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Polymer Science in Hungary, Part II. The Universities in Hungary

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Polymer Science in Hungary

Part II. The Universities in Hungary

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In the first part of this series we described the institutions where macromolecular research in the Hungarian Academy of Sciences is being carried out. In this second part we describe the research in macromolecular science that is being done at the universities in Hungary.

The universities with teaching and research in macromolecular science in Hungary are as follows:

1. Technical University of Budapest: The Department of Plastic and Rubber Industry and The Department of Organic Chemical Technology
2. Eotvos Lorand University of Science Budapest: The Department of Colloid Science: The Department of Chemical Technology
3. Kossuth Lajos University, Debrecen Department of Applied Chemistry

A. TECHNICAL UNIVERSITY OF BUDAPEST

a. History of the Technical University

The first institution which became one of the predecessors of the Technical University of Budapest, the "Institutum Geometricum" was founded by the government in August 1782. It was organized to provide training in civil engineering at a level of higher education; it was the first institution of its kind in Europe.

The second institution which became part of the Technical University or Budapest, the Industrial School of Pest, was opened in 1846. The Institutum Geometricum and the Industrial School were combined in 1850. In 1870, the then called "Jozsef Nador" Technical University was raised to the level of state universities, based on a proposal of the then Minister of Education, Jozsef Eotvos. In 1901 the Technical University also received the right to graduate their candidates with a degree of doctor of engineering.

The Technical University of Budapest is not only the largest educational institution of Hungary, but it is also a most significant research center. The greatest part or teaching and research in macromolecular science is carried out in two institutes of the Faculty of Chemical Engineering: the Department of Plastic and Rubber Industry, and the Department of Organic Chemical Technology.

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Technical University of Budapest; Main Building on the Bank of Danube.

View of Buda with the Castle Hill.

Department of Plastic and Rubber Industry

The Department of Plastic and Rubber Industry, the first academic unit in Hungary for the education of specialists in the production, processing and application of polymers, was founded in 1952 by Professor Rudolf Ballo. Engineering students could graduate with the degree of B. Sci. and M. Sci. in 3 and 5 years, respectively. Since 1964 special 2-year courses have been organized for postgraduate training.

At present 15 professors and research associates, as well as 18 technical and administrative staff are employed in the department. Polymer research is conducted by ad-hoc teams formed for the specified projects.

After Rudolf Ballo's retirement Professor Gyula Hardy, member of HAS, became head of the department. He held this position from 1959 till 1981; he was at the same time also the director of the Research Institute of Plastics. Since 1981 Dr. Jozsef Varga has been the head of this department.

The activity of the department is closely connected with the plastic industry of the country.

The main research interests of the founder, Professor Rudolf Ballo was "Heterogeneous Polymer Systems and Composites"; his group studied the preparation, characterization and properties of these materials. In the same department, the field of paints, crosslinking reactions of drying oils and the mechanism of the action of siccatives were studied under the Kalman Juhasz.

Work on "Polymerization Reactions" was started in 1959, when Professor Hardy took over the directorship of the department. The investigations focussed on the synthesis of new monomers suitable for polymers with special properties, as well as on their polymerization and copolymerization. Polymers and copolymers of N-vinylimides and those of vinyl thioacetates were investigated in order to produce biologically active materials containing $-NH_2$ and -SH groups which provided protection against radiation.

In the 60s and 70s the study of the polymerization in solid state initiated by high-energy radiation became an important activity in the department. These research activities were conducted in cooperation with research associates of the department and the Research Institute of Plastics. The staff of the Technical University (J. Varga, M. Kerekes) carried out pioneering work in the field of polymerization in two-component systems with characteristics of eutectic phases. They determined the general characteristics of the topoatactic polymerization on models of different N-vinyl compounds and acrylamides, and verified the primary role of physical factors and of their crystal structure.

