

On the second floor lived Professor Stein from the University of Massachusetts in Amherst, with his wife Judith and their 4 girls. We all were at Kyoto University for one Semester.

It was a remarkable group of scientists, involved in polymer research and teaching, an engineer, a physico-chemist and an organic chemist. The housekeeper was a man called Kohjima. None of the Japanese spoke much English and only Ferry spoke a minimal amount of Japanese which he had studied before coming to Kyoto.

Having settled in the apartment, I immediately had to show up at the University to demonstrate that I had arrived. The University was still full of tradition and formal in the spirit and style of the post war era. Furukawa was the head of the Department and had to take me to the Dean and the President and introduce me. There had never been a formally appointed University Professor from Industry at the University, especially not from abroad. The Dean, Professor Maeda, from the Agriculture Department spoke some English, but etiquette required that he addressed me in Japanese which was translated into English by the department head Furukawa and my English comments were formally translated into Japanese. Maeda later became President of the University. My visit to President Okada was similar even more formal and he presented me with the formal document of appointment. This document has become very dear to me. Once I asked Furukawa if it was a Xerox copy of sorts. Furukawa "scolded" me and explained that this was produced by a Japanese typewriter, where each symbol had to be by hand put in place. What a different time but the computer age was still 25 years away!

Next I was shown my office, a very nice office. Furukawa's secretary, Ms. Ohji had prepared a flower arrangement for me and served green tea every morning as soon as I arrived. This procedure was repeated whenever I was in the office. I was also associated with Professor Saegusa, (my age) and his young secretary Chieko Sato. I will never forget with what dedication she typed my abstract booklet, and once I had a toothache, she took me to the Kyoto University Dental Clinic. 20 years later, on my 60th birthday, ken-reki, on the occasion of the party of my "rebirth", she dressed me in the traditional crimson baby pajama bonnet and jacket.

The Department of Synthetic Chemistry consisted of 6 Kozas, as the research groups were called, headed by a Full Professor, Kyoju.

The oldest Professor was Professor Oda who was German trained, spoke little English and had his office next to mine. I visited him almost every day and spoke German with him, which he enjoyed.

Oda had started the creation of the Department of Synthetic Chemistry by spawning from his Koza the other 5 Kozas. six Kozas constituted a department. When I was in the department there were in addition to Oda, the Professors Junji Furukawa. Zen-ichi Yoshida, Kumada, Minoura, and Takeo Saegusa. The chairmanship rotated every year.

Furukawa's koza had as its jo-kyoju Shinzo Yamashita. He was responsible for the interests of Furukawa in rubber chemistry. When Furukawa retired he took over his functions and was a Professor at KIT. The Jo-shu was Jitsuo Kiji, who became a Professor at Tottori University.

Each Thursday the faculty meeting was held. I also had to attend in spite of the fact that I did not speak or understand Japanese. The seating arrangement was according to seniority. Furukawa as department head was at the head of the table. I was placed between Saegusa and Minoura. The department assistant brought in the lunch from a nearby restaurant, usually "oyako dombori" served with green tea. At the second table, also in exact order were the Assistant Professors (Jo-kyoju) and at the last table the Instructors/research associates (Jo-shu).

The next surprise came as I was preparing for the lectures. I would have to produce short manuscripts for the lectures because they would be reproduced, small pamphlets produced and distributed to students and other people that might be interested.

Fortunately I had carefully prepared my lectures. In Wilmington, as Cairns had

approved my stay in Kyoto, he also approved a list of lectures and allowed me to talk on subjects that were no longer of interest to the company. Cairns thought these subjects might be useful sales item for the DuPont Company in Japan. Weeks before I left for Japan, I designed slides and worked practically day and night to be prepared. It should be emphasized it was not a company assignment but a project encouraged (and tolerated) by the department.

Lectures in Japan were 2 hours long. The lectures in the Orient had to be such that the subject was understood by the audience. It had to be done slowly and it essential to repeat parts of your presentation.

I lectured on Wednesday. And all the students of the department came to the lectures. The objective was not only to present the lectures of scientific importance, but also to provide the lectures in English to make students aware of the sound of English. In Japan, English was taught in high schools but the students did not have much experience to actually hear English spoken. They had a great advantage since I was conversant in 3 languages, in addition to English and I knew what it meant to listen, comprehend and speak a foreign language. My European origin was consequently highly appreciated.

With the help of many we proceeded with the course, which was entitled "Aspects of Polymer Chemistry". Now after 35 years it is hard to explain what enthusiasm and friendship I created in this lecture series. It was important of the senior people the faculty in the department and other departments, to hear not one but a sequence of lectures in English. The attendees also learned what was going on in the scientific world, in the industrial world. Even though the work presented had been abandoned by DuPont it showed how in the leading research company of the US in chemistry, polymer research was approached. This was also of real importance to the contact with Japanese industry.

The lectures were given in the morning for two hours with a participation of about 50 students and faculty attending. I presented my lecture with slides but with additional explanation on the blackboard. It was difficult to see the success, as the students were struggling with the language, the subject matter and the cultural difference of lectures in Western style. I was never told at that time what the oriental style was exactly and I was not invited when a professor lectured to the students. This was Japanese etiquette and you did not ask any questions. What was not volunteered by the Professor, even for a visitor, was not needed to be answered.

It was an exciting time. A learning period was not only for my hosts and their students but it was even more important for me on the professional level and for my family and me on the personal level. We started to love Japan.

My teaching in Kyoto in 1968 was only the seed for my extensive interactions and activities in Kyoto and in Japan. As soon as I had arrived in Kyoto I was also asked to teach the same course at Osaka University, I had subsequently intensive interactions in teaching and research. I was also invited to visit and lecture in all major National Universities and in major industrial laboratories in Japan. Our stay in Kyoto was originally intended as a small course at Kyoto University. It became the stepping-stone for my extensive involvement and interaction with polymer science of Japan.

I visited Japan many times but always have considered the City of Kyoto as my "other" home. Whenever I was in Japan I gave a lecture at the University, which always included the Departments of Synthetic Chemistry and Polymer Chemistry. Furukawa had retired and Saegusa had become my contact man and partner. Our families had become good friends. Under his initiative, In 1980 Saegusa arranged for my wife and me to come again to Kyoto for a longer period, of one Semester. This time my support was provided by the Society for the Promotion of Science, Japan. Again I gave a 6-hour short course, this time on the results of our own work and surrounding subjects.

Saegusa and I had been cooperating on a number of subjects. He had hosted my former student David Tirrell for one semester. Saegusa had been my "substitute" at the University of Massachusetts when I was on sabbatical leave in Europe, teaching my courses and supervising my research group.

## **b. At Osaka University**

When I had arrived in Kyoto and had received my proper appointment, Furukawa came to me and said: "I have made arrangements for you to give the same course in Osaka University." What choice did I have but to accept this invitation with pride and satisfaction? Soon thereafter Professor Tani of the Department of Polymer Chemistry arrived in Konoe Hall at our living quarters to discuss this unexpected new arrangement. It was a great surprise but I was very happy to take this additional responsibility. My family had barely adjusted. But according to Japanese custom, the husband provided the funds and the wife handled the family - and my wife did so with love and enthusiasm.

Teaching in Osaka not only meant adjusting the course to the needs of Osaka University but also to learn --- how to get there. First to the lectures: The students and much of the younger faculty came not only from the department but also from "neighboring" departments. It looked to me as if it was easier to "penetrate"; students and junior faculty spoke to me and with me with greater ease. One of the students became not only department head at Osaka University and also President of SPSJ, another Vice President of Osaka University.

The course, as in Kyoto was exciting for me, the climate a little more relaxed and the students and younger faculty who attended the course, bright and dedicated. Although it was a course in the "books" of the University there were no exams, only discussions after every lecture, but they were more of a personal nature.

But to set it up and actually perform as a Professor and Lecturer was another Story. Professor Tani was my host. He had arranged for an office that I could use while I was at the University and for a secretary, Miss Keiko Hashimoto. She spoke some English and took care for my everyday needs. Now she is the wife of Professor Ueyama. In recent years my wife and I have been in contact with them.

To give some background. Tani was the "Organic Chemistry" Professor of the Department of Polymer Chemistry. His jo-kyoju was Takeo Araki, who became Professor in Matsue University and finally at KIT. His jo-shu was Hajime Yasuda who is now Professor at Hiroshima University. The department also included Professor Murahashi, Tadokoro, Ishida and Fukuda...There was also a Department of Engineering Science in the School of Engineering, The key Professor there was Heimei Yuki, also a Polymer Chemist.

To travel from Kyoto to Osaka on a scheduled basis was complicated especially for a "gaijin", a "Western Foreigner" who did not speak Japanese. Osaka University was about 40 km away from where we lived in Kyoto. We decided that the best way for me to go alone would be for me to take a taxi to the International Hotel in Kyoto, take a bus to the Osaka's Itami airport and take a taxi to the University. This was expensive but safe for me because I could not get lost. I did it 2 or three times and then found the best solution, and a solution that "local" people would use.

I took the bus to downtown Kyoto to the terminal of the Hankyo line at Kawaramachi/Shi-jo. I then bought a ticket for Osaka. It was important to learn the sign (in Japanese) how to buy a ticket how to find the express train at 8:37 to Osaka. It was important to detrain at Ju-so the last stop before Umeda-Osaka and take another train to Takarazuka. This was difficult because one had to change trains in Ju-so. There were 17 tracks in Ju-so station and not the track assignments were the always the same every day. The instructions were in careful details but were only in Japanese. People on the platforms were in a hurry because they were on the way to work and did not

speak enough English. Why should they? Once on the train I had to exit at Hotarugaike (fortunately the station names were also written in English!) and take a taxi to the University, the Toyonaka Campus. I was never lost! At 10:00 a.m. was my 2-hour lecture every Thursday! I barely had time to drink the traditional green tea that Miss Hashimoto had prepared. Later I mastered the walk from Hotarugaike to the University. Several Professors from the University came at the same time, showed me the way and accompanied me. What an exciting period of my life.

The first day of my course lecture, the Dean of Science of Osaka University, Professor Murahashi, took me to lunch at the faculty club of the Toyonaka campus with two or three faculty members. It was a delightful occasion. Murahashi made me feel at home at the University and I kept in contact with him over the years, even after he had retired. My wife and I once visited him in his home near Sakai-Osaka. He was in his 90s and still very alert. He had been one of the pioneers of polymer science in Japan after the war especially in the Osaka-Kansai area.

The faculty club located at the edge of the Toyonaka campus was named after a steep hill called " Matsukarayama". The club also had a number of rooms that could be used for visiting faculty. We stayed there several times, the last time when I gave my last short course at the University. In 1968, it was customary to go to the faculty club for lunch when I was at the Toyonaka Campus on Thursdays. During that time student unrests erupted in Japan, led by a leftist and highly aggressive organization "Zengakuren". It was in part directed toward University reform but also to American involvement in Vietnam.

At the latter part of my visits it became dangerous to walk to the faculty club from the Chemistry Building. Miss Keiko Hashimoto who spoke very little English, prepared sandwiches for me to keep me happy and fed. When I saw Keiko recently, we were now 30 years older and she spoke excellent English. We were amused at the situations, as they had existed in the late 60's and that were potentially dangerous,

Over the next 35 years I lectured extensively at Osaka University. The emphasis changed. While in the beginning my visits, lectures and short course presentations were initially organized by the Department of Polymer Chemistry, now Macromolecular Chemistry, the sponsorship changed to the Department of Engineering Science, although those two Departments worked closely together. They were only separated for organizational reasons based on the University structure. Koichi Hatada, the jokyoku of Professor Heimei Yuki had spent one year with me as a postdoctoral Research Fellow and took over the organization of my visits to the Toyonaka Campus.

Almost every time I visited Japan I was asked to give short course at Osaka, usually a 6-hour short course, three 2-hour lectures. These short courses had become "longer", because by 1980's or even later in 1990. The students were much more fluent in English and their comprehension was greatly improved. I spoke slightly slower but almost in a normal pace. A 6-hour course, always registered formally with the University, gave the students course credit. However, we did not bother with examinations. In addition to the lectures I always provided students with handouts and most of the time with copies of the slides. It would have been difficult to judge a subject from language comprehension. I gave the last of these short courses when I was at KIT in the fall of 1996.

I gave my last lecture at Osaka University in 2001. During the lecture period in 1996, Osaka University bestowed on me the honorary degree of Doctor of Science in special recognition for my service to the University, the first non-Japanese, to receive this honor.

### **c. At Kyoto Institute of Technology**

Kyoto was and is like home in Japan for my wife and me, especially for me. I had started my activities in Japan in Kyoto and had visited many times for various periods. I was closely associated with Kyoto University, the Departments of Synthetic Chemistry

and Polymer Chemistry and their faculty members. Kyoto also had a campus at nearby Uji, south of Kyoto, the Research Institute of Kyoto University. Kyoto University also had another important University, the Kyoto Institute of Technology.

I had visited Kyoto Institute of Technology (KIT) a few times and had written an article about the University in Polymer News with Professor Araki. The faculty of KIT came largely from Kyoto University. Among my friends at KIT was Professor Takeo Araki whom I mentioned before when he was an Associate Professor at Osaka University and Professor at Matsue University. He had joined KIT in the 1980's as Professor and his wife's father had formerly been President of the University.

I had another connection with KIT. Professor Fukui, a friend of Furukawa, whom I knew from my 1968 visit in Kyoto had retired from Kyoto University in 1981, and was selected President of KIT. He received the Nobel Prize the same year. KIT was not called by that name which for use in English. KIT is officially called Kyoto University of Crafts and Technology (Kyoto Kogyo Sen-i Daigaku). Fukui had "translated" this name into KIT, probably to mimic MIT (Massachusetts Institute of Technology). KIT is in the northern part of Kyoto in a beautiful location on the banks of the Takano River and the township of Matsugasaki. By the early 90's Fukui had also retired and was succeeded by Professor Maruyama, a former Professor of Kyoto University.

KIT consists of two parts, Architecture and Science, each part is headed by a Vice President/Dean. My friend Araki had risen to the Vice President of Science & Technology. I had become interested in the chemistry of oriental lacquers at the time that I had finished my turn as President of the Pacific Polymer Federation. The Federation had started to prepare for its second meeting in Japan, with a section on "Polymer Science and the Arts." When I visited KIT, I asked Araki to help me contact an Oriental Lacquer producer. We succeeded and our work on the components of Oriental Lacquer started in cooperation with Professor Hatada in Osaka. At the same time Araki ask me if it were possible to make an arrangement of cooperation with the

Polytechnic University. I still was very active at Poly and it was readily possible to come to this arrangement. Within a few months the agreement of cooperation between Polytechnic University and KIT was reached and signed.

In 1995 I was ready to retire from Polytechnic University and Araki asked me: "Could you care to come to KIT for one semester as a special Professor?" I immediately accepted. KIT applied for this professorship to Monbusho, the Ministry of Education, Arts and Sports and the request was granted for the fall semester 1996. The salary came directly from the Ministry and was not part of the KIT budget. The purpose was to attract senior Professors to teach in a University of slightly lower rank than the large National Universities.

As I arrived in Kyoto - my wife came about 2 weeks later- I was welcomed at the Kansai Airport by the Vice President and his wife and taken to the house in Jodo-ji on Kagura-gaoka near the famous temple Ginkagu-ji, the Silver Pavilion. The University had rented a house for us in one of the loveliest locations in Kyoto (the house was available because it had been sold and was to be reoccupied shortly after we left. I (We) had to take care of a somewhat modern, but Japanese house.

The teaching was arranged in a 20-hour course for graduate students and a 20-hour course for undergraduate students. In addition I had an obligation to go to the Japan-US Symposium on Polymer Synthesis in Sendai. I had started the sequence of these Symposia with Furukawa in 1972.

As soon as it became known that I had received the Monbusho Professorship, I was invited to be a Special Lecturer at the Annual Symposium of SPSJ in Hiroshima. I was also asked to give a short course of 6 hours at Osaka University. This was impossible to refuse because I received at the same time an honorary degree of Doctor of Science from Osaka University.

Let me first mention my responsibilities in Osaka. I had been there on many occasions. I chose to use as the title of my presentations. "Polymer Science and Technology for the 21st Century." It allowed me to give anecdotal presentations; the story of important discoveries, some of the work that my research group had done and pointed to the cooperation that had existed with the Osaka group for nearly 30 years, and most intensely during the past 15 years.

Now to KIT:

I presented first a simple introductory course in "Polymer Chemistry". For simplicity, I chose to give the lectures as "chalk talks." Even in Massachusetts I gave most of my lectures as "chalk talks", as I pointed out in an earlier chapter. Before I began my lectures at KIT, I did some homework. I "sat" in on some lectures of my Japanese colleagues to find out how they lectured to their students. I spent a few minutes in the back of the room to listen to several lecturers. Most gave talks with "overhead" projectors, based on overheads that were copies of pages from books.

I decided that I had a problem of subject matter as I presented it and a language problem. It turned out that the lectures had to be translated by my "mentor" Associate Professor Horoyo. This provided an additional problem. When lecturing to audiences in foreign countries, in Romania and in China, some of the lectures had to be translated, but this was for mature audiences. This time I was lecturing to beginning students and the lectures were translated and explained. With the help of my younger colleagues we solve our problems successfully.

As it turned out, the "chalk talks" which I used for my lectures were well selected. The students had time to copy while I WAS WRITING on the blackboard. I enjoyed this particular course very much, and the students were very appreciative. Each student had to take a written examination; I requested a short essay of some of the subjects, which the student could choose. Horoyo handled it all superbly. He graded the questions that I had submitted and we both encouraged the students for their later graduate studies.

The course for graduate students on "Aspects of Polymer Chemistry" was a little easier. The lectures did not have to be translated, but it was still challenging for me. I had initially thought I would give a course of broader topics but soon realized that I was teaching in a Japanese University. Students are committed to a research group and the knowledge of the research group, a koza, and not the knowledge that is available to the entire department. As a consequence, in lecturing one had to be careful that the entire audience was addressed, and not a special section. Checking and crosschecking that students could follow your reasoning was essential. There was the additional problem that the students only gave polite answers if the Professor, especially a "famous" Professor, asked them questions. It was difficult to ascertain the right level of comprehension in science and language. I had my "spies" in the low rank of University Instructors, research assistants and even secretaries who provided me with the information needed for the next lecture. In this course I used overhead projections so I did not have to write everything on the black board.

I realized in these courses at KIT that little had changed since my first teaching experience in Japan in 1968. Speak slowly repeat and make sure what you said was understood. The principle was not different from teaching in general.

