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Polymer Research in Austria. I: Introduction and the Facilities

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Polymer Research in Austria. I
Introduction and the Facilities in Styria: Graz and Leoben

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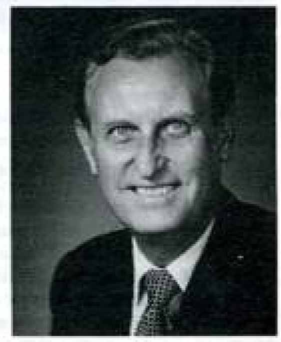


Otto Vogl, H.F. Mark-Professor at Polytechnic University

Introduction

Austria is located in the heart of Europe. To the West lie Switzerland and Liechtenstein, to the South Italy, the Southeast Yugoslavia, the East Hungary, and to the North Czechoslovakia and to the Northwest by Germany. Austria is a Federal Republic with 9 Federal States; one of the Federal States is the Capital of Vienna. Austria has a population of 7.7 million people and a area of about 32,000 square miles; in 1989, it had a GNP of about 140 billion dollars, or about 18,000 $ per capita. The Austrian Schilling is one of the strongest currencies in the world. Austria has its own crude oil, about 1.2 million tons, and has in its refinery a throughput of nearly 8.5 million tons of crude oil and other fuels. Austria has an extensive paper and cellulose industry producing about 4 million tons of various paper products per year. Plastics product production amounts to about 400,000 tons per year.

Austria has twelve Universities with about 8,000 Academic permanent positions and 180,000 students (It also has 6 Colleges of Arts with 7000 students). The expenditures for Research in Science are estimated to be 1.6 billion $.*

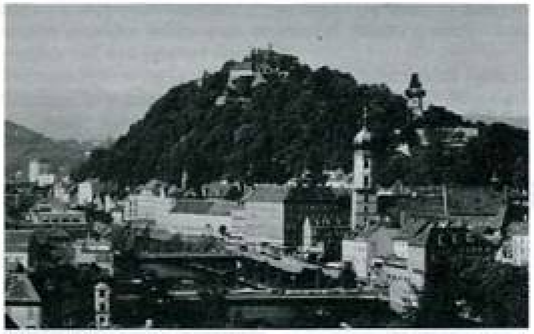
*"Austria in Figures", an Austrian Documentation, published by Federal Press Service, Vienna 1990

Polymer science has had a long tradition in Austria: research in polymer science is carried out in Universities, some research institutes, and industrial laboratories. The academic research institutions are the University and Technical University in Graz, the Technical University and University of Vienna, the University in Linz and there is also some activity at the University of Innsbruck. Herman F. Mark was active for about 5 years in the 1930's as the director of the Institute of Physical Chemistry at the University in Vienna and Otto Kratky at the same Institute in Graz developed the small angle x-ray diffraction technique.

Part I: The Styrian Facilities: Graz and Leoben

1. Graz: Karl-Franzens-University
2. Graz: Erzherzog-Johann Technical University
3. Graz: Vianova Research Center
4. Leoben: Montan University

Graz, with 280,000 inhabitants, is the capital of Styria (one of the nine states located in the central/eastern region of Austria) and the second largest town in Austria. It has two Universities, the Karl-Franzens-Universitat (founded in 1585) with 27,000 students, and the Erzherzog-Johann Technische Universitat (founded in 1864) with 11,000 students. Leoben is a small town in the mountains, it has 33,000 inhabitants; its Montan Universitat was



The "Schloβerg mit Uhrturm", the landmark of Graz.

founded in 1840 and has 2,300 students. All three institutions have research groups engaged in polymer research.

1. Graz: Karl-Franzens-University

Institute for Physical Chemistry (by Josef Schurz)

Polymer research at the Institute for Physical Chemistry began in 1946, when Dr. Otto Kratky was appointed Professor and Director of the Institute. His lifelong research was in X-ray scattering; he was the co-inventor and is now considered the father of the special field of x-ray small angle scattering (SAXS). He was interested in the scattering of such polymers as cellulose, silk and the new developing synthetic macromolecules. The range of small angle x-ray scattering methods was extended, when Kratky's student Josef Schurz, after his "Wanderjahre" at Brooklyn Polytech and in the German fiber industry returned to Graz in 1954 and introduced methods like osmometry, light scattering, and above all his special field, rheology. All these methods were then applied to natural and synthetic polymers both in the solid state and in solution with the aim of structure determinations of polymers. In these years, the Institute became Austria's cradle for two important methods: SAXS (x-ray small angle scattering) and rheology. In

Aerial view of the Karl-Franzens-University in Graz. It is situated in the center of the city and combines both old and new buildings.