This work was the basis of the investigation of "Polyimides, Acrylamide based Hydrophilic Gels, Crystallization and Structure of Polymers and of the Synthesis of Liquid Crystalline Monomers and Polymers".

Research on the "Polymerization of Vinyl Chloride and the Stabilization of PVC" was launched by Associate Professor Kalman Juhasz at the same time the production of PVC started in Hungary. One of the reasons was to increase the inherent stability of PVC by developing a "cold polymerization" process which is carried out at lower temperature. These investigations required the development and adaptation of methods suitable to determine the thermal stability of PVC and to follow the degradation processes. It was also important to investigate the effectivity of stabilizers and stabilizer compositions. New initiators (furoil peroxides and derivatives) were developed and their decomposition kinetics and polymerization activity were compared with their performance In the industrial production of PVC (Dr. Molnar).

The "Kinetics and Retardation of the Gel Effect" was investigated in block polymerization at high conversion by Imre Mondvai and his group.

"The Thermally Initiated Polymerization of Acrylamide" has been studied from the fundamental point of view since the early 70s. Important results allowed the development of practical use for hydrogels based on polyacrylamides; this work was done in cooperation with other institutes (Inorganic Chemical Laboratory of HAS, Mining Shaft-Sinking Enterprise, Geodetic and Amelioration Enterprise etc.). Polyacrylamide based gels have been successfully applied in mining and civil

engineering to solve the problem of water penetration. Investments in mining enterprises could be saved by using a procedure patented as "MAT-akril"; by using the procedure "Superaqua", water drains can be regenerated without disconnecting the system. A newer type of hydrophilic gel has been developed in the group of G. Nagy; these products are patented under the name of "Tonplast".

From the industrial point of view the development of processing technology of polymer powders for electroxerographic copying (Professor S. Doszlop) was a significant achievement.

Since the 50s, research on "Thermosetting Polymers" has a role priority in the activity of the department because of the demand of the plastic industry in Hungary. One of the points of focus was the fundamental study of the reactions that lead to "Phenol-Aldehyde Resins"; this work was the basis for developing the technology of a continuous preparation of the resins (Project Manager I. Kovacs).

Studies on "Epoxy-Resins" resulted in the development of the systems "Enovol" which are based on epoxy resins and novolac (Associate Professor I. Szollosi). These resins can be used for laminates for the electrical industry. The interrelationshsip of the reactions between the epoxy and novolac resin was elucidated by using model reactions.

The kinetics and the mechanism of the reactions of polycarbamides were investigated and their thermal and thermooxidative degradation was studied by I. Szollosi and his group.

Also in the 1970's work was started on the preparation and application of "Heat Resistant Polymers" with thermostability up to 300°C. The formation of polyimides prepared by polycyclization, polyaddition and polymerization have been studied by J. Varga, K. Belina, and M. Baksay. Some of the results include the preparation of light-sensitized polyimide intermediates (polyamic acids) suitable for photolithography; these polymers can be used for the production of thin-layer circuits. Polyimides were successfully applied for coating of surfaces on chromatographic columns. The stabilization and control of the viscosity of polyamide acid solutions were patented.

General features of polyimide formation in polyaddition and imidization for polycyclization were studied. The effect of monomer purity on the product properties were shown to be important. An interaction seems to exist between the anhydride and the solvent resulting in the formation of an intermediate which is oxygen sensitive and can have an important effect on the polyaddition reaction. A synthesis of solvent-free polyamide acids has been worked out, with which the characteristics of imidization could be further studied.

In order to perform the duties of education and research on a high level, one unit of the department had been assigned to cooperate with the Electrical Insulating Materials and Plastic Factory; it is responsible to carry out research activities in polymer processing (Project Manager: L. Zubonyai).