When I arrived at KIT, we had a welcoming party for faculty and all students, and, when I left, a farewell party. It was very amicable because I had been there for 3 months and most students started to know me. In addition, with many people I knew, faculty or staff, I had tea or lunch. They helped me whenever I needed help.

With great sentiment, I remember my morning trip to my office; I took bus #204 from near my house in Jodo-ji to Takano-bashi and walked to the University watching the Sagi (Japanese blue heron) fishing in the Takano River. Or I would take the bus #203 to Demachi-Yanagi and changed to the #4. It was shorter but I had to buy 2 bus tickets. When it rained I took a taxi home. It was a wonderful time in Kyoto 8 years ago.

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## **G. In Germany**

### **a. Universität Freiburg**

In 1972 I had been at The University of Massachusetts about 2 years. The German Department had an exchange program with the University of Freiburg, the "Freiburg Program"; the person in charge was Eva Schiffer. Our fledgling Polymer Program was pressured by the University to commit itself to become a Department. It occurred to us, I do not remember who had the original conception, that we should be involved in some aspects of the Freiburg program. There were some good reasons.

The University of Freiburg had the best-known Institute of Macromolecular Chemistry in Germany. It had been founded by Professor Hermann Staudinger, who received the 1953 Nobel Prize in Chemistry. He had received the Prize for his concept that macromolecules or polymers were long chain molecules of very high molecular weight. Our Polymer Program in Amherst aspired to achieve the same respected status in the United States. At that time Professor Hans-Joachim Cantow, was the head of the Institute of Macromolecular Chemistry.

We were ready to formally propose an agreement of cooperation between our program (soon to be a department) and the Institute of Macromolecules in Freiburg. When Cantow came for a visit to Amherst, we met in Dean Appley's house on Lincoln Avenue to establish a cooperative program between the Institute in Freiburg and our Polymer Program at the University of Massachusetts. Dean Appley was responsible for Graduate studies at the University. Eva Schiffer was also there and a number of faculty members and staff of the University, especially from our Program. An agreement was reached. I had the most interest in the project, since I was the organic polymer Professor and spoke German. Consequently I accepted the assignment of going to

Freiburg as the first Professor of this program.

In November 1973 I left Amherst to go to Freiburg for about 5 weeks. As in most cases timing was very important. I had been elected as the new Chairman of the ACS Polymer Division, for 1974, and our program was to become a department. Since both of our children were still in High School I went without my family.

I moved into a University apartment and had an office at the Institute. Unlike later teaching assignments, which required both lecturing and traveling to other institutions, the Freiburg professorship was restricted to Freiburg. It was not a formal professorship within the University of Freiburg but a professorship within the Freiburg agreement between the Universities. I gave about 8 lectures on "Special Topics in Polymer Chemistry" in the form a short course.

The Institute of Macromolecular Chemistry had two full professors: Professor Husemann (also called Husefrau, because she was a woman, one of the few woman professors in Germany)) the organic chemist and Professor Cantow the physico-chemist. Husemann was the official successor of Staudinger. Although she had a meager record of scientific achievements she had devoted her life to promote Staudinger's fame. She was the soul and organizer for the building of the new Institute. My contact man was Cantow, who was then the director of the Institute. He had come from Industry, I believe from Hoechst. Other highly respected scientists fro Freiburg had infiltrated the University of Mainz. W. Kern, the true scientific successor of Staudinger. G.V. Schulz, R.C. Schulz and ultimately H. Ringsdorf, the last graduate student of Staudinger.

I spent my time preparing my lectures and talking with my colleagues. I presented my series of lectures as it was required It was very enjoyable, because they were scientific colleagues and not competitors. I learned much during this period, and learned how other more established Institutions functioned.

I would like to mention an amusing story. I am sure today I would not do it again. One day Cantow came into my office and said., he wished to tell me something and would also like to ask me a great favor. Husemann was retiring and they were ready to appoint a successor. Everything was already fixed; Gerhard Wegner was selected as her successor. In order to follow University rules, three candidates had to be submitted. Dr. Greber from the Ciba Company in Basel was one of the candidates. He was scheduled to give his lecture the next week. He thinks he might have a chance to be appointed. One more candidate was needed to fulfill the University requirement. Since I speak German, Cantow asked me if he could submit my name as a candidate but I would not accept the position if, by accident, I was selected.. He asked me to make my regular lecture a little more formal, because the dean and the selection committee would be present. The Institute in Freiburg had been nice to me, and I wanted the cooperative program to succeed, consequently I agreed. Looking back I should not have done it. Gerhard Wegner became Husemann's successor.

## **b. Freie Universität Berlin**

For my sabbatical year I had planned to go to Strasbourg. I was also in discussion with my friend Manecke, Professor George Manecke to spend some time in Berlin. To be on the safe side, if Strasbourg did not come through, I encouraged Manecke to follow up with his proposal. He intended to apply for the Alexander von Humboldt Prize for me and if I were selected, I would go to Berlin. I received both, the professorship in Strasbourg and the Humboldt Prize for Berlin. I accepted the Humboldt Prize for half a year and went to Berlin in April 1976. My responsibility was to teach a one-hour credit course in the spring/summer semester at the Free University of Berlin in Dahlem.

We packed our belongings in our red Opel and drove to Berlin. We settled in our nice University apartment in Dahlem, within walking distance of the Institute. My office in the Institute of Organic Chemistry was right above the laboratory, where Hahn and

Strassmann had carried out their experiments to split the uranium atom nearly 40 years before.

The Humboldt Prize provided the funding for my appointment as an Adjunct Professorship of the Free University in Berlin. I prepared my 13-hour (one credit hour) course under the title "Polymer Chemistry with special emphasis on selected topics". The course content was a mixture of my introductory course from Amherst and some special topics of my own interest. I gave the lectures in English, as my German was not sufficient, to teach properly on a University level. We had a good attendance for the lectures, about 25-30 students and most of the professors of the Institute. During this period I became very friendly with Professor Kossmehl a close associate of Manecke who helped me whenever I needed help.

My wife and daughter left in August but I stayed on for another few weeks to fulfill my obligations. The life in the Berlin atmosphere of the 70's was very enjoyable and we were very happy that we had the opportunity to spend some time in Berlin. I did not get involved in any research but wrote a number of articles while I was in Berlin.

Manecke also had an appointment at the Technical University in Berlin and several of his students were located there. He was also a member of the Max Planck Institute, which was located within walking distance from the Organic Institute. Excellent and world famous physico-chemists and physicists were members of this Institute. During my stay in Berlin, I met a number of them. I was particularly interested in those who had interests in polymer science. Dahlem was also a good basis to visit scientific Institutes in East Berlin and East Germany.

### **c. Technische Universität Dresden**

We had known Professor Werner Berger from the Technical University for some time. He sent Dietmar Lehman, his Assistant to work in my laboratory as a post doc fellow in

1980. Berger also spent about 6 weeks in the summer in Amherst. He asked me if I would be interested in coming to Dresden for a month and teaching a short course. After thinking things over and discussing it with my wife we accepted under certain circumstances.

I insisted that the position would be that of a Full Professor for one month at the highest salary level that was available at that time in the GDR. The University accepted. We arrived in Dresden in the beginning of April 1982 for one month. This was a difficult time for me because of my involvement as the Vice Chairman of the IUPAC Symposium to be held in Amherst later in the year and I was extremely busy. However, most of the decision-making had been done and the organization was in the hands of the University organization. Still we felt it was a challenge that should not be missed.

We were assigned a nice apartment on the 15th floor of the student tower overlooking the City of Dresden. The day we arrived the University ball was held and we attended with pleasure. Next day I had to go and see the Rektor of the University, Professor Knauner who welcomed me to Dresden and handed me the contract.

I should mention that we were provided by a private person with a car, a Russian made Lada, soon after we had arrived. The fee was quite modest, but payable in dollars, in advance, and in cash. We were only told not to drive in the border security zone. To our question "why?" we were told the car was qualified to enter this zone while other cars that belonged to regular citizens could not.

The Department of Chemistry was headed by Professor Pippel. He worked closely with Berger on a new fiber from acrylonitrile based on lithium initiated anionic polymerization. I became slightly involved in the project although I was convinced that it would not work in practice, which turned out to be true.

I became also acquainted with Professor Gloeckner, who worked on macromolecular characterization of polymers, Professor Hans Kammer, a polymer theoretician and the organic chemist Professor Mayer, also called by his friends, the Schwefel-Mayer because of his interest in sulfur chemistry.

Again, my main duty was to present lectures in the form of a short course. It was more informal and without examinations, only a sequence of lectures, involving some of my own research interests and subjects of more general interest in polymer chemistry.

In total I gave about 10 hour lectures, one was usually presented in the morning of Tuesday right after the general "get-together" of the department, faculty and staff. Coffee and cake were served in a general meeting room. Science was primarily discussed but discussions were also carried out on bowling and other social activities.

Some of the lectures in the Department were followed by question and answer periods. The students were interested in scientific matters such as meetings that are being held abroad and a "who is who" of important polymer scientists and their interests. Subjects about the US came up sometimes in the discussions. I explained our points of view to the surprise of many. One of the Assistants left Dresden shortly after our visit and made it to West Germany. After the re-unification of Germany, he returned to Dresden as Full Professor and is now a highly regarded member of the faculty there.

In addition to our activities in Dresden at the University Jane and I also visited other Universities, Jena, Merseburg, Berlin, and the Polymer Institute in Teltow-Seehof.

## **H. Technical University Warsaw**

I had good scientific relations with the Academy of the Polish Academy, especially the branch in Lodz and also with the Academy Institute of Polymer Science in Zabrze.

In 1978 I was preparing for a scientific trip to Poland. The President of the Technical University, Professor Pacynkiewicz, whom I knew from previous meetings, asked me to give a short course at his University. I was very happy to comply and told him that, if he wished I could give a 10-hour short course at his University.

Pacynkiewicz wanted me to give a specific course in topics of unusual polymerizations and (our common interest), advances in oxirane polymerization of functional oxiranes. Pacynkiewicz had done some excellent work on oxirane polymerizations.

It was a wonderful experience. The students of the Technical University in Warsaw that attended my course were highly competent and motivated and it was a pleasure to be associated with them.

Warsaw University was a highly intellectual community and its leader, Pacynkiewicz, as a chemist, was a striking personality. Subsequently I had two of his coworkers in Amherst as my postdoctoral fellows. One, Zbigniew Florianczyk, became, after the departure of Communism from Poland, the Director of the Polymer Institute of the University.

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## H. In China

### a. At Wuhan University

In June or July 1983 I was approached and asked if I would be interested in coming to China for a month to teach polymer chemistry in selected Universities. The trip for my wife and me would be paid by the Chinese government via the World Bank. Jane and I talked it over, realizing all the other commitments that we had. Jane was setting up the business office of the ACS Polymer Division within my office in Brooklyn. I had just been appointed for the next year the Chairman of an advisory committee for the

President of Enichemica in Milan, Italy.

In September I arrived in Beijing and was ready to go. The objective and the interest of the Chinese government was to update 30 "second rate" Universities to international standards. I was assigned primarily Wuhan University and East China University in Shanghai.

It was a complicated assignment as I soon found out. From the beginning the project was ill defined and neither the Chinese authorities nor I knew exactly what was planned and what was expected. I arrived in Beijing and my Chinese colleagues arrived to discuss the matter. I believed that I would have the possibilities to discuss with my friends how to proceed. I was indeed told that it was all right to see my friends at the Institute of Chemistry and the Institute of Photochemistry in Beijing, and the Beijing Polytechnic University. The Vice President had a protégée, Liping Hu, who became my post doc fellow, and a husband who was the party secretary of the Institute of Chemistry in Beijing. Years later the University moved to Anhui.

But when I requested seeing my good acquaintance in Tianjin, Professor He, I was told that was impossible. My answer was very clear and decisive. If this is the case I will take the next available flight back to the United States. Within an hour a high-ranking representative from the Chinese Department of Education, the sponsor of my trip, showed up. I told him that I would not be restricted to do what was possible under our agreement. I was given the phone number of Professor He and it was dialed. He told me that he was very ill and not able to receive me at his University. He at that time was among the 10 most influential and competent polymer chemists in China.

It finally came out that my real appointment was in Wuhan. In our initial agreement Wuhan was one of the stops of my polymer teaching in China. I later found out that the driving force for my being invited for this task was Qian Baogong one of the Vice Presidents of the Chinese Academy. Qian Baogong was a graduate of the Brooklyn

Polytechnic University. After his graduation he had returned to China just at the time when the communists took over. He survived all the turmoil in China in the 60's and 70's. He was located in Changchun, in Northeast China and had become the head of the Institute of Applied Chemistry. For some reason his real interest was to live and work in Wuhan. He became the President of the Wuhan Branch of the Chinese Academy of Sciences. This was at that time, I suppose, a powerful position, far away from the capital Beijing and safe.

After my initial problems, my wife arrived and we visited the Great Wall and the Ming tombs and we were ready to go to Wuhan. Wuhan was a City of 4 million people, with hardly any paved roads even in the city. We were placed in the government guesthouse, a place where Mao used to stay when he was in Wuhan near the East Lake when he was in Wuhan. The lake was rather shallow and large and near the guesthouse there were hundreds of different birds, different because they were Chinese birds. Even similarities to our birds meant substantial differences. Jane, as a bird watcher had a grand time, since she had acquired a bird book in English. First I had to meet the President of the University, Professor Liu.

He was a delightful and very competent person, an inorganic chemist. He was trained in Moscow. In China the most promising scientists and teachers were trained a.) Until the early 40's, in England, b.) Until 1950 in the US and c.) From 1950 to 1960 in Russia. This combination of training caused a considerable amount of confusion in the Chinese scientific community.

Now to the teaching: I was told I should set up a polymer laboratory at the University. I had prepared for setting up basic lectures and laboratories. We actually did some of it.

I was soon asked, if could present scientific lectures and how science was done at that time in the world outside of China. I was glad to comply. What I did not know at that time was the Department at the University had already invited scientists from nearby,

even from the Institute in Lanchow, 1500 miles away to attend my lectures. Remember this was the beginning of the "opening" of China. The head of the department asked me if I would consent that the lectures be taped and I agreed. He also told me that 400 copies would be made and distributed in China where needed. I allowed them also to copy my slides.

The proceedings were as follows I was picked up with a car after breakfast, had my lecture until 11:00 to 11:30 and was brought back to the guesthouse (which seemed to have been also one of the best restaurants in town) for lunch. I was picked up again for my lecture at 2:00 p.m. for 2-2 1/2 hours. This went on for 10 days. By that time I had completed my obligations of 20 hours of lecturing.

Our reception and treatment was first class. Almost every night a 9 course "banquet". Sponsored by various organizations and companies. We were taken sightseeing - and when we needed, a new tube of toothpaste it was found in some store!

My obligation completed I wanted to return to Shanghai, my next destination. We found out that the plane for which we had reservations did not fly. Why would I want to leave? The Chinese authorities expected me to stay another week sightseeing or doing something or nothing. We were told the plane was used for something else or someone else. There was a flight with seven stops on an Antonov 24, a Russian plane that had not had spare parts for 25 years. !!

We made the usual fuss. All of a sudden, there was room for the two of us on the original plane from Wuhan to Shanghai. The military had taken over the plane. Jane and I were the only non-military persons in civilian clothes on board and we were even Caucasians and Americans. We felt safe being surrounded with colonels even a couple of lower ranking generals. We felt we were on a well-maintained aircraft.

We had arrived from Wuhan on the scheduled flight that turned out to be a military

flight. We had been "invited" and allowed to use two seats on the plane that flew once a week (on Tuesdays). We arrived in Shanghai and were met by all my friends. God knows how they knew that we were on the plane. This is the myth of the orient, the myth of China. Maybe they never found out that the scheduled flight had become a "scheduled" military flight. I should say, that Wuhan Airport was a military airport and was controlled by the military. Civilian flights were allowed to land and take off, but the military had the final "say". All these "fine" details we learned much later. "Everybody" knew but nobody told us.

## **b. At East China University**

We were in Shanghai, ready to perform at the East China University for my teaching assignment. My wife and I were placed in the Cypress Hotel, which is located between the Shanghai Airport and the Zoo. The Cypress Hotel was a Japanese built modern Hotel. It had been built on grounds, that had belonged to Mao and the mansion at the end of the property could still be seen. We were located in a suite (a double room), paid by the allotment from the World Bank, in other words, our allotment. We immediately changed to a normal comfortable double room.

My work started the next Monday morning at the East China University. The objective was that I would present a 12-hour short course on Polymer Chemistry. I was picked up in the morning to discuss the lecture schedule; my wife was invited to accompany me. I had agreed to give a 12-hour short course in one week.

Having found out that my wife was the Business Office Manager of the prestigious ACS Division of Polymer Chemistry, the interest changed. She was invited to give a lecture on "College Education in the United States". She was happy to agree. Later more on the subject.

I started my lectures with about 40 students in attendance. They were competent and

anxious to have contact with polymer science as it was taught in English. I should emphasize that in Wuhan and here in Shanghai it was not only the subject that was of interest, but to hear the subject in English.

I was very careful to present the subject slowly with careful attention to the students understanding the subject not only from the technical point of view but also from the language point of view. In 1983 I was a pioneer in teaching polymer chemistry in China. The opening for China was only 4-5 years old, main roads in Shanghai were still not paved and I did not know how the students had acquired their good language skills of English. They were very motivated and I was very delighted to have these students in my class. I had a chance to meet a few of the students outside the classroom. This was not easy task for a Westerner, an American.

More spectacular than my short course on Polymer Chemistry was the lecture that my wife, Jane C. Vogl presented. I was busy with my lecture; consequently I cannot confirm it first hand. When she arrived in the lecture room, expecting perhaps 10 or 15 people, she was confronted by an audience in excess of 250 students. Soon the lecture became a question and answer session. From outside sources it was a resounding success.

In addition to my responsibilities at East China University, I gave a few additional lectures in other Universities in Shanghai before we returned to the United States.

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## VIII. Professional Societies

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### A. The American Chemical Society

I was hired by DuPont in 1956 at a time when science and science achievements dominated the business sector of a profitable large chemical company. The scientists were working on novel, and it meant novel, scientific achievements. There was always the hope of turning some of these inventions into business successes. This is not the case any more. Emphasis was directed toward new and better Nylon, polyesters and polyolefins. The products had to be completely under the control of the inventing company.

In the '50s, the question was, how to inspire new inventions. One solution was to hire the potentially most competent scientists, if there was no direct job available "stockpile" them, give them a half-year job to learn the objective and needs of the company. This strategy and approach does not exist any more. Was it necessary and is our present approach of hiring and integrating into the company any better, more efficient - or cheaper?