1970 the II. International Congress on SAXS was held in Graz, followed in 1982 by the First European Congress on Rheology. At present, the Institute is engaged in polymer research in three main fields: x-ray scattering, light scattering, and rheology (including electrokinetics). The electronics group is most capably assisting with the development of instruments, which is also an important objective of the Institute. Four scientific instruments, which had been developed at the Institute, are now produced commercially. In the following four paragraphs, the present work of the different groups that are active in the Institute shall be outlined.

X-ray scattering (both wide angle and small angle) is done on solid polymers, such as cellulose fibers and thermoplastic polypropylene (Peter Zipper). The structure and texture of the polymers are investigated including their crystallinity. Other characteristics like inner surface, void content, pore volume, pore shape and, if appropriate, fractal dimensions are also studied (Andras Janosi). Recently, the crystalline pattern and its layer-variation in extruded polypropylene samples were determined with an extremely high resolution of 0.1 mm. Regenerated cellulose fibers, spun according to the viscose process and spun from newly discovered solvents (solvent spun) were found to differ not only in their size and shape of crystallites, but also in their fractal dimension (Josef Schurz, Jurgen Lenz).

X-ray small angle scattering in solution is carried out mainly on bipolymers with special emphasis on enzymes and nucleic acids to determine their structure; another objective is to develop structural models for their dissolved state. Recently, biorials such as enzymes (carboxylases, dehydratases), antibodies (IgG, IgM, IgA), and hemoglobins have been studied. The technologically important enzyme cellulase was also investigated; an interesting toad-shaped model was proposed for its structure (Ingrid Pilz). The radiation damage of proteins (enzymes) and measures to protect for these damages was studied by SAXS (Peter Zipper). In another group classical x-ray crystallography is done (Christoph Kratky). Although many systems are being studied, precursors and subunits of natural polymers, such as tetrapyrrolic systems (building blocks of chlorophyll and other natural polymers) and subunits of enzymes are especially investigated.

The group involved in *light scattering* (Otto Glatter) succeeded in working out effective methods that involve the Mie-region. For spherical symmetry, a radial polarisability density profile could be calculated. Polydisperse samples could be analyzed. In oil-water emulsions, the droplet size could be determined. In the field of dynamic light scattering (Laser-Doppler spectroscopy), this group was able to measure diffusion constants and electrophoretic mobility. At present the change of shape (activation) of human blood platelets is being studied. Significant changes in the diffusion constants and in the electrophoretic mobility could be detected, a consequence of changes in temperature, mechanical stress and activating agents. The Lipid IVA, an active precursor of Lipid A has been studied by quasi-elastic light scattering and small angle x-ray scattering. It could be shown that Lipid IVA forms large unilamellar vesicles with a diameter of several hundred nanometers and a membrane thickness of 4.8 nanometers. In combination with the rheology group, streaming profiles are now being studied. All these measurements have been possible by developing and constructing a new laser light scattering spectometer, which can be used for both elastic and dynamic measurements and allows also measurements at small angles. Another field of study in this group is exclusion chromatography coupled with small angle laser light scattering (SEC/LALLS) for the determination of molecular mass and molecular mass distribution. The detection is done by refractive index measurements to determine the concentration, and by LALLS to determine the molecular mass. This method has been used during the last years to characterize various polysaccharides, for example inulin, sinistrin, amylopectin, cellulose derivatives, fructans, dextran, pullulan, xanthan and schizophyllan (Anton Huber).

In the field of *rheology*, the main goal of research in the Institute is the determination of the structure of dissolved polymers by means of rheological measurements. This method is one of the main scientific activities of the Institute in Graz, and many aspects of rheology have been developed at this Institution (Josef Schurz). Polyoxyethylene in water has been studied in the state of an entanglement network solution by means of both rotational and high shear capillary viscometers (Julius Pfragner) to determine the network-characteristics as the apparent chain element and the resistance to penetration. The elastic properties are studied via normal force measurements. At present, the shear modulus at rest is measured in a prestationary creep experiment in an elastoviscometer. It is compared with the corresponding modulus calculated from both shear viscosity and first normal viscosity function for zero shear rate. In another group of experiments, dynamic measurements are being made used for the study of the rheology of erythrocytes and blood in both the normal and in pathological circumstances (Volker Ribitsch). Other biopolymers, such as the synovial fluid, hyaluronic acid, and various soluble polysaccharides are presently being studied with the help of the rheological instruments that are available in this Institute. Problems of technical interest at the present include investigations of pigment suspension, as used in the paper industry as coating colors, at very high shear rates (up to $10^6 s^{-1}$). In addition, electrokinetic studies are aimed at determining the zetapotential and the charge density of materials especially fibers (including wood pulps), planar structures, such as paper, films and plates, granulates, pigments and latices. These data are needed in the control of technical processes; and much of this work is done in cooperation with industry.

