

1990

## Polymer Science in Hungary. Part I. The Institutes of the Hungarian Academy of Sciences

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Vogl, Otto; Tudos, Ferenc; and Iring, Margit, "Polymer Science in Hungary. Part I. The Institutes of the Hungarian Academy of Sciences" (1990). *Polymer News*. 95.

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Ferenc Tudos, Margit Iring and Otto Vogl, *Polymer Science in Hungary. Part I. The Institutes of the Hungarian Academy of Sciences*, *Polymer News*, **15(6)**, 185-190 (1990)

Centers of Polymer Research

# Polymer Science in Hungary

## Part I. The Institutes of the Hungarian Academy of Sciences

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Hungary is located in the south-east of Central Europe. It borders to the west on Austria, to the north on Czechoslovakia, to the east on the Soviet Union and Romania and to the south on Yugoslavia. Hungary has an area of 93,000 km<sup>2</sup> (about one percent of Europe); the population of Hungary is 10.6 million people (about 1.5 percent of that of Europe); thus the population density is about 114 people/km<sup>2</sup>.

The capital of Hungary is Budapest; it is located on both shores of the river Danube and has a population of

about two million people; about one fifth of the population of the country lives in Budapest. Budapest, as the country's capital, plays a determining role in the economy (production, commerce, transport) of the country, consequently it is not surprising that it is not only the center of the cultural and economic, but also of the scientific life of the country. The main offices of the Hungarian Academy of Sciences, several universities, the Technical University and other technical schools of higher learning are located in Budapest.

*Polymer News*, 1990, Vol. 15, p. 185-190  
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Printed in the U.S.A.



The Central Research Institute of Chemistry of the HAS.



Building of the Hungarian Academy of Sciences (HAS).

Macromolecular research in Hungary is being carried out in several institutions in Budapest as illustrated by Table 1.

Table 1. Macromolecular Research Institutions

Institution	Authority
1. Scientific Research Institutes and Groups	Hungarian Academy of Sciences (HAS)
2. University Institutions	Ministry of Education
3. Industrial Research Institutes	Relevant Ministries
4. Developing Institutes of Big Enterprises	Relevant Companies

In the first part of this series of articles we describe the activities of macromolecular research that are carried out in the two institutions of the HAS: 1. Central Research Institute of Chemistry of the HAS, Budapest. 2. Research Laboratories of Inorganic Chemistry of the HAS, Budapest.

#### 1. CENTRAL RESEARCH INSTITUTE OF CHEMISTRY OF THE HAS, BUDAPEST

The institute was founded in 1954; pioneering work in several areas of chemical research is being carried out in this institute. The Department of Macromolecular Chemistry which is responsible for the research activities in macromolecular science has a staff of about 50 people, 25 of them have a university degree. The leader of the department is Professor Ferenc Tudos, a member of the HAS.

##### a. Department of the Polymerization Kinetics

The research activities in this division are directed by Ferenc Tudos and Tamara Bereznich-Foldes. Over the last 30 years scientists of the division dealt mainly with the systematic investigation of *elementary reactions of radical polymerization and copolymerization* in chemically inert solvents. Industrial vinyl monomers (styrene, acrylates acrylonitrile, vinyl chloride, vinyl acetate) were investigated; particularly studied was the radical polymerization of butadiene in solution.

Several specific methods were developed and equipment was redesigned to achieve high accuracy in the study of elementary reactions in polymerization processes, such as initiation, chain propagation, chain termination, chain transfer and inhibition of polymerization (Dr. A. Nagy). It has been found that the initiation and propagation constants of radical polymerization are not constant but can vary depending on subtle changes, such as concentration of monomer, or on the conversion in copolymerizations, even though the reactions proceed in inert solvents. It has also been found that every kinetic parameter which includes the chain propagation rate constant is dependent on the reaction medium in most systems investigated. These fundamental studies provided the basis of the now well accepted hot radical theory of homo- and copolymerization.