Today one might call it the stone age of polymer research. When we were making new polymers we hoped they would be useful at some time in the future. They were novel, were patented for the inventor of the company and belonged to the company.

Scientists like myself worked to find new products and new principles we spent our "off-hours" in the library in my case in the Lavoisier library of the Experimental Station. This exercise not only familiarized one with the subject but also --- provided time for daydreaming, surrounded by the knowledge of yesterday and the distinct smell of books. This was encouraged by the company, as long as it was on your time, even if it was on a subject that did not have any relationship with your assigned work in the company. The scientist was encouraged to go to scientific meetings (as long as it did not cost too much for the company). At the Central Research Department (CRD) of Du Pont, most leaders had positions of national scientific importance.

I became intrigued by such national activities - and the attendance of national and International conferences. I mentioned some of my activities in an earlier chapter.

DuPont was the dominant factor of the associations of chemists in Wilmington. Maybe 1200 scientists were employed in Wilmington by DuPont, Hercules and Atlas. They comprised a major portion of the official Philadelphia Section of the ACS

### **a. The Delaware Section**

*Polymer Group:* To fortify my experience in polymer chemistry, which had now become my major scientific objective in my scientific life, I attended all the meetings of the Delaware Section of the ACS. A substantial portion of the members of the Delaware section was comprised of polymer scientists. In 1967 I was asked to run for the position of treasurer of the section. I still do not know whether I had been nominated to "lose" or whether Nominating Committee hoped to have an efficient treasurer. I must mention, that in my University years Vienna I

had not been prepared for this kind of position. I believe that the leaders at that time in Vienna were also not prepared for positions of this kind. I lost the election. This was my first loss - and I believe my last loss of an election.

The next time I won the election handsomely and I then was interested in higher positions in the ACS Wilmington Section. In 1970 I left Wilmington and DuPont and went to Amherst, which belonged to the Connecticut Valley Section of the ACS.

*The Awards Committee:* The Delaware Section honored each year the most important scientific achievement that was accomplished by a member of the Division. It usually had to be published the year before the award was made. I was a regular participant of the local Delaware Section, attended the monthly meetings and was participating in many activities. In 1967 I was appointed the chairman of the Awards Committee, a group of people who looked over the scientific achievement made of members of the Section. This committee made sure that deserving people were nominated for the Prize of the Delaware Section. I did not realize that it was a responsible and dangerous position.

The bulk of the research of DuPont, Hercules and Atlas was done in Wilmington. Much of this work was novel, important and elegant. Furthermore some of the senior authors held important positions in their respective companies and were active or officers of the Section.

As I recollect one paper was particularly attractive. It was an elegant reaction sequence in steroid chemistry. I remember visiting with my colleague Charlie Pederson from the Elastomers Department once in a while in his small and narrow laboratory. One day he showed me a 500 cm Erlenmeyer flask containing

a dark purple solution. He told me it was a solution of potassium permanganate. I said, I have seen aqueous permanganate solutions before and he replied but what you see here is benzene solution. He had added an aromatic cyclic ether of a certain ring size to benzene and potassium permanganate. In this mixture, potassium permanganate that is normally completely insoluble in organic solvents had dissolved in a large portion. As we know, the reason for this phenomena is that the potassium ion forms a stable complex with the cyclic ether and the complexed the potassium ion of the permanganate is soluble in benzene.

I convinced the Awards committee of the novelty and importance of this work and we presented Pederson the Award of the Delaware Section of 1967 to the consternation of many potential recipients. This principle turned out to be of enormous importance and in numerous variations is used by many chemists. This was the only prize that Charlie Pederson received until 1987, when he was awarded the Nobel Prize in Chemistry.

*MARM Meeting:* The ACS held not only two annual national meetings, but also regular regional meetings. The meeting in our area was the Middle Atlantic Regional Meeting (MARM). In 1968 this meeting was assigned to the Delaware Section. Fred Wiesenberger, of the Textile Fibers Department was appointed chairman and he asked me to be his Vice Chairman. It proceeded according to the plans and Fred's strong leadership. I learned a lot about meetings and how to run meetings. And enjoyed this function very much

## **b. The Connecticut Valley Section**

The ACS consists of local Sections and of Divisions. Each member is automatically a member of a local section. To be a member of a Division the ACS

member has to select and join a Division - and where it is required must pay the dues to the Division. As I moved from Wilmington to Amherst I became a member of the Connecticut Valley Section.

The Connecticut Valley Section is a "weak" Section because it consists of Massachusetts and Connecticut but without the "plums" of the region: Boston Worcester, and the coastal strip in Connecticut including New Haven, with Yale. The central location of the Section is Hartford. About two years after I had moved to Amherst, Norbert Platzer - the perpetual nominating Chairman of the Section, (and a fellow Austrian) asked me if he could place my name for the nomination for the Chair. For some reason, I said yes, won and was the Chairman of the Connecticut Valley Section in 1974.

Very little could be done to "improve" the Section, because it served primarily the small colleges in the Hartford area. Jane and I went to most of the Colleges, some in Hartford, Wesleyan College, Trinity College and Williams College. The Chemistry Department at Williams College was not interested in us, because the Department would have rather be associated with the Rensselaer Polytechnic Institute (RPI) in New York, which the ACS did not allow.

I arranged a small financial support (\$ 75) from the Section for the Seminar speakers at each of the Colleges. Jane and I went to one good seminar at Wesleyan by Eyring's son from Utah University. Other than that the officers and the executive Committee of the Section held required regular meetings.

The high point of our activities during my function as Chairman of the Connecticut Valley Section was the Annual Symposium, held in Hartford. I selected as the subject title "Chemistry and Fashion". I had speakers from DuPont, Eastman

Kodak and a couple of other companies. I thought it was unusual, very interesting and very successful.

The only people from a large University were a number of members of the Chemistry Department of the University of Massachusetts. The star was ultimately Ron Archer, who is still active as Councilor of the Section and represents the Section superbly in ACS affairs.

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## **B. The ACS Division of Polymer Chemistry**

The Polymer Division: I had become known though the frequent attendance of the Gordon Research Conference as one of the young "Turks". At this time the relationship between persons involved in the Gordon Conference on Polymers and the ACS Polymer Division was very close.

**Program Committee:** It was at the ACS meeting in Atlantic City, in 1967, when I ran into Jack Elliott, Stretch Winslow, Jesse Hwa and I believe Bill Bailey, all regulars at the Gordon Conference on Polymers, on the famous Boardwalk. They were rushing for "The meeting" in Winslow's bedroom. I imagine about 7 or 8 people were present to discuss the future of the Division. The discussions involved the future of the division, the disastrous situation of the treasury and new directions of the Division.

The Division had gone through 3 periods: a.) The founding, b.) The stabilization and growth period, led by Winslow, Ed Fettes and Bill Bailey - and how c.) The future would develop. Much of the business of the Polymer Division was decided by relatively few "regulars" at the Gordon Conferences of Polymers in New

London, NH. As the youngest and newest man I was assigned to the program committee, where I served for two years.

*International Membership Subcommittee:* Jesse Hwa was the Membership Chairman, one of most important position in the PD. As a member of the Program Committee I had a chance to learn the trade of how these organizations were run, especially the ACS Division of Polymer Chemistry. I decided to commit myself fully to this organization.

Bill Bailey was the Secretary/Treasurer of the Division, which had already over 4,000 members. The membership fee was \$ 5 year. It paid for the preprints and the Newsletter. Under Bailey's Chairmanship in 1968, the position of the Treasurer was separated from the Secretary. Porter became Treasurer, and Kinsinger Secretary. At the same time, under Haw's recommendations, an international membership sub-committee was created and I was appointed chairman. In the fall of '68 I was on leave in Japan for a Semester. My main thrust was membership recruitment in Japan During about two years as International Subcommittee Chairman the international membership rose from 180 to 520, one third were Japanese. A success like this was fun but also difficult to achieve, I had help from the group secretary at the Central Research Department of DuPont. Mary Alice Clark had a B.A. from the Connecticut College of Women. I had to be careful not to show too much outside activity vis-a-vis the Company even though I did it all on my own time, late in the evenings and on week ends. After all I worked for a company, and then, just as is today, too much outside visibility other than for company business was dangerous for a research scientist. Even today it is still not much appreciated.

*Polymer Division in the late '60:* Let me first comment on the structure of the

Polymer Division as it was after the "Bailey rearrangement". Bill Bailey was Chairman in 1968, with Kinsinger the Secretary and Porter the Treasurer. The Chairman was elected for one-year terms and the Treasurer and Secretary for 3 Year terms. Practically speaking the two officers were almost guaranteed the Chair if they wished to have it. The Division was run by the executive committee consisting of the Chairman, the Chairman-elect (Vice Chairman), Secretary and Treasurer, Past Chairman and the two Councilors and two Alternated Councilors. They were all elected by the Division. The Alternate Councilors had no voting rights in the Executive Committee, they were just alternates, if a Councilor could not attend his assigned function. The Chairman term was de facto also 3 years.

The Chairman appointed the Chairmen of the various Committees which I used to call, his "Cabinet"; he could also appoint the replacement of an elected officer who wished to resign. Importantly, the chairman appointed the chairman of the nomination committee, which gave him considerable control over the future of the development of the Division.

As mentioned Bill Bailey had the chair in 1968 followed by Elliott in 1969. We alternated always between academic and Industrial candidates for the Chair. Kinsinger was past-chairman in 1970, Bill Gibbs in 1971, Joe Kennedy in 1972, Jesse Hwa in 1973 and I had the chair in 1974. I mentioned the various Chairmanship of the Polymer Division,

The Division had been run as an amateur organization and Jack Elliott was determined to change it into a "professional "organization. He was a Vice President at GE and interested in the theory of management, not to run an organization but more importantly, how to plan for the future, its objectives, its possibilities and achievements. He had with him a newly elected Secretary, Jesse

Hwa, a manager from Stauffer Chemicals, who was also interested in the functioning and interactions in industrial organizations. As Treasurer I joined them and for the next 6 years we "ran" the Division as a triumvirate.

### **a. Treasurer:**

I had mentioned that I had been involved in the modernization. How did it happen? As usual, by accident. Under Elliott's Chairmanship, Roger Porter was the elected treasurer. In the middle of Jack's chairmanship, Roger decided it was too much for him, he had other interests that took much of his time and he resigned. One day Elliott called me and asked me if I would like to be appointed to fill the term that Porter had left incomplete. He said the treasury was in a mess and it would need a lot of attention to straighten it out. I checked with Jane (and my 10 year old daughter Yvonne) and asked if they were willing to help. In those days it was not necessary or desirable to pay, if something had to be done to help within the family it was done. I am still grateful to them for spending hours and weeks to reorganize the treasury.

This was complicated because I had just accepted the position of a Professor at the Polymer Program at the University of Massachusetts and Porter was the Head of the Program. Porter also let his term as Alternate Councilor of the Polymer Division run out.

An additional and unusual problem was created by Bill Bailey. As Secretary/Treasurer, he tried to attract more member candidates and supposedly make book keeping easier. He created a new membership style. In 1967 he created the choice of a three-year membership. In other words, instead of paying \$ 5 per year it was possible to pay \$ 12 for three years. This was an interesting idea had

one drawback. Initially, in the first year, there was plenty of money in the treasury, but something had to be left for the second and third year.

When we obtained the material for the Treasurer, it came in open shoe boxes, crumbled checks of \$ 5 or \$ 12 checks, handwritten notes but no actual accounting, no list of members who had paid or not. I had a lot to do, and all that as my family and I were preparing to move to the University of Massachusetts and I began to prepare for a new career - but it was worth it. My wife Jane my 10year old daughter were all involved in trying to straighten out the mess. All of us learned a lot, and even had fun. The most bizarre scenarios occurred. Finally if somebody said, he had paid, we had to accept it, and if someone said he had paid for 3 years we had to accept it without any questions asked. As I look back, I believe that very few members were dishonest Sloppiness and/or incompetence in the bookkeeping was the cause of the confusion? Porter had hired a girl, who, for \$ 2/hour was suppose to take care of the affairs of the treasury. She was to keep the incoming dues in order and keep records She never did, she probably did not understand and Porter probably never took the time to check the situation. Roger resigned and I became Treasurer. After a year and a half we (Jane, my daughter and I) had the treasury in order.

We were still amateurs and when the budget was reviewed it became clear that we had to increase our dues. The preprint costs were increasing too rapidly

More people could afford to go to ACS meetings and present papers that required reprints. I still remember the first issue of the preprints. They were created under Stretch Winslow's stewardship and Chester Rosenbaum of DuPont was the first Editor. They had a rather unattractive gray cover and were meager, as compared to what we have today.

The problems that we explained were not only a question of producing the preprints, 2 issues per year, but also packaging and the cost of mailing of 5,000 issues, at a typical cost of \$ 17,000 per year. The work other than the printing was done by unpaid volunteers. Now lets go back to the cost factor of the Preprints. The page costs (at \$0.39) were slowly rising. We had instructed the Preprint Editors Lenz and later MacGrath to bring in competitive to collect competitive estimates and bids from Printers. This was probably too inconvenient for them and the Editors ignored the request and instructions of the Executive Committee and The Treasurer to paid the costs of the bills. Jack Elliott raised the following point (he had checked known statistics out). Let's raise the dues to \$ 7 from \$ 5, rather than just to \$ 6. A certain percentage of persons will drop out, they just do not wish to pay for the extra costs, but the portion (about 5-10%) is the same if you increase by one or two dollars. He was right. We pay now \$ 35, receive an electronic version and nobody complains.

The cover became more colorful, the pages size became larger and the page number was 6 pages per paper. People loved the preprints; it was the most popular Journal at that time and still is. It had the great advantage of not being refereed and printed the uncorrected results and thoughts of the author. The papers did not need to be too long just communications. Errors could be readily corrected and it was the largest polymer Journal in English. But that became unmanageable.

A major decision had to be made for the Hawaii meeting in 1979. Everyone wanted to go to Hawaii and I could see a catastrophe on the horizon. We "old" treasurers, including the then present treasurer sat down and concluded that the page number had to be reduced. I had checked with Chemical Abstracts and was

told they would only record and review articles that were 4 pages long, two-page double column were also allowable. I proposed this new format. It was accepted with relief and we had this format until the Division went to electronic publication of the Preprints a few years ago. .

Another scary factor came up when Bill Gibbs, former director of the Air Force Laboratory in Dayton, OH became Chairman in 1971. He asked me what our budget was and I said about \$ 32-35,000 annually I mentioned also that in addition we were involved in charter flights to international meetings, primarily IUPAC meetings. Henry Friedlander, a self-appointed organizer, had been organizing such flights on behalf of the Polymer Division. One year this operation had a budget of about \$ 75,000. Bill asked me if I realized that if something went wrong financially, I, as the Treasurer would be personally responsible if something went wrong. I had no idea about this situation and Bill said that we should immediately incorporate the Division to relieve the Treasurer from any personal liabilities. Gibbs spent much of his term in office to prepare the incorporation, to find the proper legal advice and had the paperwork done. We were always under the impression that we were protected under ACS rules, but this turned out not to be the case. Since then the Division, the ACS Division of Polymer Chemistry Inc. is protected by the ACS.

A few words about the Charter flights: During the early '60s flying was still very expensive and had many inconveniences regarding scheduling. Henry Friedlander's brilliant idea was to charter a plane for Division members to attend major Conferences abroad. One week was used to attend the meeting another for sightseeing or vacation, flying directly to the location of the meeting and return again as a group. In this way we flew to the IUPAC meetings in Paris in 64, to Munich for the Prague meeting in '65, to the Tokyo/Kyoto IUPAC Symposium for

\$ 460 in '66 to Louvain in '67, to Aberdeen in '73 and ultimately to Rio de Janeiro in '74. On one occasion we needed 2 planes and I was responsible for one of the planes - as Treasurer! We flew regular Boeing 707's with regular seating but first class service. Henry was a hero and could not be criticized - and nothing went badly. Still it was worrisome. Henry was very fair but on one occasion he had accidentally overcharged. I still see him sitting in one corner in the airport lounge handing out \$ 20 bills from brown bags for the overcharge. I think everybody was reimbursed. A few "important people received "free" tickets. As Treasurer of the Division it would have been a conflict of interest. I never was high enough in Henry's favors even though for Henry's flight to Brazil I was the Chairman of the Division.

By the mid '70's people had become more affluent and individual flight deals with airlines became available and travel commitments required more flexibility. As a result, Henry under the auspices of the Polymer Division did not organize any more charter flights for a group. Henry's heroic period came to an end.

I handed over about \$ 12,000 extra money to my successor as Treasurer Joe Salamone.

## **b. Chairman of the Polymer Division**

I was the Treasurer of the Polymer Group in the Delaware Section and for 4 1/2 years Treasurer of the Polymer Division. With this experience I concluded that the success of any growing organization depended on a sound Treasury. The Polymer Division also depended on the ingenuity and dedication of the Treasurer. I had, in my 4 1/2 years as Treasurer of the Polymer Division, stabilized our disastrous financial situation in the Division that I had inherited. My theorem was

that the office of the Treasurer was the heart and success of the Division.

When I took over the Division in 1974 I had to face three significant problems. The Secretary did not cooperate as required by the constitution, the Preprint Editor spent what he thought was convenient without following the instructions of the Executive Committee and more importantly was the treasury. The Treasurer paid little attention to his responsibilities.

In the election in 1973 for the officers for the chair of 1974 I was elected Chairman, Karasz the Secretary and Jim Mark the Treasurer. At that time the election of an officer depended much on his scientific reputation rather than his dedication to serve. Jim Mark was elected Treasurer because he was scientifically well known. He had no real interest in spending much time for the well being of the financial affairs of the Division. We had quite a few discussions, of how much time the treasury required. Jim felt he did not wish to spend the time necessary and decided to resign from this position

Now I had the problem of finding a dedicated young ambitious person that was well recognized to take the treasury. Fortunately, there was a young Professor at Lowell Technological University, 35 years old, who was willing to take the position of Treasurer Joseph C. Salamone. Without his competence and diligence the Division would not exist, as we know it now. It is financially sound and ready for a continuous vigorous future. He brought with him his friend and close Associate Stan Israel

Joe Salamone continued to run the Treasury in the style and spirit that I had started. Stan Israel became his successor and both Joe and Stan brought the treasury of the Polymer Division to new heights. Israel became member of the

Board of ACS before his untimely death in 2003.

In the '60s, the Polymer Division instituted Biennial Meetings, symposia in which recognized scientists reported the status of their field of research. It had been customary to hold these meetings at major Universities with other Polymer Groups. In 1972, when Joe Kennedy was the Chairman, it was held at the University of Michigan. One of the reasons to hold these symposia was to give local students easy access to major meetings. It was always assumed that the meetings were budgeted to break even. Consequently, the Treasury of the Division did not get involved, in the planning or overlooking the budget. This had always worked well and nobody gave it any thought.