Research on "Processing Technology" was started with the study of thermosetting materials; it was then extended to the processing of thermoplastics (injection-molding, extrusion) (I. Molnar, I. Mondavi, L. Zubonyai, O. Kelemen). Two specific areas were investigated: a) Study of rheology of polymer melts (I. Mondvai, L. Macskassy). b) Crystallization of polymers as a function of their thermal and mechanical history. The effect of different additives on the crystallization of polyolefins and polyolefin-based blends is being investigated (J. Varga, A. Solti, I. Molnar). Two scientific movies were made on the spherulitic and cylinderite type crystallization of polypropylene. The β-modification of polypropylene was prepared in pure form in the laboratory by proper modification of the processing conditions (J. Varga, G. Garzo, F. Toth). Final products based on β-polypropylene were produced by compression molding, injection molding and extrusion. Multicomponent systems (filled compounds and blends) of β-polypropylene were also prepared and their properties were determined.

b. Department of Organic Chemistry Technology

The Department of Chemistry Technology is the largest unit of the Faculty of Chemical Engineering of the Technical University of Budapest; it is headed by Professor Laszlo Toke. One of the independent research units of the Hungarian Academy of Sciences, under Professor Istvan, is also working in this department.

Two units are presently engaged in carrying out research on 3 projects each; 50 undergraduates and 5-10 postgraduates are involved in these activities. One of these subjects is related to the field of macromolecular chemistry and has three directions:

1. *Cellulose Chemistry*: Some aspects of the oxidation of cellulose are being studied in order to optimize processes for their use in the textile industry; the mechanism of cellulose oxidation by nitrogen dioxide is particularly investigated. Thermolysis of cellulose is also being studied; a theory has been worked out for the reactions of cellulose with active dyes (J. Frankl, I. Kovacs, I. Rusznak) The damaging effect of cellulose crosslinking by monomers with N-methylol groups on the characteristics of fibers is being investigated, and the possibilities of decreasing this effect by modification of the reaction conditions are being studied by Gy. Lepenye. Cellulose for the paper industry has for some time also been prepared from hemp. The conditions influencing the swelling of cellulose were investigated and a method for hot mercerization has been developed, and efforts are being made for its practical application (J. Reicher).

Modified polysaccharide derivatives have been obtained by oxidation of starch; optimized materials have been studied for their use as adhesives and in textile technology (E. Polyanszky).

2. *Protein Research*: The crosslinking of fibers (wool, fur) activated by singlet oxygen is being studied in order to improve the characteristics of the fibers and their processability (I. Rusznak, L. Trezl). Reactions of biological importance between the protein units of L-lysine, L-arginine with formaldehyde are being investigated. It was found that the results obtained can be utilized in agriculture and in the tobacco industry (I. Rusznak, L. Trezl).

3. *Synthetic Polymers*: Research on synthetic polymers is carried out in three directions: a.) Polyolefin-based polymer composites with 4 components were prepared: their properties and the possibilities of their application

is being investigated. The composites contain an elastomer, a tenzide and inorganic pigments in addition to polyethylene or polypropylene. The dependence of the properties of the composites as a function of their components is being evaluated. Composites adequate for specific applications are being produced and marketed under the name of MODILENE by the Tisza Chemical Work. The patented process is based on the research of Gy. Bertalan, I. Rusznak and Gy. Marosi.

The mechanism of cationic polymerization of lactams has also been studied. It was found, that amidine compounds are formed during the chain propagation reaction; the water formed during the hydrolysis complicates the kinetics. On the basis of mechanism worked out in detail, a kinetic model was developed (P. Anna, Gy. Bertalan).

The preparation of polyacrylate dispersions with monomers containing functional groups was studied. Dispersions applicable in paper and leather industry have been prepared by P. Anna, Gy. Bertalan and Gy. Marosi.

About 200 articles were published and 15 inventions were patented in Hungary and other countries from the research done in the Department of Organic Chemical Technology in the field of macromolecular chemistry.