Institute of Organic Chemistry (by Bernd Trathnigg)

Polymer research at the Institute of Organic Chemistry started when A. Zinke and his coworkers studied natural resins and their degradation products as early as 1918-23. In 1929 the first of many patents was granted to H. Hönel, who in the subsequent years performed extensive investigations on phenolic resins and polyesters (glyptals). Before World War II mainly phenol-formaldehyde-resins and polyesters were investigated; in 1939 several patents were granted to Zinke for the synthesis of resinous alkyl-substituted phenols and to H. Honel for synthetic varnish and lacquer resins from phenol and formaldehyde. Between 1941 and 1957 A. Zinke, F. Hanus, G. Zigeuner and their coworkers published numerous papers on the hardening process of phenol formaldehyde resins. Several patents were also granted to H. Honel for soluble phenol-formaldehyde resins ("resols") and urea-formaldehyde resins (1952) and their hardening and for coatings made from these polymers. Later, G. Zigeuner investigated urea-formaldehyde resins (1952) and reactions of resols and resitols.

In 1974, Junek and Trathnigg started investigations on (meth)acrylic polymers and on the improvement of adhesion of lacquers on metallic surfaces. Furthermore, the application of

Bernd Trathnigg, leader of the polymer group at the Institute of Organic Chemistry at Graz University (Head: Hans Junek).

density measurements according to the mechanical oscillator method was applied to polymer characterization, especially for detection in GPC and for polymerization kinetics. A density detector for liquid chromatography was developed. The synthesis and polymerization of spiro-orthoesters was investigated, some of them were found to expand on polymerization.

Further work was devoted to the transesterification of phthalates, the synthesis of monomeric and polymeric enaminoketone ligands. The Cobalt-chelates of these ligands were found to bind reversibly to molecular oxygen. Functional azo-initiators were investigated for the preparing of hydroxy-terminated polybutadiene and the decomposition kinetics of these polymers were investigated. The degradation of poly(hydroxybutyric acid) was also studied as was its use in drug formulations. GPC with coupled density and RI-detection was used for the determination of the chemical composition of copolymers together with their molecular weight distribution.

2. Graz: Erzherzog-Johann Technical University

Institute for Chemical Technology of Organic Materials (by Klaus Hummel)

The Institute for Chemical Technology of Organic Materials is exclusively concerned with topics of polymer chemistry. This is reflected in the course requirements and the scientific research activity. The Institute was established only in 1979, but preceding institutions had contributed to the field of macromolecules, for example, when the Institute was under the direction of Professor A. Wacek, work in lignine and cellulose chemistry had a very considerable macromolecular component.

At present the permanent scientific staff consists of one full professor (K. Hummel), two associate professors (F. Stelzer, M.G. Martl) and five assistants. There are also adjunct professors from the rubber and cellulose industry. The laboratory courses include topics such as processing and recycling of polymeric materials and polymers in electronics. The main fields of activity in research are the synthesis, modification, cross-linking and degradation of polymers. Some of the current work will be described in the following section.

Degradation of soluble polymers by olefin metathesis:

The structure investigation of unsaturated polymers by metathesis degradation and the identification of the products by combined

Klaus Hummel, Head of the Institute for Chemical Technology of Organic Materials at the Technical University of Graz.

gas chromatography/mass spectrometry has been developed at this institute. It is a means for elucidating the structure of copolymers and also subsequently to determine the structure of modified polymers with CC double bonds in the backbone. Recent publications have presented new investigations of copolymers containing nitrogen or silicon atoms in the chain. Calculations have also been developed which provide the theoretical bases for the metathesis degradation based on the principle of a carbene mechanism for the polymer degradation.