The Chairman of the Michigan Biennial was Charlie Overberger, head of the Chemistry Department and recently appointed Vice President of Research at the University. We believed that nothing could go wrong, but it did. At the end of the Symposium, the finances of the meeting were \$ 3,000 in the red. Kennedy, as Chairman said, that the Division would not cover the losses. We had a few unpleasant weeks of discussion. Kennedy finally agreed to pay half the debt from the Treasury.

This was a warning because the next Biennial was contemplated for Syracuse University. At this point Jesse Hwa was Secretary and Chairman elect; he took over and sent out a long questionnaire asking the members of the Polymer Division where and when would they wish to have the Symposium held. The answer was clear: around Thanksgiving in the South and it was determined that the meeting had to be financially self-sufficient. The next Biennial was held in Tampa/St. Petersburg, FL and it was a success. Biennials have been held in this style ever since. Jack Elliott the then Chairman of the Division had appointed me

to complete the term of the last Treasurer, I had been appointed to fill the term had resigned and was then elected for a full term.

After Kennedy, Jesse Hwa, the Secretary, was elected Chairman and Frank Karasz the new secretary.

For the next election in 1972, Jack Koenig and myself were nominated for the Chair. I still remember, when I heard the combination I was concerned and went to see my friend Elliott. Koenig was a friend from DuPont; in fact we were, for some time, in laboratories next to each other. He had left DuPont in the early '60's and became a Professor at Case Western University and a very well known expert in spectroscopy. Jack said: if you cannot win the election, you are not worth being chairman. We have to have 2 opponents each of whom can run the Division successfully. Fortunately, I obtained 63% of the votes and was ready to become chairman in 1974.

I will briefly summarize what was done during my chairmanship, some of it important, some of it trivial. I added three Committees to the activities of the Polymer Division: a.) The Awards Committee; b.) The Archives Committee and c.) The International Committee.

a.) The Awards Committee was charged with creating an Award given by the Polymer Division, independent of the ACS. It was conceived as an Award for service in the Division and outstanding innovative scientific accomplishments and I appointed Carl Wooten as the chairman.

b.) The 25 year celebration led me to recognize that it was important to have permanent records kept in archives by experienced people. The Chairman should have served personally the Division for some time and have direct knowledge of its development.

c.) The International Committee was to be responsible for foreign affairs of the Division. The Chairman was to know activities abroad and was in part involved and personally known to International polymer organizations and some of its key members. (Vogl)

Several more events sharpened during the year of my chairmanship. Of the trivias: we redesigned the stationary of the Division. Previously it had black letters and only the Chairman, voce Chairman and secretary shoed on the letter Head. The new design was in the blue that we still have with all the Executive Committee with addresses on the left hand side. Three years later, under Stannett's stewardship, a competition was held and the present logo became the official standard of the Division.

The friendship of the Division of Polymer Chemistry with PMSE was at its peak. Clara Craver was the Chairwoman. Clara and I held a joint dinner of the two executive committees at the ACS meeting honoring Speed Marvel at his 80th birthday with a giant birthday cake.

I appointed Ulrich to oversee our celebration of the 25th year of the creation of the Division of Polymer Chemistry. Kostner, the Chairman of the Paints and Varnishes Division in 1949 allowed the steering committee, Mark, Marvel and Flory to form a provisional Polymer Division, which was later formally accepted by the ACS as a separate Division The picture of the former Chairmen of the Division who attended the ceremony still holds a prominent place in my office.

1974 was also the year of 2 IUPAC Symposia, the official one in Madrid the other in Rio. Most people went on the charter flight to Rio de Janeiro. Few went to the official IUPAC sponsored Meeting in Madrid. The Meeting in Rio with the beaches

of Copacabana and Ipanema and a side trip to Brasilia was a great success and the meeting was enjoyed by everybody.

### **c. The Macromolecular Secretariat**

It was not long after I had joined the "active group" of the ACS Polymer Division I wrote Jack Elliott a letter. Again I was young and idealistic, Elliott was the Chairman-elect of the Division. In this letter I expressed my view of cooperation of interest groups, almost like a tribal society, in other words, regional cooperation. I expressed three points: To create a.) A loose cooperation of Divisions within the ACS; b.) Cooperation with polymer interested groups in the US such as SPE and c.) An organization or Federation of Polymer interested groups within the Pacific area.

a.) was a success and became in 5 years the "Macromolecular Secretariat" within the ACS. b.) was a total failure and c.) was also a success and became 20 years later the Pacific Polymer Federation.

First the Macromolecular Secretariat. I was still young and inexperienced. I had to convince Jack Elliott that it was a worthwhile undertaking. I succeeded and with his leadership we put together this organization, which was first called "Secretariat for Macromolecules". Today the ACS has at my last count about 20 "Secretariats". Ours was the first and more importantly the first conceived and difficult to put together.

Jack and I decided it should include in addition to the Polymer division, the paint and Plastics Division, (now PMSE), the Colloid Division, the Cellulose Division and most importantly the Rubber Division. They were semi-autonomous from the ACS, held their meetings not at the time or location of the ACS meetings. Most

importantly, they had money, great industrial support and a closely-knit "in"-group.

Elliott convinced first Ken Edwards from what is now PMSE and Egon Matejevic, Head of the Colloid Division and the Cellulose Division. The Rubber Division finally also agreed. I believe Eli Dannenberg of Cabot was leading it at that time.

We decided we should hold a joint meeting to demonstrate the cooperation of the new organization. We selected Eli M. Pearce to be the Chairman and gave him the title "Acrylonitrile in Polymeric Materials". In 1973, this subject was of interest at that time to all Divisions and promoted ABS and acrylic fibers.

In the mean time I was busy negotiating with all the Divisions and writing the constitution.. Again I learned a lot. From all these activities and got to know quite a few people.

Jack Elliott was elected the first "General Secretary". I believe he served 3 one year terms He was highly committed and wanted to be sure that the beginning of the new venture was successful. He was followed by Ken Edwards and I was elected the third "General Secretary". You can see how my responsibilities increased rapidly toward the middle of the '70's.

I am showing some correspondence relation to the creation of the Macromolecular Secretariat and its constitution

American Chemical Society

MACROMOLECULAR SECRETARIAT

January 31, 1979

Dean Vivian T. Stannett  
Graduate School

North Carolina State University, Raleigh, NC 27650

Dear Vivian:

When the Macromolecular Secretariat was formed under the initiation of Otto Vogl about seven years ago, the sponsoring Divisions agreed to the operation of the Secretariat according to bylaws, which were approved by the sponsoring Divisions. Last year, Professor Otto Vogl, one of the founding Secretaries, was asked to obtain the official copy of the. Bylaws and reissue the bylaws so that the current representatives of the sponsoring Divisions could each have a reference copy.

I am enclosing copies of the bylaws provided by Professor Vogl. With reference to this copy, only three editorial changes have been suggested: the name "Macromolecular Secretariat" has been proposed in place of the original "Secretariat for Macromolecules"; the title "General Secretary" has been proposed in place of "Secretary"; and the name of @ Division has been corrected. The first follows current common usage. The second clarifies correspondence with the ACS and C and E. News. The Rubber Division now holds an inactive status with the Secretariat largely because the Rubber Division meetings are not currently coincident with the ACS National

Meetings. The Rubber Division did participate in the 1978 Sym-posium.

Copies of the bylaws are provided with this letter to the officially designated representatives of the current sponsoring Divisions.

Very truly yours ,

F. E. Bailey

FEB: 11

cc: Dr. H. M. Chang  
Dr. L. Nowacki  
Dr. E. M. Pearce  
Dr. E. J. Soltes

Dr. Kurt Thies  
Dr. E. J. Vandenberg  
Dr. T. F. Yen  
Dr. Otto Vogl

**UNION CARBIDE CORPORATION**  
P. O. BOX B361, SOUTH CHARLESTON, W. VA, 25303  
RESEARCH AND DEVELOPMENT DEPARTMENT  
Technical Center

November 3, 1983

Dr, L. Guy Donaruma, Provost

The Polytechnic Institute of New York  
333 Jay Street  
Brooklyn, New York 11201

Dear Guy:        Enclosed is a copy of the bylaws of the Macromolecular Secretariat which you, requested and which were located for us at ACS Headquarters by Barbara Hodsdon

With best regards.

Fred Bailey

cc:     Jane Vogl, Business Manager John Schaefgen, Secretary Elect:  
         Macromolecular Secretariat

## BYLAWS OF THE, MACROMOLECULAR SECRETARIAT

of the

## AMERICAN CHEMICAL SOCIETY

### Article 1

#### Name and Objectives

Sec. 1., The name of this organization shall be the Macromolecular secretariat.

sec. 2. The object of the Secretariat is to encourage the generation of science and technology of Macromolecules for the benefit of man-kind-by:

- a.     Promoting the cooperation of American Chemical Society Divisions concerned with various aspects of synthesis, characterization, understanding and use of Macromolecules.
- b.     Organizing forms of multi-divisional participation in discussion of selected topics in macromolecular chemistry.

- C. Encouraging the active participation of several divisions in presenting a comprehensive view ranging from science to technology on selected subjects. 1
- d. Provide a mechanism for integrating the activities of divisions concerned with macromolecules and encourage comprehensive coverage of the subject by the American Chemical Society.

## Article II

### Members

Sec. 1. Charter membership in the Secretariat is made available to those divisions with substantial interest in macromolecules. These are: Polymer Division, Organic Coatings and Plastics Division, Rubber-Division Cellulose Paper and Textile Division, and Colloid and Surface Chemistry Division.

## Article III

### Organization and Administration

Sec. 1. The fiscal year of the Secretariat is from January 1 to December 31.

#### Sec. 2. Officers:

The officers of the Secretariat are the General Secretary and the General Secretary-Elect, each to serve for a term of one year and to be chosen from among the representatives in the Secretariat and by the representatives of the Secretariat.

#### Duties of the Officers

##### General Secretary

The duties of the General Secretary are to preside at meetings of the Secretariat and to administer the current years' business.

##### General Secretary-Elect

The duties of the General Secretary-Elect are to plan the following years' business and to act for the General Secretary in his absence.

## Article IV

### Meetings

Sec. 1. The Secretariat will meet at each fall meeting of the American Chemical Society and at least one, other time during the course of the year. The Secretariat must report its activities to member divisions in an annual report.

## Article V

### Amendments of Bylaws

Sec. 1. Any member division of the Secretariat may propose a change in the Bylaws by submitting the proposal in writing to the Secretary before June 1. The Secretary will inform the other member divisions of the proposal and solicit their vote by October 1. The amendment will be approved by a majority of the member divisions.

Sec. 2. The Secretariat may be disbanded by majority vote of the member divisions but with the understanding that program commitments must be honored.

Sec. 2. Other divisions may become members of the Secretariat by applying to the Secretariat; their membership to be approved by majority vote of the governing bodies of the member divisions.

Sec. 3. Each member division shall appoint two representatives to the Secretariat.

Sec. 4. Non-member divisions may participate in the activities of the Secretariat on a temporary basis or on specific projects.

Sec. 5. A member-division may withdraw from the Secretariat by notifying the General Secretary no later than the fall meeting prior to the year of withdrawal.

## **Expo Osaka 1970**

I mentioned Professor Seizo Okamura (b. 1914) of Kyoto University It was his fundamental idea that brought me to teach in Kyoto in 1968. Although we were never actually associated with his research group in a working relation Okamura

influenced me as an older and wise "friend". He taught me Japanese Art, block-printing and went with my wife and me to a fabulous Hiroshige exhibition in Kyoto Kaikan in 1980. I still have 2 Hiroshige block-prints in my living room. He advised me what structure the Pacific Polymer Federation might be most favorable. I did not like it at that time but he was right.

Most importantly, Okamura arranged for my first official appointment in Japan. The world exposition was planned for 1970 in Osaka. The whole of the northern Osaka suburbs was a "big dig", which became SenRi the new town.

Among the big celebrations that planned was to deposit, deep in the earth a time capsule called Time Capsule EXPO 1970. The capsule was to contain 2,060 items representing how life was in the 20th century. It was proposed to open the capsule in 5000 years. The capsules had an internal diameter of 1 meter and was 1,275 meter high and a volume of 5000,000 cubic centimeters, and a weight of 1,600 kilograms. The material was similar to 22AT stainless steel.

Capsule Shape Sphere. Size Internal diameter: 1 meter

Height: 1.275 meters, Capacity 500,000 cubic centimeters

Weight 1,600 kilograms, Material Similar to 22AT stainless steel, Number of items 2,060.

The capsule was to be placed deep in Osaka Castle Park. The entire project was supported by The Mainichi Newspapers and the Matsushita Electric Industrial Co., Ltd.

How did Okamura and I fit into that picture. Okamura had become the chairman of the committee to select plastics materials (polymers) that should be included in

the 2000 items. Okamura asked me to be a member of this committee. For me this was a great honor and I enjoyed very much being part of this committee. It was the first appointment from abroad, and an appointment sanctioned by the Osaka Expo 1970 Committee and the government of Japan.

Who knows where exactly the capsule is located, if it ever will be found and under what conditions. For my services I was presented with a copy of the capsule, 5 centimeter in diameter and embedded in transparent acrylics.

### **C. Foreign Secretary**

During my time as Chairman of the Polymer Division, one of my major objective was to make the Polymer Division the predominant organization on Polymer Science in the U.S.A. The easier and equally important thrust was to have the Polymer Division as the organization to represent U.S. Polymer Science abroad. I intended to have official interaction of the Division with organizations in various countries and encourage and facilitate the recognition of individuals abroad. For my own interest and to publicize the Division I arranged many meetings abroad. I also made contact with leaders of organizations of various countries, and organized or created Seminars and symposia. I served the Division in this capacity for 15 years. Some people called me jokingly the Metternich (the sometimes controversial Austrian politician who presided at the Vienna conference in 1815 and was an important politician in Europe for 33 years) of Polymer Science

.Otto Vogl, International and Interdisciplinary Cooperation of Polymer Scientists, Polymer Reaction Series Volume 5 (Japan) 2, (1972) (T. Saegusa, T. Otsu and T. Higashimura, Eds.).

# 1. Agreements

## a. The SPSJ-ACS Polymer Division Agreement

I mentioned in earlier part of the book how I got involved in Japan and Polymer Science and in teaching and lecturing in Japan. I became involved in numerous other activities. The Society of Polymer Science Japan had been found in 1965 with the legendary Sakurada of Kyoto as the first President and Sobue the second President. My leading role in Polymerization of higher aldehydes did not hurt. Furukawa with Saegusa had a program on acetaldehyde Polymerization, so had Tani and Sobue in Tokyo. They all started the year after my first patent (the Belgian Patent appeared) came out. They all used modified aluminum or zinc alkyls as catalyst (as did Vandenberg in the US).

This was a first stepping-stone since these modified catalysts were excellent catalysts for oxirane polymerizations. We used them for the polymerization of functional (carbomethoxylated) oxiranes.

As the Japanese polymer chemists coalesced, some rules developed. The Presidency was normally held for 2 years by the Kanto (Tokyo region, usually Tokyo Institute of Technology) and the Kansai region (Osaka-Kyoto region but usually Kyoto University). Furukawa was well known throughout the country, because he had powerful friends in Industry: Mitsui Chemicals, Mitsubishi Chemicals, Sumitomo, Japan Synthetic Rubber, Asahi Chemicals and several more. The leaders knew each other, were about the same age and had helped form Japanese polymer science after the original polymer generation after the war had become the administrative leaders in the chemical world in Japan. This was the world that became accepted even though I was only a simple chemist at

DuPont. I was however a promising young man in professional politics. I was the Chairman of the international membership committee. I was also recently appointed the Treasurer of the Polymer Division, which guaranteed the chairmanship in a few years.

The two organizations, the SPSJ and the Polymer Division in the US had about the same number of members the SPSJ perhaps 30% more members. What is more important, the SPSJ was better organized. They had and have one spring meeting and one Fall Symposium. But almost every Polymer Scientist attended the meetings with an attendance of 2500 to 3000 members attending. Every student would go and be seen. Major Professors presented 20 to 25 oral presentations and posters. The peak period began in the mid 70's

As the membership sub chairman and treasurer of the Polymer Division I targeted the Japanese polymer community a main objective. During about 2 years we recruited about 200 Japanese members of the Polymer Division, as Affiliate Members.

This was not my only interest for developing a close relationship between polymer scientists of the US and Japan

The Polymer Division had developed under the organizational talent of Henri Friedlander Charter flights to various places which hosted these Symposia on Macromolecules: Paris, Louvain, Amsterdam, Rio de Janeiro and Japan. In these days there were no special flight reductions. To have cheap flights you needed to arrange for a Charter Flight. Japan in 1966 WAS FAR AWAY and few partners know their counterparts. Henri arranged the flight for \$ 460 round-trip and everybody came. Our Japanese colleagues were happy to welcome us. This was

the first leg of our connection. The second was my visit 2 years later. Furukawa was my counterpart.

It had become clear that the interaction with the Japanese polymer chemist had to be done in 2 separate but interacting steps for the US -Japan seminar we had to deal with the Kyoto community. They were the primary actor. With the SPSJ the organization was in Tokyo. Not only that I was also restricted. I could arrange the seminar almost single-handedly with the support of a few friends, as long as I guaranteed a free trip to Japan - and as long as I did the work.

The agreement between the organizations. As the agreements approached, a few items became important. The Japanese side: through my friends in Kyoto and Tokyo were very within SPSJ was relatively quickly reached that the principle of an agreement was sound Sobue was followed as President of SPSJ by Shu Kambara for the years 1972/3 and Iwakura 1974/5.

By sheer chance the IUPAC Macromolecular Symposium was in 1973 in Aberdeen. We created an ad hoc committee with Kambara and myself who was the chairman-elect of the Polymer Division.

During 1972/3 the US-Japan meeting was also defined, formalized and scheduled. Shu Kambara was not an organic chemist but his successor Iwakura was. He was not only influential, but also from Tokyo (and worked in the area of high temperature polymers). We quickly reached the final agreement, which was signed during the meeting at Lake Kawaguchi-ko .

I had to go to the Executive Committee of the Polymer Division, which at that time had 7 members; most of them were my friends. We agreed that this was also

useful for us. We had to create an International Committee and I was appointed the Foreign Secretary, a position that I held for almost 15 years.