If one takes into account that the kinetic parameters (which are included in the chain propagation constants) depend also on the medium (type and concentration), the anomalies which had been found in the parameters of the rate equation of bicomponent radical copolymerization, could be clarified. The cross termination parameter  $\phi$  was found to be constant if the solvent dependences of the  $r_1$ ,  $r_2$ ,  $p_1$  and  $p_2$  parameters were also taken into consideration. The now well known and generally utilized *new linear graphic method*, the so-called *Kelen-Tudos method* (K-T equation) for the determination of copolymerization constants was developed. This new method can predict with relative ease and accuracy whether the system under study could be treated by the classical rate equation. Using the K-T equation, several thousand data from the literature data which describe radical copolymerizations were re-investigated; it was found that only about 17% of the copolymer systems can be described by the classical rate equation.

The accuracy of the results could considerably be improved by the novel equipment developed for the determination of absolute rate constants of chain propagation and termination. This equipment enabled the determination of the rate constants with a much lower error limit.

In the studies of *polycondensation kinetics*, progress has been achieved in the investigation of well-known polymer systems. Most of them had not yet been studied kinetically (e.g. furan-resins, phenol-formaldehyde resins). Some of these systems can now be investigated by a newly developed technique of gel permeation chromatog-



raphy; these studies are conducted by Zsuzsanna Laszlo-Hedvig and her group. This kinetic approach to polycondensation research was found to be applicable to practical problems of the manufacture of industrial polymers, primarily crosslinked polymers.

The mechanism of polycondensation reactions was investigated in great detail; considerable progress was made in the condensation systems of acid catalyzed furfuryl alcohol and furfuryl alcohol-formaldehyde. The ratio of methylene to methylene ether linkages in polymers prepared under various reaction conditions was carefully determined. The role of "active" and "inactive" reaction intermediates was identified (Dr. M. Szesztay).

Other polyaddition reactions were investigated from the theoretical and from the practical point of view. New information was obtained on the thermal properties of acid catalyzed epoxy model systems, as well as on the relationship between the thermal behavior and stability of the catalyst as it applies to the mechanism of the polyaddition reactions.

The experience gained from the kinetic investigations allowed its application to applied research; it provided the solutions to important problems. Among the goals were significant objectives for the production of antistatic and flame resistant polyacrylonitrile (PAN) fibers, for water-purifying gels and for furane resins used in foundries.

In the Central Research Institute of Chemistry research has also been carried out for about 20 years to further understand the mechanism of the degradation of polyolefins and PVC (autooxidation, photodegradation and physical aging).

The project leader for the research on polyolefin oxidation is Dr. Margit Iring and the research effort of her group is focused on the following questions: a) Is the simplified mechanism for the oxidation of liquid hydrocarbons also valid for the polyolefin oxidation, and what are the limits of its application; b) Some features of the mechanism and kinetics of the oxidation, characteristic to polyolefins, need to be clarified particularly important is the determination as to how much influence does the macromolecular and supermolecular structure have on this oxidation; c) How can the oxidation products of the polyolefin autooxidation be best characterized (qualitatively and quantitatively) and how can the mechanism of their formation be best described.

In order to find answers to these questions, the following investigations were carried out: The rate of oxidation in the condensed phase was studied as a function of various transport processes (estimation of the kinetic region) and of kinetic reaction parameters. Some characteristic properties of elementary processes of the oxidation reactions are clearly related to the polymeric character of the polyolefins such as: a.) dependence of the primary initiation step of oxidation on the polymer structure; b.) formation and decomposition kinetics of polymeric hydroperoxides; c.) relationship between different subtle differences in the chemical structure of the macromolecules and the incorporation of oxygen into the polymer; d.) the structure of the reaction products formed during the polyolefin oxidation; e.) the way reaction products are formed and the effect of the polymer on the structure of the reaction products and/or on the ratio of the individual products; f.)

the effect of the physical state of the reaction on the rate and mechanism of oxidation (studies of the oxidation of polyolefins in solution, as compared to the oxidation in the condensed phase) g.) the effects of structural and stereo-regularity and polymer orientation.