Application of metathesis degradation to crosslinked polymers:

The study of metathesis reactions on low-molecular-weight olefins facilitated the elucidation of the structure of crosslink and substitution sites present in polymer structures, especially when they are present in low concentrations. It is now possible to discriminate between various types of chemically possible crosslinks. Crosslinked polymer blends were also investigated by the technique of metathesis degradation. In addition, metathesis degradation was found to be a valuable method for the determination of fillers in rubber vulcanizates.

The influence of magnetic fields on chemical reactions of macromolecules:

The investigations of the influence of magnetic field on chemical reaction of macromolecules were primarily concerned with the development of precise experimental procedures using the statistical evaluation of the measurements. Some effects of the magnetic field in enzyme reactions which had been found by other authors could not be confirmed. However, a magnetic field effect was observed in the crosslinking of polybutadiene by peroxides and in the photo-crosslinking of butadiene-styrene copolymers. This effect is explicable by the radical pair theory. In connection with the magnetic field influence, photo-crosslinking by pulsed monochromatic radiation of an excimer-laser was investigated in a more general way.

Electrically conducting polymers:

Conjugated polymers are frequently synthesized via precursor routes. The behavior of thin films of poly(acetylene) and poly(p-phenylene) as the simplest members of this type is suitable to explain the conduction mechanism. By special processing of the pre-polymers it was possible to vary the crystallinity of the films from completely amorphous to a high degree of crystallinity. Pronounced anisotropy of the physical characteristics could be achieved. At present, the ring opening metathesis polymerization of cycloolefins using special transition metal catalysts is being investigated for the synthesis of new specialty polymers and copolymers with interesting properties for future technological applications, e.g. in potential optoelectronics or in molecular electronics applications.

Monte Carlo simulation of modification and crosslinking reactions of polymers:

Modification of 1,4-polybutadiene, copolymers from butadiene and monoolefins and common polyalkenylenes were investigated with suitable computer programs. In most cases, the reaction sequence was a mono- or disubstitution reaction at the C atoms coupled with a partial double bond shift. This is one portion of the radical crosslinking reaction with peroxides. Investigations were carried out in order to verify whether the behavior of a macromolecule is different from that of a low molecular weight model compound. Of special interest is the question if the polymer becomes colored in the visible light by random reactions.

3. Graz: Research Center Vianova Kunstharz AG (by Wolfgang Daimer)

Wolfgang Daimer, group leader of research and development at the Research Center Vianova Kunstharz AG (Director: Merten Schlingmann).

Founded in 1948, the VIANOVA-Kunstharz AG was the brainchild of Dr. Herbert Hönel, a native of Graz. Hönel was 58 years old at the time, and had already acquired a considerable reputation as a scientist in research with his numerous innovations in the field of synthetic resins and especially his discovery of alkyl phenolic resins which are reactive to vegetable oils. The new Company began to produce synthetic resins for the paint industry, as binders for paints and surface coatings. With the Company's Latin name VIANOVA, the founder indicated that he was setting out on a "new path" in paint technology, based on the principle of water based solvents. The revolutionary concept that water could replace the highly flammable, health-threatening and expensive organic paint-solvents required a restructuring of the polymeric binders: along the polymer backbone carboxyl groups were attached by covalent bonding; the carboxylic acid groups were neutralized which converted the whole polymer into a water dilutable polyelectrolyte (anionic polymers). In the case of cationic polymers this principle is reversed—the basic functions were attached to the polymer backbone and acids were used for the neutralization of the basic group.

Watersoluble paint polymers presented two fundamental challenges in development:

a) to synthesize a polymer backbone stable against hydrolysis with no saponifiable groups, in order to guarantee the long life of the paint under aqueous conditions

b) to discover suitable crosslinking mechanisms for hardening the water-soluble paint binder, after their application to the substrate, into a water-resistant coating layer with three-dimensional crosslinked structure

The first of these objectives was achieved by steadily reducing all ester linkages. For anionic polymers, this finally led to the Diels-Alder synthesis involving maleic anhydride using liquid diene oligomers. For cationic polymers it is now possible to react glycidyl functional prepolymers with primary or secondary amines.

The choice of a suitable crosslinking mechanism depended chiefly on the way in which the coating was applied. Possible methods range from oxidative drying at ambient temperature using the oxygen in the air through forced curing in ovens at temperatures of up to 20° C to spontaneous polymerization curing under ultra-violet radiation.