What did it mean to have an agreement of cooperation? First of all the scientists became to know each other, personal consultation were readily arranged and scientific contacts were established. Many functions are easier done within a framework that can be referred to as an established and reliable organization. Key persons involved in the establishment of the agreement reached high positions. Bill Bailey became the President of the ACS, Furukawa the President of SPSJ and Tsuruta the President of SPSJ and the Japanese Chemical Society.

The first tangible interaction was the joint US-Japan Symposium in Palm Springs in 1978. With Tsuruta and Bailey as the co-chairmen. This was a very effective meeting in a beautiful surrounding. It was organized by the expert organizer of ACS meetings Barbara Hodsdon, assisted by Jane Vogl Almost 400 people attended this meeting representing all aspects of Polymer Science.

We were now in the 1980's and it had become possible to interact closely between the polymer scientists of the US and Japan.

A number of industrial Japanese chemists spent one or two years in the U.S. It was almost obligatory for a Japanese a Jo-kyoju or Jo-shu to spent a year abroad. These sabbatical abroad did not only probed scientific interaction, but more importantly perfected their knowledge of the English language which became more an more the instrument of publication in written form and oral presentation.

We planned the second meeting in Kyoto in 1985 with Saegusa and myself as

the co-chairmen. It was held in the Heian Kaikan, a beautiful Hotel, a former mansion of an aristocrat and court official. Heian Kaikan was just across the street of the Imperial Palace. It also was a success but did not have the glamour of the first meeting. Time had changed, people had changed and interests had changed.

The SPSJ had become involved in temporary interactions with Korea, China, Russia and the commitment became too diluted. While this meant that our cooperation should continue, a new framework needed for the continued cooperation.

Otto Vogl, History of the Conception of the U.S.-Japan Seminar on Polymer Synthesis, J. Macromol. Sci.,-Pure and Applied Chemistry, A31(11), xv (1994)

## **b. The U.S. - German Agreement**

Having reached an agreement of cooperation with the SPSJ, our International Committee started to explore the possibility and need for cooperation with polymer organization. We explored these ideas with Hartwig Cherdrone and Hans Schnell, the Chairman of the Polymer Division of the German Chemical Society. We found that there would be sufficient common interest to warrant an official agreement. Schnell, Cherdrone and I met for dinner in Cherdrone's house in Wiesbaden and initialed the agreement.

We immediately started to plan for a meeting in Freiburg or surrounding with Joe Salamone as the US-Chairman of the meeting. The formal application was discouraged and ignored by NSF but some later meetings took place outside of our agreement and it was finally abandoned.

## **c. The U.S.-Italian Agreement**

A considerable amount of interaction existed with our colleagues in Italy but all on a one to one basis. Polymer Science played important role in the science education in Italy. There were schools in Milan, Rome, Turin and Padova where various aspects of Polymer Science and Engineering were taught. Montecatini, Enichemica, SIR and some other smaller companies were the motors for these developments. A number of scientists were needed for the development of polypropylene and several industrial scientists came from these schools. The polymer community was more organized according to their school "families". A polymer group that included academic and industrial scientists still existed.

It was with this group that I made contact. I was consulting for Montedison, had a nice office on Largo Donegani, and Professor Allegra who had just been promoted to Professor was the chairman of the Italy Polymer organization. After a few discussions with our colleagues on the committee, we came to the conclusion that an agreement of cooperation between the Polymer Division and the Italian Polymer Association could be reached.

The agreement of cooperation was signed in my Montedison office in Milan Italy. Not much came out of our agreement. The Italian group was dispersed and had too many individualistic - The US Polymer Division had become involved in domestic affairs. Looking back, there was probably no need for a formal cooperation with the Italian group. In such a small group people could make their academic and professional contacts individually.

## **2. Symposium Organizations**

## Background

I mentioned in an earlier part of the book how I became involved in Japan and Polymer Science and in teaching and lecturing in Japan. I became involved in numerous other activities. The Society of Polymer Science Japan had been founded in the '50s with the legendary Sakurada of Kyoto as the first President and Sobue the second President. My leading role in Polymerization of higher aldehydes did not hurt. Furukawa with Saegusa had a program on acetaldehyde Polymerization, so had Tani and Sobue in Tokyo.

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This was not my only interest for developing a close relationship between polymer scientists of the US and Japan.

The Polymer Division had developed under the organizational talent of Henri Friedlander Charter flights to various places which hosted Symposia on Macromolecules: Paris, Amsterdam, Rio de Janeiro and Japan In those days there were no special flight reductions. To have inexpensive flights you needed to arrange for a Charter Flight, Japan in 1966 WAS FAR AWAY and few scientists in similar fields of research know their counterparts. Henry arranged a charter flight to Japan for \$ 460 round-trip. Our Japanese colleagues were happy to welcome us. This was the first leg of our connection. The second was my visit 2 years later. Furukawa was my counterpart. One day I suggested to him to have a US-Japan Seminar, not too large with perhaps 15 scientists from each side.

## **a. U.S.-Japan Seminars on Polymer Synthesis**

In the late '60's I became acquainted with Kyoto and Kyoto University. Faculty members of Kyoto University at that time provided much of the leadership in Polymer Science in Japan. In the Fall semester 1968 we lived with other academic families in Konoe Hall, the faculty guest house of Kyoto University: Stein, from Amherst and Ferry from Wisconsin were our immediate neighbors. While I was still at DuPont they had already established some interaction, both scientific and personal, with their counterparts in Kyoto. In 1965 a small "family seminar" was held on polymer physics in Kyoto. Stein and Ferry attended this meeting.

I had become very friendly with Furukawa, my official host at Kyoto University, and his right hand man Saegusa. For a short period I traveled with both throughout Japan on business. I became very familiar with the functioning of the Japanese academic and industrial communities. At one of the breakfast meetings I asked the group (which also included Professor Tsuruta, of Tokyo University and a former coworker of Furukawa) what we should do to develop closer relationships between polymer scientists in Japan and the US. Mind you there were other older Professors that had interacted with individual Japanese scientists and who had taken young academic Japanese scientists into their laboratories. Bill Bailey and Charlie Overberger were among them. They provided a temporary home for young Japanese scientists in their laboratories giving them opportunities to improve their English language, which was highly appreciated in Japan.

My family and I soon became interested and fascinated with Japanese culture and Art and the Kyoto way of life. I learned to know the Japanese school system,

especially fine points in the University system, that had been reorganized only 20 years before, shortly after the war.

At one breakfast meeting I suggested developing a formal system of cooperation between key polymer organizations of the US (ACS Polymer Division) and Japan (SPSJ). My proposal was thought to be an interesting idea but at that time was not "do-able". A few practical reasons clearly showed the limitations. Only the highest-ranking people of the communities could afford to travel such long distances. The workhorse of flying long distances was the B 707 air plane which required two stops, had limited capacity for passengers and was consequently very expensive.

The obvious language of communication was English. Few Japanese had learned English sufficiently well as few had spent some time abroad. There were a number of other limitations or restrictions to go ahead with such a project. We finally concluded that the easiest solution would be to hold a US-Japan Seminar on Polymer Synthesis in Japan as soon as feasible. Furukawa and Vogl were authorized to explore the possibilities.

As one were starting to prepare to translate our ideas into practice, new obstacles arose. The Vietnam War wound down but still many US soldiers were in transfer in Japan, especially in the Southern island of in Kyushu. Although Japan profited economically enormously from the transshipment for the war - the younger generation did not see it that way. Anti-Americanism arose, led by active leftish students at Universities and had caused frequent strikes. When I visited Kyushu University in the fall of 1968, a tragic accident happened. One of the US Phantom jets crashed into the 6th floor of the new computer center that was being built and was not yet finished. To make things worse, my friend and host Professor Chujo

Aso was the University negotiator with the striking students. Do not ask me how I gave my lecture, but I did!

We concluded that we had to postpone our Seminar at least for 3 years! A certain Anti-Americanism of the student body influenced the possible decision-making. In the mean time I started to assemble the team that had the technical competence, interest in Japan Polymer Science, and had scientific results to present. We decided to have about 15 official participants but also a few observers from industry. It must be remembered that this kind of interaction was totally new territory. It was anticipated that the support would come from the National Science Foundation (NSF) in Washington and the Society for the Promotion of Science (SPS) in Tokyo.

The joint proposal Japan - US Seminar of Polymer Synthesis was prepared and submitted to the two institutions. The proposed meeting was under the co-chairmen ship of Junji Furukawa and Otto Vogl. The meeting was scheduled for the Mountain View Hotel at Kawaguchi-ko (Lake Kawaguchi) near Hakone. The proposal received a lukewarm reception in Tokyo and was rejected by the NSF. In the meantime I was appointed Professor at the University of Massachusetts and elected Treasurer of the ACS Polymer Division. The second application was received much more favorably but it still was postponed until 1972.

Much of the organization in Japan was done by Furukawa's Associate Professor Saegusa. The arrangement was that NSF paid for the selected academic participants to go to Tokyo, the local expenses were handled by SPS. They also paid for the Japanese academic participants. A few industrial observers were also admitted. The observers provided some input of industrial scientific and technical interests. Industrial organizations also provided some additional financial

contributions that were needed for the smooth proceeding of the seminars. The seminar was planned to be one week long. There was a Welcoming Reception and, after 4 days, a Farewell Party. After the second day of meetings, one rest day was provided for a bus trip to the surrounding Japanese countryside to allow the scientists to become better personally acquainted. The first excursion from Hakone included the Suntory Winery in Kofu, the small wine growing region in Japan (Furukawa had been a school friend of the research director of Suntory). This excursion was so inspiring that it was decided that subsequent meetings were to be held in wine growing areas or at least in places where spirits reigned. On another occasion we had our banquet in a famous farmhouse/restaurant in the countryside, an hour from our meeting place.

These comments should only provide you with the atmosphere that existed when one started a new and unusual undertaking. Today I am no longer involved in the organization of U.S.-Japan Seminars on polymer synthesis, which are still held every 3 years, and I understand an application to host such a seminar is automatically approved and funded.

For the first US-Japan Seminar we assembled on a Sunday morning at the Dai-ichi Hotel in Tokyo. Americans attending were, M. Chiesla the U.S. Manager of NSF in Japan, W.J. Bailey, J.K. Stille, D.P. Tate, M. Litt, R.W. Lenz, H.J. Harwood, and from US, industry, P. Dreyfuss, Patricia Dreyfuss, J.M. Prasser, R. Pariser, N. Calderon, From Japan: J. Furukawa, T. Saegusa, T. Tsuruta, H. Hirai, A. Yamamoto, T. Otsu, Y. Iwakura, H. Hayashi, H. Tani, M. Asada, H. Yuki, N. Ise, N. Yamazaki, T. Kunitake, F. Toda, M. Takeda, and from the Japanese industry, J. Inomata, H. Maki, H. Morikawa, R. Sakatori. The SPSJ was

represented by Vice President Takeda (Science University, Tokyo) and Y Iwakura, President-elect of SPSJ.

The Seminar almost failed in the last moment. A number of our American colleagues, for most the first time in Japan, had wandered around Tokyo trying to find their way back to the Dai-Ichi Hotel. The bus was loaded, the big sign US-Japan Seminar was glowing in the front of the BUS --- suddenly a large explosion occurred 3-or 4 street blocks away in the Mitsui Building affecting the 7th and 8th floors. We did not know whether this was an accident or the beginning of a large organized Anti-American demonstration. To be sure, we took the label off the bus counted our participants- and since nobody was missing, drove off as quickly as we could to our destination in Hakone near Mount Fuji.

The meeting Hotel was at a gorgeous location at the foot of Mount Fuji, the weather was beautiful, and we were ready to begin our meeting. The official picture, which is always necessary in Japan, was taken. How nice it is now to look a picture, which was taken over 30 years ago. How young the participants looked! The President elect of SPSJ, Professor Iwakura (the picture of his grand-uncle, once Prime Minister of Japan is still on the Y 1,000 bank note) was there. One of the Vic e-presidents of SPSJ, Takeda, of the Science University gave the "After Dinner" talk.

When we negotiated the meeting structure we included an excursion to interesting and stimulating places. We agreed to visit a wine-growing region in Kofu. Forty years ago only about 4-500 acres of grapes were grown in Japan.

For our excursion, the Suntory winery in Kofu, one hour by bus from the meeting site, was selected. We not only admired the modern way of making wine in

relative modest quantities, but the company invited us to an excellent Japanese banquet dinner and provided, most importantly, a supply of Suntory Old the famous Japanese Scotch whisky for the banquet and for the meeting of the Executive Board of the Seminar. It was anticipated that the organization and success of the second meeting (this time in the US) required the necessary inspiration and ingenuity for a successful future of U.S.A.-Japan cooperation in polymer synthesis.

The Board meeting on Tuesday night was a lengthy affair but we finally accepted the title of my proposal and called it "Functional Polymers" with Joseph C. Kennedy and Takeo Saegusa as the co-chairmen.

The first US-Japan Seminar on polymer synthesis in Hakone was a great success. Preparation for the future meetings was made and we were ready for the next Symposium. This time called Japan-U.S.A. Seminar on "Functional Polymers." Politeness and etiquette required that the guest country and the guest chairman were always mentioned first.

The preparation and execution of the second Seminar was in the hands of Saegusa and Kennedy. Five years passed until the next seminar was held, this time in the U.S.A. Finally we realized that NSF wished to have us organize such seminars as spontaneously conceived innovative meetings, not held officially on a regular basis and not "just" a continuation. Of course, that is exactly what we intended to do and did. Consequently we used venue changes and different titles and invited the program director of NSF to the meeting. They accepted gladly!!

Another reason why the next meeting was delayed seemed to have been that Kennedy did not want to be bothered with the substantial inconvenience of

organizing a meeting. The fact remains; the meeting was organized by Stille in his "territory" in Pingree Park, Colorado, near Fort Collins where Colorado State University was located. Pingree Park was a mountain retreat of Colorado State University, 9,000 ft high in the Rocky Mountains. It was a lovely location, although it violated the initial agreement, because it was not near a wine growing location. This was remedied by a substantial donation of the liquid refreshment from the Suntory Brewery.

Slowly I lost my influence in the organization of the meetings. I was still on the organizing committees and later as contributor to the seminars and an observer at the meetings of the organizing committees. The next U.S.-Japan Seminar was in Shin-Osaka under K. Hayashi and John K. Stille. The seminar was held shortly before the tragic and untimely death of John Stille in a plane crash.

At this meeting I introduced my "star" student David Tirrell, who, for over 10 years propagated my interests. Eli M. Pearce brought the meeting back to wine country in the Napa valley. Together with H. Hirai, Pearce organized the seminar in Yountsville CA. in 1987. That meeting in the U.S. was followed by the Seminar in Tokyo in 1990 under David A. Tirrell and Eishun Tsushida as co-chairmen. Again a slight violation of our initial agreement regarding the excursion location occurred. In the beginning of the bus tour to the countryside we stopped at the JOEL laboratories followed by a visit to the Suntory Brewery (not winery). But as in so many cases agreements have to be stretched in order to be successful.

The now regularly scheduled Seminars have retained their individual novelty, with new initiatives, new participants and other changes during the 20 years of their existence. The U.S.-Japan Seminars are solidly established. Perhaps the most interesting scientifically exciting, and historically most important meeting was held

in Sonoma Valley CA chaired by Virgil Percec and Yukio Imanishi in Santa Rosa, CA. in 1993. It was the 6th meeting and had brought the U.S. and Japanese polymer scientists together for a smooth cooperation both scientifically and personally.

I was in Japan in 1996 for 3 months as Monbusho Professor when the next Seminar in Sendai was held. It was the last meeting in which I participated. I had seen almost 2 generations of young scientists passing through this learning process of the participation in these meetings, maturing and becoming famous scientists.

It was time for me to retire from active participation at these meetings.

Otto Vogl, History of the Conception of the U.S.-Japan Seminar on Polymer Synthesis, J. Macromol. Sci., - Pure and Applied Chemistry, A31(11), xv (1994)

1st Seminar, Unsolved Problems in Ionic Polymerization, Junji Furukawa and Otto Vogl, Fuji Hakone October 1974

Journal of Macromolecular Science,- Chemistry, A9(5), 1975

2nd Seminar, Functional Polymers, Joseph P. Kennedy and Takeo Saegusa, Pingree Park, CO

Journal of Macromolecular Science, - Chemistry, A13(3), 1979

3rd Seminar, Synthesis and Reactions of Oligomers and End-reactive Polymers, K. Hayashi and John K. Stille, Shin Osaka, 1983,

Journal of Macromolecular Science, -Chemistry, A21(8&9), 1984

4th Seminar, Synthesis and Reactions of Specialty Polymers, Eli. M. Pearce and H. Hirai, Yountsville, CA 1987

Journal of Macromolecular Science, -Pure and Applied Chemistry, A25(5-7), 1988

5th Seminar, Advanced Materials Based on Macromolecules, E. Tsushida and David. A. Tirrell, Tokyo, 1990

Journal of Macromolecular Science, -Chemistry, A28(11&12), 1991

6th Seminar, Macromolecular Design for Advanced Materials, Virgil Percec and Yukio Imanishi, Santa Rosa CA, November 6-12, 1993, Journal of Macromolecular Science, - Pure and Applied Chemistry, A31(11) 1994, Polymer News, 19(9), 289-296 (1994)

7th Seminar, S. Inoue and Krystof Matyjaszewski, Sendai, October 1996  
Macromolecular Architecture and Engineering, Polymer News, 22(7), 252-257 (1997),  
Progress in Polymer Science, 23(2), 125-141 (1998)

8th Seminar, Jean Pierre Ferchet and Shiro Kobayashi, Journal of Polymer Science. Chemistry Edition.

## **b. The U.S.-Romanian Seminars**

As I started my work at the University of Massachusetts I decided that I wished to finish my work on the side chain crystallization of higher aliphatic isotactic polyaldehydes, which I had, began at DuPont. One young scientist from Iasi had written to Roger Porter in 1972 and asked if he could work for him for a year. Porter's interest did not coincide with what Negulescu could deliver and he asked me if I were interested in following up on this proposition. I had some support funds available and we agreed that he would work for me. Ioan became one of my most devoted coworkers and friends.

During the year that we worked together I established a contact with Professor C. I. Simionescu, director of the Institute of Macromolecular Chemistry in Iasi, Rektor (President) of the Technical University in Iasi, Vice President of the Romanian Academy of Sciences and President of the Iasi branch of the Romanian Academy of Sciences and the "Mr. Polymer" in Romania. In this case I do not know who made the actual proposal but I suppose it went like this. I was preparing the details of the first US-Japan Seminar and Simionescu probably mentioned why couldn't we have such a Seminar in Romania.

I was under the impression that it should be possible to organize such a seminar

in the north of Romania. I contacted a number of my friends and found a considerable amount of enthusiasm, should there be a certain amount of side seeing included, organize by the Romanian side, and should there be a "return" meeting in the US. The later was NSF requirement.