2. EOTVOS LORAND UNIVERSITY OF SCIENCE, BUDAPEST

a. History of the University

The predecessor of the University was founded in 1635 in Nagyszombat. Originally it was a Jesuit University with two faculties: The Faculty of Theology and the Faculty of Arts. In 1667 a Faculty of Law and in 1769 a Faculty of Medicine was added. After the Jesuit Order was dissolved, the University moved to Buda in 1777 and to Pest in 1778.

After World War I the University was named after its founder: Peter Pazmany, cardinal-archbishop of Esztergom. In the 20th century the rapid development of science together with some practical reasons necessitated the transformation of the old university. The Faculty of Medicine was reorganized into an independent University of Medicine, the Faculty of Theology became an independent Theological Seminary. In 1949 the Faculty of Arts was divided into two faculties. The Faculty of Science was organized to undertake teaching and research in the entire field of the sciences. The university now was renamed after Lorand Eotvos, a world-famous physicist, and professor of the university

The building of the Eotvos Lorand University of Sciences on the Museum Ring was erected between 1880 and 1883 by Imre Steindl and Antal Weber. This building housed (until 1989) the chairs dealing with natural sciences; among them are the chairs in chemistry dealing with macromolecular research. This year, the research groups associated with these chairs moved to a new, modern building on the Buda side of the city, the right side of river Danube, near the Polytechnical University.

b. Department of Colloid Science.

The Department of Colloid Science was founded in 1939. The first professor of colloid science and the head of the department was Professor Aladar Buzagh. Since the early 1950's and under his leadership polymer research and education has become a part of the activities. At the present time the department is headed by Professor Sandor Rohrsetzer.

The research activities in the field of macromolecular science is focused on three major areas: i. thermodynamics of polymer solutions and gels, ii. structure and properties of macromolecular systems, and iii. interactions of polymers with colloids of different types.

Since the mid 1960s Professor Miklos Nagy has carried out intensive research on dilute solution properties of water soluble macromolecules, as well as on the thermodynamics of preferential solvatation involving polymers. The interaction of synthetic macromolecules with enzymes was also part of his research interest. Later, Miklos Nagy turned his attention to polymer gels, prepared by crosslinking of well-characterized linear macromolecules. The formation and the properties of physical

Eötvos Lorand University (ELTE), Budapest; the Old Chemistry Building.

The New Chemistry Building of ELTE.

gels obtained by association of poly(vinyl alcohol-vinyl acetate) block copolymers are also being studied in cooperation with his coworker Dr. Judit Gyorgyi-Edelenyi.

Associate Professor Miklos Zrinyi is concerned with the thermodynamic properties of neutral polymer gels with special emphasis on the collapse phenomena. His research interest also includes the effect of fillers on their effectiveness of reinforcement and that of other heterogeneities of colloidal size on the mechanical properties of dry and swollen polymer networks. In cooperation with Professor Hans-Georg Kilian (Department of Experimental Physics, University of Ulm, FRG), they are dealing with the non-Gaussian theory of polymer networks. The objective of this research is to study the influence of the morphological characteristics (size, shape and degree of aggregation) of the filler particles as well as the strength of adhesive forces that act between the surface of the filler particles and the matrix polymer as they effect the mechanical and swelling properties or filled networks.

Associate Professor Ferenc Horkay is particularly interested in the structure-property relationships of polymer gels. He is studying the osmotic and mechanical behavior of chemically crosslinked network systems equilibrated with thermodynamically good-, theta- and poor solvents. His work in this area is being carried out in close collaboration with Professor Erik Geissler and Dr. Anne-Marie Hecht (Laboratoire de Spectrometrie Physique, University of Grenoble, France); it is involved with the microscopic and macroscopic characterization of swollen polyacrylamide, poly(vinyl acetate), polystyrene, and poly(dimethylsiloxane) networks. Radiation scattering (dynamic light scattering, small angle X-ray scattering) experiments are used to characterize structural heterogeneities that had developed during the formation of the networks; these investigations are combined with the study of macroscopic swelling pressure and of shear modulus measurements.