Besides finding solutions to basic problems like these, the main focus of VIANOVA's Research and Development is based on developing products with all the different combinations of properties required for paint binders depending upon the conditions under which they are used. It is obvious, for example, that a coating designed for application to wood must possess elasticity and abrasion-resistance, whereas for the three paint layers applied to a car-body the chief requirements are corrosion protection against salt, resistance to damage by flying stone chips when travelling at higher speed, and permanent gloss retention regardless of the change of climatic conditions. The Company's modern Research Centre in Graz employs 35 graduated scientists and a technical staff of 160 to work on solutions for such problems. The results of this Research and Development go straight into VIANOVA's own synthetic resin production, with an annual capacity of 40,000 t, or else are marketed by means of international licences. Including production and sales divisions, VIANOVA - since 1968 a part of the Hoechst group - has 550 employees and an annual turn-over of 110 million dollars (1989).

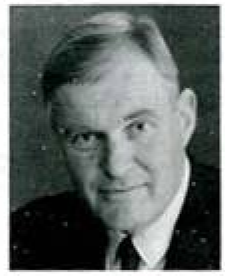
Herbert Honel, who died in June 1990 at the age of 100, could look back on a successful "new path". The early 1960's saw the breakthrough in industrial automotive painting of the waterdilutable binders marketed under the name "RESYDROL". It was the polyelectrolytic qualities of these materials that first made possible the process of electrodeposition coating, today a standard procedure world-wide, which provides greatly increased corrosion protection. Besides significant savings to the economy, the replacement of organic paint solvents reduces the emission of atmospheric pollutants, a major ecological benefit which will guarantee watersoluble coatings an increasingly leading position in the market-place of the future.

4. Leoben: Montan-University (by Klaus Lederer)

The Montan University Leoben (MU Leoben), the well-known Austrian University of Mining and Metallurgy was founded in 1840. In 1970 the University created a program of Polymer Engineering and Science to train engineers for the transformation and application of polymer materials. Taking into account the specific situation of the respective Austrian industry and the international development, the curriculum was designed to include an education in general engineering during the first 5 semesters, followed by special training in polymer engineering and science during additional 4 semesters, with the main subjects:

- Chemistry of Polymer Materials
- Transformation and Technology of Polymer Materials
- Physics and Testing of Polymer Materials
- Design of Parts made of Plastics, Rubbers and Composites

The final 10th semester is fully devoted for the actual work on the master's thesis. About 5-10% of the graduates then proceed to the program (5-8 semesters) to get the Dr.mont. (= Doktor der montanistischen Wissenschaften) degree, a specialty of the MU Leoben. Since 1975, over 180 engineers have graduated and about 80% are now working in the Austrian polymer industry, predominantly in companies involved in polymer processing and in polymer production. Some are also active in the industry producing machinery for polymer processing, e.g. for injection molding, and for sports articles (ski, tennis). The close cooperation with industry made it possible to start the whole polymer engineering program with two professors only, Prof. J. Koppelmann (Chemical and Physical Technology of Polymer Materials) and Prof. W. Knappe (Polymer Processing; succeeded in 1989 by Prof. G.R. Langecker) which were assisted by a number of adjunct professor and lecturers from industry and from other institutions.



Klaus Lederer, Head of the Institute for Chemistry of Polymer Materials at the Montan University Leoben.

As judged by the professional success of its graduates and the close cooperation with the Austrian polymer industry, polymer engineering has been steadily developing into a now well established branch of science and engineering at the MU Loeben. In recent years, about one third of the freshman at MU Leoben go into polymer engineering (about 100 students per year); this program is now distributed over four institutes.

It is most appropriate that the special role of chemistry in this program is now described in more detail. In addition to the core program in chemistry, chemical aspects are also covered in lectures of rubber technology, fiber technology and the technology of lacquers and varnishes. The research in the Institute for Chemistry of Polymer Materials (Klaus Lederer), which was newly established in 1989, is mainly devoted to molecular characterization of synthetic polymers, the characterization of the polymer matrix in composites and the characterization of additives, impurities and degradation products. This field of investigation is considered to be a key factor for polymer engineers to enter various subjects of special interest: chemical reactions during processing, chemical processes during aging, quality control of raw materials, investigation of chemical reasons for the damage of polymer materials, chemical aspects of recycling. The institute, which has evolved from a small research group of the former Institute of Chemical and Physical Technology of Plastics, is extensively involved in international cooperation, e.g. IUPAC working party on the characterization of commercial polymers, and participates in the joint national research program "Research Emphasis Plastic Materials".