First I had to go to Romania and explore the situation and possibilities. What could I use from the experience with Japan, how different was it to run a meeting in a communist country - but with a very influential person as my counter part. I arrived in Bucharest from Tokyo, having changed planes in Moscow. The latter was a 4-hour flight with a propeller drive aircraft. In the middle of the flight, over Charkov, in Russia, we had to fly through a very bumpy thunderstorm and most people thought it was the end of the world. In addition, some people had brought some chicken (beautiful brown chicken) in cages and placed them in the overhead racks. In the excitement of one of the larger bumps, one of the cages opened and the chickens were loose in the airplane. It took a while until they were safely returned to their boxes. Still the Schnitzel and beer that was served thereafter were excellent.

Arrived in Bucharest at 2 a.m. I was met NY my friend Ioan and his colleague Denes (of Hungarian decent). Foreigners from the West always had to be met by 2 people who were obliged to write two separate, independent reports to the police. Ioan and I had to send Ferenc for some beer in order to speak a few uncensored sentences alone. The next morning I saw the President of the Academy, the powerful head of the Institute of Physical Chemistry Murgulescu, who was also the speaker of the house in parliament (but lost both positions a little later - because he was an intellectual and not a "worker"). I had to give my lecture in a large Hall with dozens of microphones. It had to be translated into Romanian. Translation during a scientific lecture delivery requires a different style

of delivery, which was completely new to me.

The train took us in 5 hours to Iasi where we were now the guest of the Macromolecular Institute. Simionescu handed me over to his "star" student, Virgil Percec, without his skill tact and cleverness. He is now a famous Professor at the University of Pennsylvania. He took me sightseeing to check out the places where we could go with the seminar participants. We went to the northern part of Romania, the Bukovina with its famous Monasteries, Voronets Moldavitsa Suceavina, Putna, and of course also those in Iasi and surrounding. There are many interesting stories to tell about our trip. Part of the Bukovina used to belong to the Austrian Part of the Austro-Hungarian Monarchy and still had some of the fundamentals of the cultural heritage from that time.

But now we were in a land that was organized as a strictly organized communist state. Simionescu had a great deal of influence in Iasi and Suceva, the provincial capital. I had to come back and make a short trip to those places that the delegation was to visit. To begin with I had to have coffee with the governor in Suceva. We then were, now with the official car and the young secretary to firm up everything with the monks and nuns, visits lunch and dinner. In the countryside a carefully balanced coexistence prevailed between the church and the party (government).

WE applied to NSF and were told that the Academy in Iasi had also applied to their government - but nothing happened. We had the approval of NSF with the proviso that the approval from Bucharest would be coming under the same conditions. When the approval finally came, it was more than generous. The US Romanian conditions were thawing and when it came to the opening and the banquet, not only the US Ambassador came to Iasi and the head of the polymer

Division of NSF Paul Lindenmayer but also the governor from Suceva, the mayor of Iasi and some minor party entourage. The S.R Romania- U.S.A. meeting, chaired but Professors Cristofer I Simionescu and Otto Vogl entitled "Unsolved Problems of Co- and Graft Polymerizations" was a great success. It was published in the Journal of Polymer Science, Polymer Symposia, 64 (1978)) as special issue.

Since the meeting provided a highly successful format for the interaction of the polymer scientists of the two countries, it was decided to hold a Second Romania-U.S. Seminar on Polymer Science, with the title of "New and Modified Polymers." with Joseph C. Salamone and Viorica Dobrescu as the co-chairmen. The original agreement stipulated that the second seminar was to be held in the US "in a few years". First, the travel expenses for the seminar was extensive for the Romanian participants. Probably inspired by our first successful US-Romanian meeting and the upcoming IUPAC Symposium on Macromolecular Chemistry in Amherst MA (with me as the co-organizer) inspired the Romanian Polymer community to hold the following meeting in Bucharest. Last but not least, Romania was a country governed by a communist regime, which tightened its grip on the country. One of the consequences severe travel restrictions for most people especially scientists to go abroad for the most justifiable reasons.

The organizers compromised on the last point and agreed to hold the meeting in Constanza on the Black Sea Coast. But even this proposal has to be abandoned and the second US-Romanian Seminar was held the week after the IUPAC Symposium on Macromolecules, also in Bucharest, Romania, on September 10-15, 1983. The Seminar was held immediately following the 29th IUPAC Macromolecular Symposium 'The proceeding " New and Modified Polymers", of the US-Romanian Seminar Bucharest, September 10-15, 1983, was published in

Journal of Macromolecular Science-Chemistry, A22(5-7) 1986 with Joseph C. Salamone and Viorica Dobrescu as the guest Editors.

This meeting was sponsored by the Division of International Programs of the National Science Foundation and by the Romanian National Council for Science and Technology. We were very pleased to have at the opening ceremony Mr. M. Florescu, Minister, Secretary of State, in the National Council for Science and Technology of Romania; Mr. N. Barbulescu, Deputy Minister of Chemical Industry of Romania; Madame Maria Ionescu, General Director of the Central Institute of Chemistry of Romania, and Mr. David B. Funderburk, U.S. Ambassador to Romania. The American participants were: Salamone, O. Vogl, V.T. Stannett, E. J. Vandenberg, F.P. Boettcher, W.H. Daly, J.A. Moore, S.C. Israel, R.M. Ottenbrite, T. St Pierre, G.L. Brode, and C.L. McCormick.

The organization of such a seminar is usually complex and requires the cooperation of many organizations and offices. The included Deborah L. Wince of the Division of International Programs of the National Science Foundation; Professor I. Ursu, First Vice President of the National Council for Science and Technology of Romania; and Professor Mircea Malitza, Ambassador of the Socialist Republic of Romania to the United States. Actually the meeting could not have been held without the consensus of Elena Ceausescu.

Even so, the meeting was a success because many Romanian colleagues made important acquaintances, for many these contacts changed their life forever.

As another cases, the interactions had been established and additional follow-ups could be done on a personal basis and no further US-Romanian Seminars on Polymer Science were held.

RADICAL CO- AND GRAFT POLYMERIZATIONS: Unsolved Problems, J. D. Wiley (Interscience), 1978 (with C. Simionescu).

Viorica Dobrescu and Otto Vogl, Second S.R. Romania-U.S.A. Seminar on Polymer Science, Polymer News, 9, 343-345 (1984)

### **c. Euro-American Seminars (Oxford Meetings)**

I was involved in 4 meetings in England. Two in connection with Pergamon Press and two as the Chairman of the International Committee of the Polymer Division.

In 1985 in Birmingham I was the opening speaker of the Pergamon sponsored Symposium, "Specialty Polymers, and also a few years later in Cambridge I was one of the Plenary lecturers.

In the mid 80's, my friend Roger Epton from Wolverhampton Technical University had become the General Secretary of the Moretonhempstaed Conferences. I had attended the second conference in 1962 and gave my first polyaldehyde talk.

In 1986, Geoffrey Eastman was the chairman of the Polymer Group of the UK and charged to organize the annual meeting in Oxford. The meeting was called: Macromolecules '86: An international Conference on Functional Polymers and Biopolymers The US Polymer Division had offered to cosponsor this meeting. It was organized under the co-chairmanship of the Polymer Division and the Macro Group UK (a joint association of the Royal Society of Chemistry and The Society of Chemical Industry of the UK) we called it the Euro-American Conference of Polymers or "the first Oxford Conference". The conference was held in St. Johns and Trinity colleges at Oxford University from September 15-19, 1986.

This was a truly cooperative conference because the business offices of the two Organizations were active and involved in the organization and handled the registration together. Of the 300 participants, 40% were from the UK 34% from continental Europe and the remainder from the USA.

The Symposium consisted of 2 Plenary Lectures, 60 Papers and 50 posters. Since the Symposium was a= such a success a second Euro-American (Oxford) conference was scheduled a 3 years later with Roger Epton and Otto Vogl as the co-chairmen. It was held in a similar style and attracted again a substantial number of participants. These meetings were primarily successful because they were held in the lovely atmosphere of Oxford University.

The Euro-American conferences seemed to have been established, and the stewardship was given to Burton C. Anderson (DuPont) and Alan Amas of Aston University. For some reason the conference was moved to Canterbury from Oxford. It was a serious mistake and did not achieve the success that we had been accustomed to the Euro-American meetings in Oxford. Oxford University had a magic flair.

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## **C. The Pacific Polymer Federation**

### **a. Founding**

As interaction between the SPSJ and PD was proceeding for the second joint Symposium in Japan, many items necessary for a successful cooperation had to be defined and clarified.

Since this meeting was in Japan, much of the work fell on our Japanese colleagues especially those in Kyoto, and financial resources had to be made available for the initial work. These preparations were under the Presidency of Saegusa. One day we sat down and talked about the structure and our cooperation, which was over 10 years old.

The ACS Polymer Division, as many other organizations, was run on the initiative of one person or a small group of people. The SPSJ worked more on the consensus principle. A number of initiatives for meetings and cooperative efforts had been developed which the SPSJ was obligated to support. Political conflicts and interests were shifting especially in the Far East.

Saegusa told me that bilateral US-Japan meetings between PD and SPSJ might not be needed any longer. They had fulfilled their purpose of getting people acquainted. Some of the direct communications had been established. Japanese scientists could afford to attend ACS meetings. Most importantly, SPSJ had become more and more involved in bi-lateral contacts with scientists of other nations in closer proximity. These thoughts seemed to be reasonable as we discussed the organization of the 2nd US-Japan meeting in Kyoto.

In 1984 there was a meeting in Hawaii. I had lunch with my friend Fukui and his wife at a restaurant overlooking the lobby of the Hotel Waikiki. I had known Fukui since my first stay in Japan 15 years before. Fukui had received the Nobel Prize in 1981 and I was by chance present at the Award Presentation in Stockholm. During lunch I looked down to the ground floor and noticed Saegusa, of SPSJ and O'Donnell, the Chairman of the Polymer

Division of the Australian Institute of Chemists walking by in deep discussion. This gave me an idea.

**The Creation of PPF:** I was thinking: since bilateral interactions of scientific organizations on a National Bases had fulfilled their usefulness, why not think in regional terms. If we included Australia in our bilateral organization, that would create an organization Polymer Scientists from the Pacific Rim countries. The SPSJ had about 12,000 members the ACS Polymer Division about 9,000, the Polymer Division of the Royal Institute of Chemistry of Australia (ARIC) about 600 very dedicated members.

The same day I located Saegusa and O'Donnell and found them very interested in this idea. O'Donnell was the chairman on the Polymer Division (PD) of RAIC and Saegusa the President of the SPSJ. I was still the "Foreign Secretary" of the PD 10 years after I had held the chairmanship. Such circumstances can facilitate development of organizations. I was not inexperienced in organizing an idea into a workable and legally do-able organization.

I wrote the first drafts for the formation of the Macromolecular Secretariat of the ACS in 1970 and played a key role in the drafting of the agreement to form CUMIRP, the Center of University of Massachusetts Industrial Cooperative Program on Polymer Research. This agreement and the subsequent draft had to reflect the position and objective of the organization. a.) It was to be a regional organization that provided a forum to interact as groups and ultimately as individuals; b.) It was a mechanism of interaction in the fastest growing region of the world, the Pacific Rim, and in the fast growing scientific and technical subject, Polymer Science.

Practically speaking it was an extension of the SPSJ-PD agreement to extend it to a regional scale with the rather small Australian Polymer group providing the glue.

We did not know if the organization would be a "strong" organization, or a weaker organization, which the PPF turned out to be which was the only solution. I still remember one day when I was in Kyoto. Seizo Okamura who was very influential in the polymer world of Japan invited me to have lunch with him at the delightful Japanese style Brighton Hotel. After the normal assurances of friendship he told me: I like your idea of your idea of creating an association of national polymer organizations of the Pacific Rim, but it cannot be a "strong" organization. SPSJ will agree very happily to a weak organization. We would never agree on the formation of some organization in which we would not have control over our individual members. English would obviously be the primary language, but it is better not defined. Have we not seen this principle many times in recent politics??

A strong organization would take the membership as a whole and it would become an organization with strong American leadership, perhaps even dominance. And then there would be the financing of such an organization. High membership fees that are necessary are unaffordable especially for young scientists. That would limit participation from far away countries. (I had been thinking of Tokyo or Japan as the headquarter of the organization and as the regular meeting place Hawaii).

What is now the Pacific Polymer Federation (PPF) became the Federation or Confederation of organization of national organizations whose representatives and officers were elected (not appointed in some obscure ways) by their members The national organizations had to be organized,

had to have a constitution and officers, were primarily interested in Polymer Science and bordered on the Pacific Ocean.

The establishment of the PPF had started with discussions of Saegusa, O'Donnell and Vogl at a meeting in Hawaii in December 1984; at that time the concept of a regional scientific organization was conceived. We decided to explore with the parent organizations (which became the Founding Members) to determine if it were possible to devise a Constitution, which could incorporate all the interests of the polymer-oriented organizations of the Pacific Basin. Much of the individual writing was done prior to and during the U.S. - Japan Seminar in October 1985, and at the Annual Meeting of the Society of Polymer Science, Japan in May 1986, at which time all parties were present. In New York, in September 1987 and at the Annual Meeting of the Polymer Division of the Australian Institute of Chemistry in February 1987 the details of the Constitution and the subsequent understandings were worked out and a final agreement to establish the Pacific Polymer Federation was reached. Bill Bailey, the recent President of the ACS helped us to obtain the cooperation of the ACS. Earl Tyner, Esq, who had been a patent attorney at DuPont and who had written my patent cases at DuPont and was then a member of a law firm in Crystal City, VA, made sure that the constitution was legally correct. All these negotiations were done before the benefits of Fax machines were available and much thought went into the preparation of the document. At the same time, the organizations and individuals involved in the negotiations had time to realize how important the development of the PPF was for Polymer Science and for the interests of polymer oriented organizations and individuals of the Pacific region.

Some Polymer Groups or Divisions of larger national organizations were usually associated with Chemical Societies, the Division of Polymer Chemistry with the

ACS, and the Polymer Division in Australia with the RAIC. Japan had its own separate Society SPSJ. Other polymer groups were not formally organized and depended on the ambitions and initiative of individuals to become functional. In such cases the concern arose: What might happen if something were to happen to these key individuals. Even for a "weak" organization, the permanence had to be carefully investigated and secured. One of the purposes and objectives of the PPF was to have orderly cooperation among the individual national polymer organizations. Some of the later members of PPF did not have organized polymer groups and some not even a defined chemical society. This was the case in Thailand or Vietnam.

In addition to the organization of the individual groups and their differences, money became a problem. Since it was clear that much of the initiative the PPF was in American hands the people responsible for the creation had to have funds to travel to meetings. Our own home organization the PD said you are on your own. The organization was in the hands of Joe Salamone, Stan Israel and myself with Jane C. Vogl tending the office and the funds. That required the foundation of PPF Inc. the money holding Foundation of the US part of the PPF to be created, with the 4 of us as directors.

First we went to industry to support our undertaking and received support of about \$ 65,000 from E.I. Du Pont de Nemours & Co., Ford Motor Company, Exxon Chemical Company, Himont Incorporated, Merck & Co., Inc., BASF Corporation, Hoechst Celanese Research Division, The Proctor & Gamble Company, Rohm and Haas Company, Polaroid Corporation, The Dow Chemical Company, Allied Signal. PPG Industries, Inc., General Electric Company, Amoco Corporation, and International Business Machines.

Polytechnic University through my Mark Chair complex provided office space and

telephone service and the rest was provided from the funds that had been collected. Actively involved in the founding of PPF were Ray Ottenbrite and Bill Bailey who was particularly important for the writing of the constitution. About 10 years before he had been ACS President and was very familiar with the internal functioning of ACS, what could be done and what should not be attempted.

It was a good idea to start with Funding Members only. It was enough of a headache to agree on the wording and the fine points of preparing of the constitution. Each of the organizations had to take into account their own way of thinking. The SPSJ was a typical oriental organization with its own tradition while Australia had British structure. Every important scientist had spent some time for study or on their sabbatical leave in the UK. The PPF creation was for the Australians a great opportunity to become more oriented toward Japan and the USA and ultimately the PPF Inc. funded the creation of PPF.

We had to write the constitution. Fortunately with our efficient drive to raise funds for this new organization, we, the founders, had enough funds to travel to negotiate the necessary fine points for the creation of PPF.

I still remember the trip that Joe Salamone, Stan Israel and I took to Australia and New Zealand. With Neil Edmund, the head of the New Zealand Polymer group of New Zealand, we agreed that New Zealand would act as an autonomous, organization but part of Australia. A delicately agreed upon important achievement at the beginning of the organization. Stan, Joe and I spend three days in Auckland to meet polymer scientists and to reach the agreement.

The negotiations for the writing of the constitution were done in different places: In Brooklyn, with Abe, (It must be remembered Abe received his PhD in Brooklyn Poly, worked at Showa Denko, and while being Professor at the Tokyo Institute of Technology, spent regular periods with IBM in California) and in Australia. As I

had mentioned, Salamone, Israel and I had made a "fact-finding tour", Bob Shanks had become the President of the Polymer group ARIC. The annual meeting was on Phillips Island near Melbourne and I was the plenary speaker. At the appropriate time in Japan in the morning, Bob said to me. Now you pick up the phone and tell them we agree with the SPSJ on all the items that were still in question.

This was in the beginning of February, it was hot at the meeting sites, about 40°C but we celebrated our achievements. Philips Island is the main sanctuary of the Koala bears, the symbol of Australia and the hundreds of penguins who have large nesting grounds on the island.

We had agreed that the signing ceremony would be in the fall of 1987 during the Annual Symposium of SPSJ in Tokyo; Riihiro Chujo of the Tokyo Institute of Technology was the local chairman.

It was an eventful period. I stayed at the Akasaka Prince Hotel near the meeting site. The signing was scheduled for the morning Monday October 19, 1987 In the International House in Roppongi, Tokyo. The ceremony was joyfully celebrated; we still have the videotapes of all the events when the Pacific Polymer Federation was born. Who can forget that day, in the US called the black Monday? The New York Stock Market plummeted 23%. It was also a joyful day because my friend Charlie Pederson received the Nobel Prize for his invention of cyclic ethers as complexing agents of the cations of inorganic salts.