Professor Sandor Rohrsetzer with Associate Professor Ferenc Csempesz and Dr. Peter Kovacs are interested in the interaction of polymers with colloids such as with hydrophobic sols and with latex particles. They are investigating the structure of the adsorption layer formed by competitive adsorption of neutral polymers on solid surface from binary mixtures; its effect on the stability of colloidal dispersions is also being investigated.

c. Institute of Chemical Technology.

The Institute of Chemical Technology in the Faculty of Natural Sciences has a total number of 12 scientists who are involved in teaching and research. The main task of this group is to teach chemical engineering and to carry out research for the chemical industry.

Up to 1973, the Institute was directed by Professor Arpad Gerecs. The primary objective of their research is involved with diverse research topics connected to the organic chemical technology. (Synthesis of organic compounds of potential medicinal activity, research on carbohydrates and alkaloids, investigation of technology problems for the production in the chemical industry). In addition, the research group associated with the chair is doing research on separation techniques in aqueous solutions.

Macromolecular research within the Institute began early. Since 1973, the director of the Institute is Professor Ferenc Tudos and under his leadership work on polymer research has intensified.

One of the research groups associated with the chair under the direction of Professor Bela Zsadon, is dealing with natural polymers and with synthetic polymers based on natural polymers. Their work is involved with the preparation of new macromolecules, the fractionation of biologically active natural polymers applicable for medicinal use and for the medicinal industry. Research is also being carried out on cyclodextrines, on the preparation of modified polymers from cyclodextrines and on the exploration of the applicability of cyclodextrine polymers.

Cyclodextrines are non-reducing malto-oligo-saccharides with ring structures; they are known for their ability to form inclusion complexes. Polymeric products can be prepared by binding the cyclodextrine molecules either to one another or to a polymer matrix (immobilization), or by polymerizing their polymerizable derivatives. The research is investigating the preparation of water-soluble, linear polymers of cyclodextrines and of their crosslinked structures and their swelling behavior in water. These polymeric products combine polymer properties with the complex forming ability of cyclodextrine.

Water soluble cyclodextrine polymers give, complexes with organic molecules which are readily soluble in water, thus keeping them in solution; they are also capable of absorbing their vapors and prevent their diffusion. Cyclodextrine polymers substituted with acidic or basic groups are worth special attention. Some of them have the effects of protecting colloids or they can be used as partial substitution for gelatine in photoemulsions.

When water-soluble cyclodextrine are crosslinked, they swell substantially in water. Pearl shaped products based on these crosslinked cyclodextrines are worthy of attention. They have several useful application: e.g. for adsorption of vapors, as antiseptic powders for wound treatments and for various other separation techniques.

Perhaps the most interesting application of cyclodextrine polymers is their use as immobile phase in chromatography. The pearl type polymers prepared in the Institute are mostly used for chromatographic separations based on the formation of inclusion complexes; in addition, they are studied for their potential in gel permeation chromatography and ion exchange chromatography. The most interesting application for these polymers is their use for the separation of optical isomers (antipodes, epimers, diastereoisomers); these principles are based on the formation of inclusion complexes of diastereoisomers of different stabilities on a stable chiral phase. This method can also be used for preparative purposes; its potential importance is in the preparation or purification of biologically active substances. The working group achieved good results in the chromatography of indole alkaloids.

The other part of macromolecular research being carried out in the Institute for Chemical Technology is focused on the utilization of industrial hydrocarbon mixtures and in the plastic industry. The so-called pyrogasoline is formed in the production of ethylene. This type of research is being carried out in the Institute since 1974 under the direction of Professor Ferenc Tudos. The

Kossuth Lajos University, Debrecen; Chemistry Building.

research group studied first the utilization of the C4 fraction of the gasoline pyrolysis products, later they investigated the pyrogasoline free of the C5 fraction and its use in the plastic industry.