Research on kinetics of PVC degradation is carried out under the guidance of Professor F. Tudos and Professor T. Kelen, in cooperation with Dr. T.T. Nagy, Dr. B. Turcsanyi and Dr. B. Ivan.

PVC degradation has two characteristic features. First, the study of the kinetics of the loss of HCl; of equal importance is the investigation of the kinetics of the polyene formation (primarily based on spectrophotometric measurements). Second, most of the degradation experiments are carried out in dilute solutions of PVC assuming well defined, homogeneous reaction conditions: these reactions must be translated into the more realistic and important condensed phase.

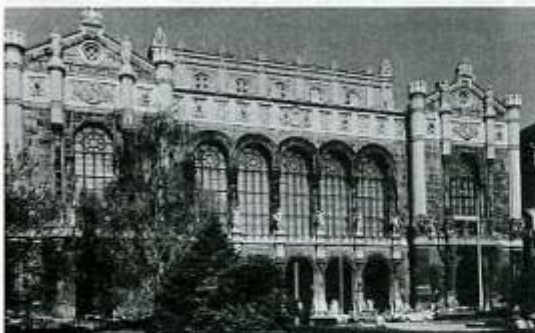
Several important results have been obtained; among them are the kinetic determination of the structural defects in PVC, the investigation of secondary reactions of polyenes and the demonstration of the connections between thermal and thermooxidative processes in PVC degradation.

In the investigation of the kinetics and mechanism of PVC stabilization the two main types of thermal stabilizers, metal soaps and tin containing stabilizers were studied. From the results of this work, the generally accepted mechanistic theories of stabilizer action in PVC had to be modified.

Like everywhere else in the world, interest in polymer blends and composites has increased in the last few years also in Hungary. Since the interactions on the interphases influence significantly the properties of heterogeneous polymer systems, extensive research is being done in this field also in the Central Research Institute of Chemistry (Project Leader: Dr. Bela Pukanszky). It has been established that in composites the interphases can be regarded as a separate phase. The percentage of this interphase as a part of the total system depends on the size of the contracting surfaces, while its properties are determined by the strength of the interaction and by the property difference of the constituting components, e.g. polymer and filler. The interphase reactions are further complicated by the fact that the effect of the interphase on the properties of the individual components depends also on the extent of deformation of the individual phases. (Various properties show a significantly different dependence on the contact surfaces than on other influencing factors.)

The final goal of the research on composites and nonmiscible blends is to establish quantitative correlations between interface interactions and composite (or blend) properties. The measurement of the elastic module is an important type of measurement. Since elastic modules are measured at approximately zero deformation, interface effects are difficult to detect. Quantitative correlations could be established, however, between the tensile yield stress and the thermodynamic parameters characterizing polymer/filler interaction in thermoplastic composites. (Tensile yield stress is determined by the decrease of the effective load-bearing cross-section and by interface interactions). The correlation could be extended





The Municipal Concert Hall in Pest.



View of Pest (left-bank side of Budapest) with the Elisabeth Bridge.

to the prediction of the dependence of tensile strength on the composition, if the decrease of specimen cross-section and the effect of orientation was also taken into consideration.

Modification of the interaction on the interphase is a well-established way to modify composite properties. The surface treatment of a filler by a non-reactive organic compound reduces its surface tension and also the polymer/filler interaction. A close correlation was found between the reversible work of adhesion and the mechanical properties of the composites; with decreasing adhesion the strength decreased but the elongation increased. Composites of higher strength could also be produced, if the filler was treated with a polymeric material as long as the interdiffusion of the interphase and the polymer matrix was possible.

Interface interactions are especially important in multicomponent systems, where the mutual wettability of the components determines the properties of the poly-

meric system. In PP/EPDM/CaCO<sub>3</sub> composites, different structures and consequently widely differing properties could be observed and prepared.

The role of the interphase is equally important in polymer blends. Further research will be directed to the application of the same principles in blends to establish a correlation between miscibility, interphase interactions and mechanical properties of the blends.