**The Constitution:** The Constitution of the Pacific Polymer Federation was signed on October 19, 1987 in Tokyo, Japan at the Inter-national House in Roppongi, Tokyo by the Chairman of the Division of Polymer Chemistry, AC S, R. Eby, and the Chair-man of the Foreign Affairs Committee, O. Vogl; by the President of the

Society of Polymer Science Japan, M. Takayanagi; Chairman and Vice President for International Affairs, A. Abe. For the Polymer Division of the Royal Australian Institute of Chemistry, Chairman D. Hill and Chairman of the International Committee, J. O'Donnell signed the Constitution.

The PPF was created as an organization to advance and benefit polymer science and technology in the Pacific Basin; it has as its objectives to encourage and facilitate: i.) Interaction between polymer organizations of the Pacific Basin; and ii.) Exchange of scientific knowledge, by participation in national meetings, and by visits of polymer scientists of the Pacific. The membership of the PPF is open to all societies and associations of scientists and engineers, which have at least part of their activities devoted to polymer science and/or technology.

It was very gratifying to see a regional organization involving the Polymer Scientists of the Pacific region come into being. Polymer Science was recognized on this occasion as one of the fast growing scientific and technological disciplines and the Pacific Basin the fastest growing region scientifically, technologically and economically in the world. It was only logical, that the organizations of the region found mechanisms of cooperation facilitating the interaction between individual scientists. Since the first years of interaction between the organizations and Council Members, representing the organizations, a great deal has been accomplished which proves that the concept, the dream of a smoothly functioning regional cooperation in polymer science could be established.

## PACIFIC POLYMER FEDERATION

### CONSTITUTION

#### 1. NAMES AND OBJECTIVE

1.1 The name of the organization shall be the **Pacific Polymer Federation**, hereafter called the FEDERATION; it shall be an organization to advance and benefit polymer science and technology.

1.2 The objectives of the FEDERATION shall be to encourage and facilitate:

- i. Interaction between polymer organizations involving the Pacific.
- ii. Exchange of scientific knowledge, participation in national polymer meetings, and visits **by** polymer scientists of the Pacific.

## 2. MEMBERSHIP OF THE FEDERATION

2.1 The Founding members of the FEDERATION shall be: (i) The Society of Polymer Science, Japan;

(ii) The Division of Polymer Chemistry, Inc., American Chemical Society,- (iii) The Polymer Division of the Royal Australian Chemical Institute.

2.2 Membership of the FEDERATION shall be open to all societies and associations of scientists and engineers, geographically situated in, or near, the Pacific Basin, which have at least part of their activities devoted to polymer science and/or technology.

2.3 Member organizations shall not be committed by any action in conflict with their charters, constitutions, or bylaws or those of their parent organizations.

2.4 Other societies or associations, meeting the requirements of Section 2.2, shall be encouraged to join the FEDERATION. The societies or associations may apply to join the FEDERATION by send-ing its application to the Council (defined by Section 3.2). The organization will be admitted by a vote of at least two-thirds of the Council. The membership will become effective on January 1 following the vote of admission.

2.5 There shall be no regular annual subscription required of member organizations.

2.6 A member organization may resign from the FEDERATION by submitting its resignation in writing to the President of the FEDERATION at least one year in advance.

## 3. ORGANIZATION AND ADMINISTRATION

3.1 The operating year shall be from January 1 through December 31.

### 3.2 Council

- i. The FEDERATION shall be administered by a Council consisting of a maximum of ten members- the Council members shall serve for a two-year term.
- ii. Each of the Founding organizations shall have two representatives, and each of the Nonfounding organizations shall have one representative on the Council.
- iii. When the number of the Council members reaches ten, the Council will establish a

rotation of the Council seats among the representatives of the Nonfounding organizations; the composition of the Council shall be reconsidered after ten years.

iv. The Council shall elect a President, a Vice-President, and a Secretary-Treasurer for a term of two years. One reelection shall be permitted.

v. The Council shall appoint all committees and committee members to conduct such matters as may be delegated to them.

### 3.3 Duties of the Council

i. The Council shall conduct all the business of the FEDERATION. The Council shall meet at least once per year.

ii. Decisions of the Council must be by a majority vote, with a minimum of one half of the total Council members constituting a quorum for the vote, provided at least one member of each of the Founding organizations is present.

iii. No Council decisions requiring a specific course of action by a participating organization shall be valid without the approval of the members or proxy delegates of that organization.

iv. Expenses of the Council members incurred through participation in Council meetings may be provided by the treasury of the FEDERATION or the member organization.

### 3.4 Officers

The officers of the FEDERATION shall be the President, the Vice-President, and the Secretary/ Treasurer.

### 3.5 President

i. The President shall be elected by the FEDERATION Council as stated in Section 3.2.

iv. The President shall be the chairman of the Council.

ii. The duties of the President shall be to coordinate the activities of the FEDERATION and to maintain contact with the member organization through their representatives on the Council. The President shall prepare an annual report on the activities of the FEDERATION.

iii. In the case of the President's inability to serve, his duties shall be assumed by the Vice President.

### 3.6 Vice-President

The Vice-President shall be elected by the FEDERATION Council from its members as stated in Section 3.2.iv. In the absence of the President, the duties of that office shall be assumed by the Vice-President.

### 3.7 Secretary-Treasurer

The Secretary-Treasurer shall be elected by the FEDERATION Council from its members as stated in Section 3.2.iv.

### 3.8 Committees

All committees and committee members shall be appointed by the Council. Expenses incurred in performing their duties will be borne when possible by the organizations to which the individual members belong.

## 4. FINANCIAL BUSINESS

The FEDERATION shall cover its activities through the support by external funds. Such funds may be used for attendance of representatives at Council meetings, and/or to sponsor FEDERATION activities. The President shall report the financial status of the FEDERATION at every Council meeting. The extent of the activities of the FEDERATION shall be determined annually by the Council of the FEDERATION.

## 5. OPERATION OF THE FEDERATION

5.1. The Council of the FEDERATION shall be operated by regularly scheduled meetings and by correspondence. Council meetings shall be scheduled by agreement of a majority of the Council. The member organization may appoint properly qualified proxy delegate(s), who will have voting right(s), to attend meetings of the Council.

5.2 The FEDERATION may organize international meetings or conferences on any aspect of polymer science and technology. The organization of conferences may involve all or some of the member organizations of the FEDERATION. These may be of the following types:

i. Meetings of international standing and interest organized by national bodies and sponsored by the FEDERATION:

To achieve FEDERATION sponsorship, a plan of the meeting must be submitted to the President of the FEDERATION for consideration by the Council, which may suggest modifications before approval is given. The financial management of the meeting shall be the responsibility of the organizing national body. Members of all national bodies affiliated to the FEDERATION who wish to attend a meeting sponsored by the FEDERATION shall be treated as if they were members of the organizing national body.

ii. Meetings of international interest, conceived and promoted by the Council:

Although the initiative of such meetings shall reside with the Council, the organization of such meetings shall be delegated to the Council members of the chosen country of venue. The financing of the meetings, together with the acceptance of any profit or loss, may be accepted by the participating body or bodies of the hosting country. Alternatively, financing may be organized by the Council through external funding.

5.3 The policy of the FEDERATION toward publication of the proceedings of any of its meetings shall be determined principally by the publication policy of the organizing national body or bodies. Prominent recognition of the FEDERATION sponsorship shall accompany all such publications.

5.4 The FEDERATION may produce a bulletin (or other forms of information) for distribution to members and other interested organizations.

5.5 The Council may plan and execute other activities of interest to the FEDERATION.

## 6. AMENDMENTS OF THE CONSTITUTION

Any member organization of the FEDERATION may propose an amendment to the Constitution of the FEDERATION by submitting it in writing to the President of the FEDERATION. Adoption of an amendment to the Constitution shall require an affirmative vote of two-thirds of the Council.

## 7. DISSOLUTION OF THE FEDERATION

The FEDERATION may be dissolved only by a unanimous vote of the Council of the FEDERATION. Prior to dissolution of the FEDERATION all debts of the FEDERATION must be discharged and all its affairs settled.

### **b. President of PPF**

Otto Vogl was elected the first President of the PPF, Takeo Saegusa, Vice President, James O'Donnell, Deputy Vice President and J.C. Salamone Secretary/Treasurer. The President was charged to set up the PPF, and particularly to organize the First Pacific Polymer Conference (PPC-1) in December 1989 in Maui, Hawaii.

During this period the organization had started to function smoothly, several committees have been created; the most active committee initially was the Membership Committee, which was responsible to approach to, and contact of potential new members for the Organization.

After the constitution was signed in 1987, the structure of the organization was established.

Founding Members: The Society of Polymer Science, Japan; The Division of

Polymer Chemistry, American Chemical Society; The Polymer Division, The Royal Australian Chemical Institute.

President Otto Vogl, Vice President: Takeo Saegusa, Deputy Vice President James H. O'Donnell Secretary/Treasurer Joseph C. Salamone

Soon a number of organizations bordering the Pacific applied for membership to the PPF and were admitted

New Members: Macromolecular Science and Engineering Division, Chemical Institute of Canada; The Society of Polymer Science, Korea; Polymer and Industrial Section, Malaysian Institute of Chemistry; The Polymer Group, New Zealand Institute of Chemistry; Polymer Division, Chinese Chemical Society.

Members of the Council consisted of Akihiro Abe, Japan; David J.T. Hill. Australia; Ramlee Karim, Malaysia, Chung Yup Kim, Korea, Martin Navratil, Canada, Renyuan Qian, China

A number of Committees, including councilors from all member countries were established:

Membership: J.H. O'Donnell, Chairman, T. Saegusa, Ramlee Karim

First Pacific Polymer Conference: O. Vogl, Chairman, T. Saegusa, Vice-Chairman, J.H. O'Donnell, Vice-Chairman

Information (Newsletter): G.S. Kirshenbaum, Chairman, K. Hatada, G.A. George, J. Vogl, T. Takahiko

PPC-1 Organizing Committee: J.C. Salamone, Chairman

Publication: B.C. Anderson, Y. Imanishi, Co-Chairmen, A. Abe, D. Hill, B.C. Anderson, J.C. Vogl, S.C. Israel, A. Logathetis, J.C. Vogl, T. Takahiko.

Finance: O. Vogl, Chairman, J. Nottke, Y. Furuyama.

At the end of my Presidency two more organizations joined the PPF as new Members: Singapore Plastics and Rubber Institute and American Physical Society

Committees were rearranged

Membership: C.Y. Kim, Chairman; T. Saegusa, R. Karim

Information: G.S. Kirshenbaum, Chairman; K. Hatada, G.A.

George, J.C. Vogl, T. Takahiko

Publication: B.C. Anderson, Y. Imanishi, Co-Chairmen; A. Logathetis, J.C. Vogl

Finance: J. Nottke, Chairman; O. Vogl, Y. Furuyama

By-Laws: R. Karim, Chairman; D.J.T. Hill

Awards: J.H. O'Donnell, Chairman; M. Navratil

Conferences: K. Wynne, Chairman; J.C. Salamone

Second Pacific Polymer Conference: T. Saegusa, Chairman, and J.H. O'Donnell, Vice Chairmen, J.C. Salamone

During the first year, several polymer-oriented organizations of the Pacific Basin applied for membership in the PPF. At the Council Meeting in August of 1988 in Kyoto, Japan, the Macromolecular Science and Engineering Division, Chemical Institute of Canada; The Society of Polymer Science, Korea; the Polymer and Industrial Section, Malaysian Institute of Chemistry were admitted as new members. At the Council Meeting in Brisbane, Australia in February 1989, the Polymer Group, New Zealand Institute of Chemistry was admitted as a new member of the PPF and the Polymer Division, Chinese Chemical Society became a new member of the Federation. The Polymer Society of Singapore and the Division of High Polymers, American Physical Society have also shown interest in joining the Pacific Polymer Federation.

Throughout the year numerous Council Meetings were held whenever a major

scientific meeting attracted the presence of a number of Council Members of the PPF. It was organized by the President of PPF. The formal meeting were held during the Pacific Federation Conference (PPC) meetings. In the next few pages I am recording the Minutes of some typical PPF Council Meetings.

The **first Meeting of the PPF Council** was held in Kyoto on Saturday, July 31, 1988. It was attended by the 6 Councilors of the PPF, O. Vogl, T. Saegusa, J.H. O'Donnell, J.C. Salamone, Hill and Abe. Also present were T. Takahiko and Jane C. Vogl representing the Business Offices of the SPSJ and the Division of Polymer Chemistry. At the meeting of the Council in Tokyo of 1987, which constituted the formation of the FED-ERATION one of the most important tasks was to form a FEDERATION truly representing the Pacific region. O'Donnell was appointed chairman of the Membership Committee. Key organizations were contacted by O'Donnell and Vogl, an application form was designed and by the first Council meeting in Kyoto, 3 applications were on hand that could be handled by the Council. The Macromolecular Science and Engineering Division of the Chemical Institute of Canada, the Society of Polymer Science of Korea and the Malaysian Polymer Division were admitted and were invited to provide the Councilor for their admission date, January 1989.

During the Council Meeting other important decisions were made; an Information Committee, a Finance Committee, and a Publication Committee were established. The Information Committee (Guise) was charged to prepare a Newsletter in early 1989, the Publication Committee (Anderson) to be responsible for the Pacific Polymer Preprints, the publication of the Maui Meeting. The President had started a fundraising campaign to support the operation of the PPF and to have funds available for the preparation of the PPF-1 in Maui.

The Secretary/Treasurer was made responsible for the incorporation of the PPF and the establishment of an independent tax-free status of the PPF. As the

Chairman of the Organizing Committee, he set in motion all the necessary activities in connection with the First Pacific Polymer Conference in Maui. Selection of the Hotel in Maui for the First Pacific Polymer Conference was agreed on, as were the contract with the Hotel, the fee structure, time schedule and preparation of a First Circular; the effect of the First Flyer was discussed. Most of these responsibilities were in the hands of Jane C. Vogl, the Coordinator and Manager of the Maui Conference.

The second Meeting of the Council of the PPF was held near Brisbane, Queensland, Australia, February 3-5, 1989. The time was selected after the Annual Meeting of the Polymer Division of the Royal Australian Institute of Chemistry at Griffith University in Brisbane. Present were O. Vogl, T. Saegusa, J. O'Donnell, J.C Salamone, A. Abe, D. Hill and representing the new Members of the PPF, R. Karim from Malaysia, N. Edmonds from New Zealand and Chang (for Professor Ahn) from Korea. The most important decision of the Council Meeting was the admittance of China (based on an application by Qian Renyuan, the head of the Polymer Division of the Chinese Chemical Society into the PPF.

Much of the meeting was concerned with the organization of the Maui meeting - the arrangement of the Invited Speakers, nearly 150 contributed Papers and 100 Posters, and the Session Chairmen. It was considered essential, that the time schedule for the preparation of the meeting be rigorously followed. The Meeting will be held at the Royal Lahaina Resort in Maui and was expected to attract at least 400 participants. O. Vogl announced that Mrs. Glenn Ulyot (Barbara Hodsdon) was engaged to handle the registration for the U.S.A. for the Maui Meeting.

In addition it was agreed that some wording in the Constitution might have to be clarified and O'Donnell was charged to look into the matter. It was also found

desirable to establish a separate committee with the responsibility to disseminate information of polymer activities, new developments in polymer education etc. within the Pacific region.

Although the next formal Meeting of the Council of the PPF was to be held in Maui, December 1989, the President was authorized to call meetings that consisted only of part of the Council members, when convenient, especially if it could be done in connection with an International meeting and in a country that has recently joined the PPF. June 1989 in Seoul, Korea and July 1990 in Montreal, Canada were considered possible occasions.

The most important activity of the PPF in the year 1988 was the First Pacific Polymer Conference, which was planned to be held at the Royal Lahaina Resort in Maui, Hawaii, December 12 - 15, 1989. It was the first Conference organized by the "Pacific Polymer Federation." The Conference Program consisted of 5 Key Note Speakers, 35 Invited Lecturers and 250 Contributed Papers, presented in Oral and Poster form. It was expected that about 500 scientists would participate in the Conference.

Maui, Hawaii was selected as the site of the PPC-1 by the Council of PPF because of its geographical situation, its natural beauty **and** peaceful atmosphere. We believed these favorable conditions would promote the interaction of scientists, both industrial and academic, and will present the opportunity for them to meet with each other harmoniously, establish scientific cooperation and lasting friendships.

**First Pacific Polymer Conference (PPC-1)** was held at the Royal Lahaina Resort in Maui, Hawaii from December 12 to 15, 1989. The Conference Committee consisted of O. Vogl, Chairman; T. Saegusa and J.H. O'Donnell, Vice

Chairmen; it was organized by the Organizing Committee, J.C. Salamone, Chairman, with A. Abe, D.J.T. Hill, B.C. Anderson, S.C. Israel, J.C. Vogl and T. Takahiko as Committee Members. Jane C. Vogl was the Conference Manager and Barbara Hodsdon-Ullyot was the Conference Coordinator. PPC-1 was attended by 401 participants and 101 accompanying guests; 19 countries were represented. They came from over 100 Universities and colleges and from over 100 different companies. It consisted of 5 key note addresses: two by the Nobel laureates of Chemistry in 1981: Kenichi Fukui, Institute of Fundamental Chemistry, Kyoto, Japan, and Roald Hofman, USA

### **c. Growth of the Organization**

My responsibilities in my last year (1990) as President were concentrated on new applications for new members in the PPF, a trip to visit the member organizations on their home grounds and preparation for transferring the Presidency to Takeo Saegusa, the representative of SPSJ. T. Saegusa was President in 1991/1992 and organized and chaired PPC-2 in 1993 in Otsu, near Kyoto, Japan. The next President was James H. O'Donnell. He asked to hold the Presidency for only one year, 1993, and held PPC-3 on the Gold Coast of Australia, near Brisbane.

The next President was Joseph C. Salamone for 1994/1995 and PPC-4 was held in Kauai, Hawaii, U.S.A. He was followed as President of PPF by Chul Yup Kim (Korea) in 1996/1997. PPC-5 was held in Kyongju, the old imperial capitol of Korea. With Wang Fosong as President for 1998/1999 PPC-6 was in Guangzhou. For 2000-2001 T. Ogawa of Mexico was President. The Mexican polymer community held PPC-7 in Oaxaca. PPC-8 was held in Bangkok, Thailand while the Presidency of PPF was Supawan Tantayanon. The Presidency for 2004/2005 will be in the hands of James, E. MacGrath, U.S.A. and the PPC-9 will again be in

Hawaii.

During the later years I still attended the PPC meetings. I presented a plenary lecture and one "after dinner" talk. Now it is time that the young generation to make their contributions.