The high temperature pyrolysis of gasoline gives ethylene and propylene and about 25% (250,000 tons per year in Hungary) of pyrogasoline which contains alkenyl-aromatic compounds. More profitable than purely energetic utilization is the so-called complex utilization, in which at first the alkenyl-aromatic substances, (which are formed in the olefin production) are enriched by suitably performed distillations. They then are polymerized with radical initiators to industrially useful products. Thus, for example, by the enrichment and polymerization of styrene, which amounts to about 6-8 percent of the pyrogasoline, a substantial part of the demand in polystyrene can be satisfied. In the higher fractions of pyrogasoline, methylstyrenes and indene are present, the enrichment, isolation of the monomers and their (co)polymerization provide a subtle supply of these industrially utilizable copolymers.

The copolymerization of styrene and other polymerizable components of the enriched pyrogasoline fraction (e.g. phenylacetylene) up to high conversion was of special interest. It could be verified that phenylacetylene does not inhibit the polymerization of styrene in such industrial hydrocarbon mixtures. The occurring of gel effect in these mixtures and in the case of pure styrene is being investigated.

In connection with the study of polymerization kinetics, the research group of gas chromatography, led by Dr. Tibor Toth, worked out several gas chromatographic methods for the qualitative and quantitative determination of pyrogasoline fractions. They also studied pyrolysis gas chromatographic analysis of some copolymers obtained from pyrofractions, and supplied direct and very useful data about the composition of copolymers obtained.

3. Kossuth Lajos University, Debrecen

a. History of the University.

The University is located in Debrecen, Hungary's fourth largest city which is more than 600 years old. The City Council of Debrecen has always maintained two cultural institutions, the Protestant College and the printing house. At the end or the last century the College had three faculties. The State University which was founded in 1912 took over the Protestant College and added one additional faculty, the Faculty of Medicine. The University moved to its new location in 1932.

The present system of the university was organized after World War II. In 1949 the Protestant Church took over the Theological Faculty, the Faculty of Law suspended its activity, and the Faculty of Medicine was organized as an independent university in 1951. In 1952 the University, with only two faculties, was named after Lajos Kossuth, the Hungarian reformer-politician. In 1969 the chemistry department moved into a new and modern building.

b. Department of Applied Chemistry

Polymer research at the Kossuth Lajos University was started by Professor Tibor Kelen, after he became head of the Department of Applied Chemistry in 1985. Together

Evangelic church on the Castle Hill of Buda (right-bank side of Budapest).

with his coworkers, Dr. Istvan Majoros, Dr. Lajos Gulyas, and Laszlo Sipos the investigation of the preparation of "Three-arm Star and Linear Telechelic Polyisobutylenes" using new cationic initiating systems was started. In connection with this work, Dr. Lajos Balogh developed a novel method for direct monitoring of ionic processes based on the simultaneous measuring of temperature, conductivity and permittivity.

A different subject of investigation involves the work of Agnes Pongracz and Dr. Janos Borbely. "Free-radical Polymerization and Copolymerization of Vinyl Monomers" (e.g. acrylates, methacrylates, styrene). In order to obtain information about the mechanism of the copolymerization, NMR and ESR spectroscopy is used extensively to determine the chemical structure of the copolymers and the monomer sequence distribution. In addition to NMR spectroscopy, DSC, GPC and other techniques are used to characterize various polymers.

Dr. Jeno Borda is carrying out research on "Recycling of Polyurethanes".

"Processing and Technical Properties of Plastic Materials" is another subject of study in the department. Dr. Magdolna D. Fehervari is studying the mechanical properties of polyolefins, the effects of the modification of the product quality by use of fillers and the weatherability of pigmented and filled polymer systems.

A cooperative program is underway between the Hungarian Academy of Sciences and NSF, a common research program with Professor J.P. Kennedy of the University of Akron in the field of cationic polymerization. From Debrecen, Dr. Miklos Zsuga and Dr. Sandor Nemes have been involved in this project.

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