The division dealing with the *synthesis and investigation of biologically active polymers, polymer prodrugs* (Dr. M. Azori as its head) was established ten years ago. The aim of their work was and is to produce polymer-bound drugs with improved (prolonged and/or selective) therapeutic activity.

For polymer carriers, either synthetic (poly-N-vinylpyrrolidone-co-maleic acid) or natural macromolecules (dextrane) are investigated. The physico-chemical properties of the polymers, the possibility of covalent bond formation between polymer chain and the pharmaceutically active molecule, as well as the connection between the chemical structure of the macromolecules and their biological properties are being investigated.

Among the drugs attached to the polymer chain directly or through a spacer group are anticancer agents, biological alkylating agents and antimetabolites, but also antirheumatics and antiarrhythmic drug molecules.

The release of bioactive materials from functional polymer derivatives are studied in vitro conditions in the presence or absence of enzymes.

The enzymatic fission of oligopeptide spacer groups and the influence of chemical structure of the side chain and of the macromolecule on the rate of release of active groups are also studied by model reactions. Results of these investigations have been reported in over 20 publications.

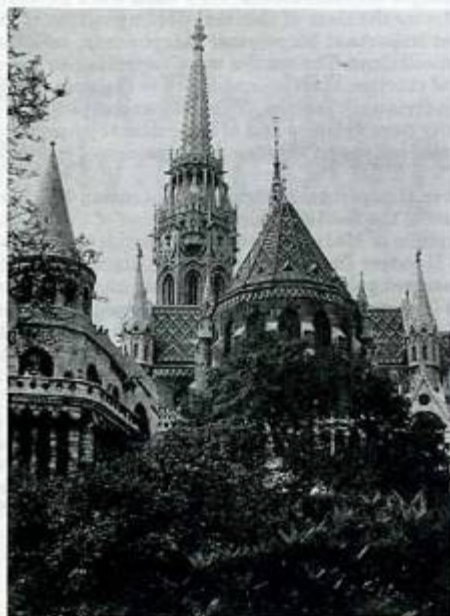
The laboratory of *electron spin resonance (ESR)* (Dr. A. Rockenbauer as the head) is involved in the development of spin labelling and spin trapping techniques in order to study the physical and chemical properties of polymeric systems. Various computer programs have been developed for the interpretation of the variations of spectra, differences caused by the conformational changes of macromolecules. Kinetic ESR methods are applied for the investigation of free radical reactions of hindered amine light stabilizers. Mechanically produced orientations are also studied in polymer composites.

#### Scientific cooperations

The Department of Macromolecular Chemistry has extensive contacts with several International macromolecular research centers. One active program of cooperation exists with the Department of Biological Sciences, University of Keele (United Kingdom) on the synthesis and characterization of biologically active polymers. The main objective of this cooperative research program is to study the interaction and possible penetration of polymers into the cells.

Scientific cooperation also is under way with two universities in the USA. Since 1987 cooperative research has been in existence between the laboratories of Professor Otto Vogl, Polytechnic University, New York and Professor Ferenc Tudos. The work is involved with the "Ther-





*Fisherman's Bastion with Matthias Church.*

mal Oxidative Degradation of Head to Head and Head to Tail Polyolefins and Poly(vinyl halides)"; its objective is to compare the thermal oxidation behavior of polymers containing the same units in the polymer structure but in different arrangement [head-to-head (H-H) and head-to-tail (H-T) polymers].

A cooperation has also existed for several years between the Department of Macromolecular Chemistry of Professor F. Tudos and the laboratory of Professor J.P. Kennedy at the Polymer Institute of the University of Akron. This work was concerned with the investigation of "The Kinetics and the Mechanism of Cationic Polymerization". Research was undertaken to evaluate the inifer technique, a chain transfer method recently discovered in cationic polymerization, to elaborate the quasiliving cationic polymerization technique and to understand the conditions under which cationic polymerization is living (Mrs. A. Fehervari, Professor T. Kelen, Drs. B. Ivan, G. Kaszas, M. Gyor, Zs. Fodor and A. Nagy). In addition to this main research objective, work was also carried out in the modification of PVC and other polymers (B. Ivan, B. Pukanszky). B. Ivan has carried out research on living-cationic polymerization and on the synthesis of new amphiphilic networks for potential biomedical applications.