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## D. The American Institute of Chemists

In 1984 I received the Chemical Pioneer Award of the American Institute of Chemists (AICh). In actual fact I shared the Award with Allan Hay. He received it

for the synthesis and technical use of poly(2,6-dimethyl phenylene oxide and I for the polymerization of higher aldehydes. I was very honored and pleased. The AICh was undergoing some sort of reorganization and was asked to take over the Chairmanship of the Committee responsible for the Pioneer Award. I enjoyed doing it since I had responsibility of the Awards Committee in the Delaware Section. I served for three years.

I was preparing for the signing of the agreement and had my hands full. The Chairman of the Nominating Committee of the AICh approached me and asked me if I would not mind running for the Chair of AICh. As I had done in the past I said no. He persuaded me I should run for the presidency of AICh. My opponent and likely winner would be the present Secretary who had served the AICh in the past in several capacities. To be sure they would like somebody capable of running the organization, in case the election went wrong.

It almost did. Without campaigning I lost by 23 votes out of 1,500.

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## **E. The Austrian Chemical Society**

### *Honorary Member*

As a student in chemistry at the University of Vienna and other Universities it was customary if not mandatory to join the Austria Chemical Society. I believed I joined in 1947 as I was beginning as a Ph.D. student. To be a member did not have any special privileges. It was however one of the questions that was asked when one applied for a job related to Chemistry.

Today the society has a membership of about 1800 members. As compared to

the US, the membership of the ACS per capita is about 3-4 times as large as that in Austria.

The student membership at the Austrian Chemical Society helped me enormously. I learned "to get involved", became interested in an organization other than the University - but I did not become interested in political activities which many students in the post war period.

I went to my first annual meeting of the Austrian Chemical Society in Linz. We slept in bunk beds, 8 students per cabin in an old ship that was moored in the Danube. I learned how to go to meetings, what to look for in meetings, and learned to like foreign speakers. One speaker stayed particularly in my mind. He was from Milan, Italy and spoke of carbonylation of olefins and oxidation of hydrocarbons. His German was very poor and I had difficulty understanding his presentation. He worked on the borderline of polymer chemistry and chemical technology, subjects we did not have at the University of Vienna. Later he had a great deal of influence on my professional life. His name was GIULIO NATTA and he received the Nobel Prize in 1964 for the discovery of polypropylene. Thirty years later, his granddaughter Giulia, stayed with us in Amherst for part of the summer.

A couple of years later, in 1950 there was an International Congress in Microchemistry in Graz. Graz was the Mecca of Microchemistry: Emich was a well-known inorganic chemistry and Pregl had received the Nobel Prize for his work on Organic Microanalysis. I still remember a few interesting circumstances. We had some nice excursions around Graz, the Schlossberg and the banquet. By then my friend Karl Schloegl spent the evening at the party after the diner, we spend a pleasant evening with a French family. We were ready to go home, the

last tramway had left and we did not have enough money for the taxi - so we walked. Mr. Materet and family walked with us. When we came home to our hotel, we heard the news that the Korean War had started

Mr. Marteret had a pharmaceutical company and, when I asked him, he provided me with a large sample of pomegranate bark, enough for me to spend two years to determine the structure of the alkaloids of the bark. My friend Giuseppe Bianchetti and I worked out the structure of the alkaloid-pelletierin. When it came to publish our results I wrote Mr. Marteret and asked him how to acknowledge his contribution. He said, mention the name of our company *Prolabo* but not m: *Je suis le president* (I am the the President of the firm)

I paid my annual membership fee to the Austrian Chemical Society regularly and faithfully. In he '80's when I was appointed to the Board of Directors of Chemie, Linz, the large Austrian Chemical Company and the International "Beirat" of the Doppler Foundation in Vienna I became again more interested in the Austrian Chemical Society.

In 1999, I was honored by the Society by being elected an Honorary Member, an honor that I share with such greats in Chemistry as Albert Eschenmoser of the ETH in Zurich and Max Perutz, (also from Vienna) who worked in Cambridge, England, who received the Nobel Prize in 1963 for the structure determination of proteins especially hemoglobin.

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## IX. Appendix

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[A. List of Publications: 1994-2004](#)

[B. Names of Co-Authors](#)

[C. Names of Students, Post Doctoral Research Fellows and Visitina Scientists](#)

[D. Curriculum Vitae 2005: Otto Vogl](#)

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### A. List of Publications: 1994-2004

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### b.) Otto Vogl 1927-

Schüler von F. Galinowsky

Promoviert 1950, Assistent am II. Chemischen Institut ab 1948

Professor University of Massachusetts 1970-1983

Professor Polytechnic University, Brooklyn, 1983-1996

Dissertation: Über zweifach ungesättigte Sterinalkohole

### 1. Friedrich Galinowsky 1904-1958

Schüler von E. Späth

Promoviert 1932, Assistent am 2. Chem. Institut ab 1937/38 Habilitiert 1945

Dissertation: Zur Kenntnis des Aconitins. Über die Konstitution des Cytisins.

### 2. Ernst Späth 1886-1946

Schüler von R. Wegscheider.

Promoviert 1910, Assistent am 1. Chem. Institut ab 1910, o. Professor ab 1921

Dissertation: Über Abkömmlinge des Aldols und Crotonaldehyds, Über die Anlagerung von Säureanhydride an Aldehyde und Ketone.

Schwergewicht seiner Arbeiten: Alkaloide

### 3. Rudolf Wegscheider 1851-1935

Schüler von L. Barth v. Barthenau.

Promoviert 1882, Habilitiert 1897, o. Professor ab 1902, leitet das 1. Chem. Institut ab 1902

Dissertation: Über Derivate und Constitution der Opiansäure und Hemipiansäure

Wegscheider arbeitete anfangs als Organiker mit Schwerpunkt Alkaloide, ab 1902 hauptsächlich als Physikochemiker.

### 4. Ludwig Barth v. Barthenau 1839-1890

Schüler von H. Hlasiwetz

Promoviert in Innsbruck 1860 Habil. 1862 Assistent in Innsbruck 1863, o. Prof. in

Innsbruck 1867, Berufung nach Wien 1876. Leitet das 1. Chem. Institut 1877-1890

Schwergewicht seiner Arbeiten: Mehrwertige Phenole. Protocatechusäure, aromatische Sulfosäuren, Kresole, Alkalischmelze verschiedener Phenolderivate.

### 5. Heinrich Hlasiwetz 1825-1875

Schüler von J. Redtenbacher F. Rochleder

1848 Magister der Pharmazie und 1850 Doktor der Chemie in Prag. 1851 Professor in

Innsbruck und 1867-1875 Professor an der T.H. Wien.

Schwergewicht seiner Arbeiten: Chemie von Naturstoffen, besonders von natürlichen Harzen Quercetrin, Phloroglucin, Untersuchung mehrwertiger Phenole, identifiziert erstmalig Resorcin als 1,3-Derivat

### 6. Friedrich Rochleder 1819-1875

Schüler von N. Jacquin und J. Redtenbacher. 1842 Postgrad Studium bei Liebig.

1845 Prof. an Technischer Akademie in Lemberg, 1849-1870 Prof. in Prag, 1870-1875 Leitet das Chem. Institut in Wien.

Schwergewicht seiner Arbeiten: Naturstoffe: Coffein und Theobromin, Roßkastanien, Rubaceen, Ericineen etc. Rochleder galt lange als der führende Phytochemiker seiner Zeit.

### 7. Josef Redtenbacher 1802-1870

Schüler von N. Jacquin Postgrad Studium 1839-1840 bei Liebig

1840-1848 Professor in Prag. Gründet in Prag das erste organische Forschungslaboratorium in Österreich. Seine Schüler besetzten die Lehrkanzeln an allen österr. Universitäten 1849-1870

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Josef Varga	Ferenc Vass	Sh.S. Vezirov
Jane C. Vogl	Petr Vondracek	W. Wada
Ch. Wandrey	Henry Warson	Gilbert Weill
Robert Weiser	Dexi Weng	E. Westhead
H.W. Williams	J.S. Wood	Shikang Wu
Meiyan Wu	G. Wunderlich	Yusuf Yagci
Akiro Yamada	Bunichiro Yamada	T. Yamaguchi
Masahide Yamamoto	Y. Yamashita	Tetsuki Yamaoka
M.D. Yandell	Shilin Yang	A. Yavrouvian
Z. Ye	Shohei Yoshida	Tongyin Yu
Himei Yuki	H. Yuyama	Fu Xi
S.S. Xie	Mao Xu	Peter Zarras
Chiongli Zhang	Hanmin Zhang	Jingyun Zhang
Z. Zhang	Qifen Zhou	S. Zhu
A. Zilkha		

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## **C. Names of Students, Post Doctoral Research Fellows and Visitina Scientists Dr. Vogl's Group 1970 - 1995**

### **Amherst**

H.J. Chang	October 1970 *	E. Schacht	September 1974
N. Vaidyanath	May 1971 @	R. Campbell	January 1975 *
K. Tada	April 1971 0	L.S. Corley	January 1975 *
C. Dudgeon	June 1971 *	W. Deits	February 1975*

D. Bailey	January 1972 *	H. Inoue	April 1975 0
D. Stevenson	August 1972 0	S. Lund	August 1975 @
A. Sicree	September 1971 0	Sh.Vezirov	September 1975 0
D. Lipp	November 1971*	S. Bollens	June 1976 @
T. Tanaka	February 1972 0	M. Helbig	June 1976 0
R.A. Gaudiana	October 1972 0	S. Grossman	June 1976 *
B. Yamada	December 1972 0	A. Stolarczyk	July 1976 0
D. Hurley	January 1973 0	G.F. Lunardon	September 197
I. I. Negulescu	February 1973 0	S. Keinath	September 1976 @
L. Demejo	February 1973 *	J. Muggee	November 1977 *
J. Starr	February 1973 *	D. Bansleben	November 1977 *
A. Beeber	February 1973 *	R. Blanks	November 1977 *
P. Kubisa	March 1973 0	H. Kawaguchi	November 1977 0
D. Roberts	July 1973 !	A. Yamada	February 1978 0
K. Hatada	October 1973	W. Harris	April 1978 0
T. Teshirogi	March 1974 0	Y. Vogl	June 1978 @
E. Vogl	June 1974 @	W. Isabelle	July 1978 @
D. Tirrell	July 1974*	M. Iwasaki	September 1978
		Y. Sumida	October 1978 0
		M. Purgett	November 1978 *

S. Yoshida November 1978 0 W. Dickstein December 1981 @

M. Malanga November 1978 \* P. Patton December 1981 @

Z. Florjanczyk November 1978 0 G.D. Jaycox December 1981 \*

P. Grosso June 1979 \*

M. Kitayama September 1979 0 **Brooklyn**

W. Pradellok November 1979 0 W. Cheung April 1983 @

R. Alward November 1979 @ A. Bittelin August 1983 0

L. Rosati November 1979 \* S. K. Fu August 1983 0

R. Grossman November 1979 \* J. Zhang December 1983 0

T. Kondo	December 1979 0	P. Gomez	January 1984 0
T. Florianczyk	February 1980 0	Liping Hu	April 1984 0
M. Demers	June 1980 @	M. Nanasawa	April 1984 0
Y. Okahata	August 1980 0	T. Doyle	May 1985 *
Z. Nir	August 1980 0	S.Z. Zhu	September 1985 0
C. Sullivan	December 1980 @	A. Sustic	October 1985 *
T. Ouchi	March 1981 0	C.L. Zhang	December 1985 0
D. Fair	August 1981 0	J. Bartus	November 1986 0
D. Lohmann	August 1981 0	P. Zarras	November 1986 *
E. Borsig	November 1981 0	L. Kiliman	May 1987 *
P. Loeffler	November 1981 0	F. Vass	November 1987 0
F. Xi	November 1981 0	E. Foldes	January 1988 0
S.S. Xie	November 1981 0	Heiping Chang	November 1988 0
Shanjun Li	November 1981 0	G. Deak	November 1988 0
		S.K. Chun	June 1989 @
		F.W.H. Kruger	July 1990 0
		W. Ulbert	July 1990 @
		L. Stoeber	August 1991 *
		Meifang Qin	February 1992 *
		J. Crawford	June 1994 @

*Visiting Professors**Associated Masters Students.*

V. Zubov	Moscow 1975	G. Sheldrick
W. Berger	Dresden 1979	A.J. Reisman
G. Hardy	Budapest 1976	K. Neeld
T. Saegusa	Kyoto 1977	A. Padwa
A. C. Albertsson	Stockholm 1982	N. Desai
Z. Janovic	Zagreb 1981	
S.L. Yang	Hanzhou 1986	

A. Zilkha,

Jerusalem 1994

0 Post Doctoral Research Associate      \* Student for Full Degree (Ph.D.)

@ Association with Group      ! Graduate Student

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## D. Curriculum Vitae 2005: Otto Vogl

BORN      November 6, 1927, Traiskirchen, Austria, Naturalized 1959.      Father,  
 Franz Vogl, mother, Leopoldine, née Scholz. Married to      the former K. Jane  
 Cunningham of Sag Harbor, NY; two      children, Eric and Yvonne and 6  
 grandchildren

### EDUCATION:

1950	Ph.D., University of Vienna
1953-1955	University of Michigan, Research Associate
1955-1956	Princeton University, Research Associate

### EMPLOYMENT:

1948-1955	University of Vienna (Austria), Instructor of Analytical Chemistry
1956-1970	E.I. Du Pont de Nemours & Co., Polychemicals, Central Research Department
1970-1983	University of Massachusetts, Professor of Polymer Science and Engineering
1983-Present	University of Massachusetts, Professor Emeritus
1983-1995	Polytechnic University, Herman F. Mark Professor of Polymer Science
1996--	Polytechnic University, Herman F. Mark Professor, Emeritus

### ACADEMY MEMBERSHIPS:

1985	Foreign Member, Academy of Sciences, Austria
1985-92	Foreign Member, Academy of Sciences, GDR
1994	Foreign Member, The Royal Swedish Academy of Sciences, Sweden

### HONORARY DEGREES:

1983	Dr. rer. nat., honoris causa, University of Jena, Germany
1992	Dr. honoris causa, Polytechnic Institute of Iasi, Romania
1996	Dr. honoris causa, Osaka University, Japan

2001	Dr. Sc. honoris causa. Academy of Sciences, Slovak Republic
2005	Dr. honoris causa, Montanuniversity Leoben, Leoben Austria

#### HONORARY MEMBERSHIPS

1993	Slovak Chemical Society, Bratislava, Slovak Republic
1996	Society of Plastics and Rubber Engineers, Zagreb, Croatia
1999	Austrian Chemical Society, Vienna, Austria
2004	Society of Polymer Science, Japan

#### GUEST PROFESSORSHIPS:

1968 & 1980	Kyoto University (Japan), Department of Synthetic Chemistry
1968 & 1996	Osaka University (Japan), Department of Polymer Chemistry
1971, 1987, 1990	Royal Institute of Technology (Sweden), Department of
1998	Polymer Technology
1973	University of Freiburg (Germany), Institute of Macromolecular Chemistry
1976	University of Louis Pasteur, Strasbourg (France), Centre de Recherches sur les Macromolécules
1977	Free University of Berlin (Germany), Institute of Organic Chemistry
1982	Technical University Dresden (Germany), Department of Chemistry
1984	Wuhan University, Wuhan China
1984	East China Normal University, Shanghai, China
1996	Monbusho Professor, Kyoto Institute of Technology, Kyoto, Japan

#### AWARDS and MEDALS:

Medal of the City of Iasi (1976); Fulbright Fellowship (1976); Humboldt Prize, Germany (1977); Senior Scientist Fellowship, JSPS, Japan (1980); W.H. Rauscher Memorial Lectureship, R.P.I. (1985); Distinguished Service Award, ACS, Division of Polymer Chemistry (1985); Mobay Lectureship, University of Pittsburgh (1985); Doebereiner Medal, University of Jena (1985); Gold Medal of the City of Vienna (1986); Medal of the University of Helsinki, Finland (1987); Exner Medal, Austrian Trade Association (1987); Medal of Texas A&M University (1988); Mark Medal, Austrian Research Institute for Chemistry and Physics (1989); Golden Ring of Honor, City of Traiskirchen (1989); ACS Award in Applied Polymer Chemistry (1990); Distinguished Award of the Society of Polymer Science, Japan (1991); H. Coanda Medal, I. Class, Society of Inventors, Romania (1993); Life Member, SPSJ, Japan (1993); Distinguished Service Award, Pacific Polymer Federation (1993), ACS Polymer Division, Mark Award (2000), Golden Honorary Diploma, University of Vienna (2000), Honorary Cross for Arts and Sciences, Republic of Austria (2000), Kulturpreis, City of Traiskirchen (2002), Honorary Medal, Slovak Academy of Sciences, Polymer Institute (2003).

#### RESEARCH INTERESTS:

Functional polymers, polymerizable and polymeric stabilizers, physiologically active polymers, spacer effects in polymeric structures, reactions on polymers, aldehyde polymerization, helical polymers, optically active polymers, stereoregular oligomers of addition polymers, general concept of stereospecific polymerization, structure/property relationship of unusual polymers and polymer blends, optical properties of solids including optical properties, the single polymer helix, oriental lacquers, chiral crystallization and chiral nucleation.

## PROFESSIONAL ACTIVITIES:

Pacific Polymer Federation: President 1987-1990  
National Academy of Sciences: Chairman, NRC Committee on  
Macromolecular Chemistry, 1977-1979  
Member, ad hoc Committee for National Needs in Polymer Science and Engineering, 1980-1981  
NSF, International Division: Advisory Committee, 1981-1984  
ACS Division of Polymer Chemistry: Chairman, 1974  
ACS Connecticut Valley Section: Chairman, 1974  
Secretariat for Macromolecules: General Secretary, 1976  
Gorden Research Conference: Polymers, Chairman, 1981

PUBLICATIONS: Author and co-author of over 630 articles, including 465 scientific papers, and several book chapters. about 50 U.S. and foreign patents; edited ten books

## ADVISORY or EDITORIAL BOARDS, Past and Present::

Journal of Polymer Science, Polymer Chemistry Edition; Journal of Macromolecular Science, Pure & Applied Chemistry (Special Advisor); Journal of Macromolecular Science, Reviews; Polymer (London); Macromolecules (1966-1978); Die Makromolekulare Chemie; Monatshefte fuer Chemie (American Editor); Polymer News; Macromolecular Synthesis; Valchemist (1973-1976); Del. Chem. Bulletin (1968-1970); Journal of Bioactive and Compatible Polymers; Acta Polymerica; Polimeri (Zagreb), Journal of Polymer Materials (India); Current Topics in Polymer Science, European Polymer Journal; Oesterreichische Chemiker Zeitung.

HONORARY EDITOR-IN-CHIEF FOR LIFE: Progress in Polymer Science.

### OFFICE

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### HOME

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