## 2. Research Laboratory for Inorganic Chemistry of HAS

The Research Laboratory for Inorganic Chemistry is working within the Research Laboratories for Natural

Sciences of the Hungarian Academy of Sciences. Polymer research work is being done in all its three departments. The director of the Research Laboratories is Dr. Tamas Szekely.

Most of the polymer research is carried out in the Macromolecular Department (Department Head: Ferenc Till). The Department is dealing with the "Thermal Behavior and the Thermal Decomposition of Polymers", in order to clarify the chemical structure of polymers and especially their fine structure. The department has a computer controlled thermogravimeter mass-spectrometer (TG/MS), a DSC instrument, a direct current heated pyrolyzer and a Curie point pyrolyzer (both can be attached directly to a gas chromatograph), a GC/MS, an LC and several GC instruments.

At the Department of Solid State Chemistry of the laboratory (Department Head Dr. Imre Bertoti) research on surface chemistry is in progress using ESCA techniques, also for polymer samples (Project Manager: Dr. Andras Toth). The changes in the chemical bond structures of polymers produced by thermal treatment or ion bombardment are measured on the surface of polyimide and methyl-phenyl-cyanopropyl siloxanes. It was found that the siloxane component of block copolymer membranes was enriched on the surface, especially in those cases, where the membrane had been cast from a solution of a good solvent for the siloxane part of the blockcopolymers.



*Building in which the Laboratory for Inorganic Chemistry of the HAS is located.*

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## Centers of Polymer Research

At the Department of Electrochemistry (Department Head: Dr. Bela Lengyel), physico-chemical studies of "Anticorrosive Plastics Coatings" is carried out (Project Manager: Ferenc Janasz). The interaction of the corrosion caused by impurities within the layer structure and the electric properties of polyacrylate and acrylate-urethane copolymer coatings are being studied.

### International Cooperations

A close Hungarian-American cooperation is in effect in the investigation of reaction kinetics of "The Mechanism of the Thermal Decomposition of Cellulose and Cellulose-like Materials" (Project Manager: Gabor Varhegyi). A recent project "The role of homolytic and heterolytic reactions in thermal decomposition of cellulose and lignin containing materials", between HAS and NSF involves as a partner institution the Natural Energy Institute of the University of Hawaii. The thermal decomposition of cellulose and lignin containing materials was studied as a function of the thermal treatment and of the addition of inorganic salts to the sample. The objective of this work is to acquire basic chemical knowledge for the utilization of cellulose and lignin containing agricultural waste and by-products.

The experimental basis of the research was the simul-

taneous performance of thermogravimetric and mass-spectroscopic measurements. New data were gathered about the mechanism of thermal decomposition of the two most important biopolymer components, cellulose and hemicellulose. The results were supported by calculations of reaction kinetics and fitted to the possibly existing individual reaction. Thermal decomposition of chemically pure samples and of agricultural by-products was carried out in the absence and presence of inorganic salts.

Another Hungarian-American cooperation has been developed in the field of "Characterization of the Chemical Structure of Macromolecules" by chemical pyrolysis (Project Manager Dr. Marianne Blazso). In the last three years, several polysilane homopolymer and copolymer samples (prepared in the Chemical Engineering Department of the University of Wisconsin) were investigated by analytical pyrolysis. The main products of thermal decomposition of polysilanes were found to be cyclic tetramers and pentamers. Under the conditions of the pyrolysis process, the chemical structure of these decomposition products corresponds to tetra- and pentasilane sequences originally existing in the polymer chain. Thus, the sequence distribution of silane copolymers containing two different kinds of substituents can be characterized by analytical pyrolysis.