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Centers of Polymer Chemistry in Czechoslovakia 1: Institute of Macromolecular Chemistry, Prague, Czechoslovakia

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Centers of Polymer Research

Polymer Chemistry in Czechoslovakia I: Institute of Macromolecular Chemistry Prague, Czechoslovakia

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Czechoslovakia is located in the heart of Europe. To the north it borders Poland and the German Democratic Republic, to the west the Federal Republic of Germany, to the south Austria and Hungary, and to the east the Soviet Union. Czechoslovakia has about 15 million inhabitants and consists of two states, the Czech Socialist Republic and the Slovak Socialist Republic, both of which are united in the Federation of the Czechoslovak Socialist Republic. The Czech Socialist Republic has two provinces; Bohemia and Moravia. Prague, a city of 1.2 million inhabitants, is the capital of Czechoslovakia and the Czech Socialist Republic; it is often called the "Golden City" because of its many spires and towers topped with gold. The origins of the country and of Prague can be traced to the early 8th Century.

Polymer chemistry has a long and important history in Czechoslovakia, where much has been accomplished in this

field, particularly in the Institute of Macromolecular Chemistry in Prague. The Institute belongs to the Czechoslovak Academy of Sciences, the highest scientific institution of the Czechoslovak Socialist Republic. Many prominent scientists are members of the Czechoslovak Academy of Science. The Academy has the facilities and financial resources to sponsor research in its scientific institutions; many scientists work or study for advanced degrees. This work provides advanced knowledge for science in Czechoslovakia.

The Institute of Macromolecular Chemistry was conceived in 1956 by a decision of the Presidium of the Czechoslovak Academy of Sciences and the Government; both considered the development of macromolecular science in Czechoslovakia of fundamental importance. The buildings of the Institute were erected in the years 1960 to 1963, the laboratories started functioning in early 1962.

The work in the Institute of Macromolecular Chemistry has, as its main objective, scientific research (both theoretical and experimental) in the field of macromolecular chemistry, macromolecular physical chemistry, and macromolecular physics.

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Centers of Polymer Research

The Institute is directly responsible for an extensive conference program and cosponsors many meetings and symposia in Prague. Two major events in polymer science organized by the Institute of Macromolecular Chemistry were the IUPAC Macromolecular Symposia in 1967 and 1965. Since 1967, numerous conferences (so-called Microsymposia) on macromolecular science have been held in Prague. These meetings, organized by the Institute of Macromolecular Chemistry, have a high international reputation. In addition, workshops and other conferences, often under the sponsorship of IUPAC, are organized each year.

The Institute of Macromolecular Chemistry also has a considerable educational program for advanced and lesser degrees. Members of the Institute publish extensively in the scientific literature; about 100 to 150 papers each year are the results of the scientific activities.

The scientific work of the Institute is focused on fundamental research in two major areas: (a) formation and transformation of macromolecular compounds and systems, particularly the study of new functionalities and novel properties of functional macromolecules, and (b) the structure and property relationship of macromolecular compounds and model systems for macromolecular compounds. The work at the Institute is carried out in cooperation with other institutions of higher learning in Prague and with research and industrial laboratories both in Czechoslovakia and abroad.



Prague, View of the Castle

A new director Vladimír Kubánek, was recently appointed to head the Institute, the third director since its founding. Until 1969, the first director was Oto Wichterle; until 1985, the second was Karel Frimml.

The Institute consists of six research departments which are each subdivided into 4 laboratories. Each laboratory employs from ten to fifteen people, of whom three to five are graduates and/or senior scientists.

The administration of the Institute consists of the (a) general section with the Director and the Secretariat, an office for foreign relations, and a department of invention; (b) department of scientific information including library, printing and copying services, and the conference secretary; (c) technical section which is responsible for designing and testing, a mechanical workshop, a glass-blowing shop, and a shop for the maintenance of laboratory equipment; and (d) administrative section, which is responsible for administrative matters, accounting, providing supplies, and the operation of the Institute cafeteria.

The Institute comprises the Departments of Polymerization Reactions, Polymer Modification and Analysis, and Special Polymers and Their Application.

The Department of Polymerization Reactions under the direction of Jiří Trekoval, who is also Deputy Director of the Institute, is working on reaction kinetics and mechanism of ionic and radical polymerizations involving olefins, vinyl monomers, and various types of lactams.

Jiří Trekoval is also the head of the Laboratory of Anionic Polymerization. His group is studying the anionic polymerization of acrylates, methacrylates, and dienes. Complicated sets of elementary reactions and their mechanisms are studied using model reactions with metalloesters; oligomerization reactions are being investigated in a flow reactor. Long reaction periods are being investigated also by infrared techniques. Structure and physical properties of polymethacrylates were found to depend on the type of ester and on the polymerization conditions. The transmetalation reaction between alcoholates and other organometallic compounds has been investigated and applied for the synthesis of organometallic compounds. The polymerization of dienes with organolithium compounds and subsequent termination with suitable compounds is being studied with the objective of regulating the molecular weight and developing syntheses of functionalized polydienes.

The Laboratory of Cationic Polymerizations, headed by Miroslav Marek, is involved in the investigation of initiation and transfer reactions in the cationic polymerization of olefins and vinyl monomers by Lewis acids both at very low temperatures and by photochemical initiation. For these purposes, interactions between olefins and electron acceptors are being studied as well as the structure of intermediates of the photolysis of charge transfer complexes. Thermodynamic parameters of the interactions between monomers and Lewis acids are being determined by spectral measurements down to -90°C . The synthesis of defined oligomers and macromers based on isobutylene, styrene, butadiene, and alpha-olefins is being carried out by controlled initiation and transfer reactions.

The Laboratory of Polymer Transformations and Heterogeneous Polymerizations (under Stanislav Ševčík) is concerned with polymers and copolymers of vinyl chloride and hydrophilic polymers based on methacrylates. Reactions on polymers are being studied from the point of view of the ef-



Institute of Macromolecular Chemistry, Prague

fects or regularity of polymer chains and of the medium. The kinetics of suspension polymerization and copolymerization of vinyl chloride with 1-olefins in a pressurized reactor can be followed by means of an automated apparatus which allows the determination of the monomer concentration in the liquid as well as in the gaseous phases. The polymer structure and properties are correlated with their composition and the polymerization conditions. The initiation reaction of the thermal dehydrochlorination of poly(vinyl chloride) has been evaluated by model reaction studies.

The Laboratory of Polyamides, under the leadership of Jan Šebenda, is involved with the synthesis and the study of the properties of polyamides based on lactams. The effects of ring size, substitution, and the reaction medium are being studied under conditions of anionic, cationic, and hydrolytic polymerization. Anionic polymerization of lactams on functionalized polymers is used for the synthesis of block copolymers. The kinetics of elementary reactions is being determined for the design of anionic initiating systems of defined activity and lifetime. A new type of cationic polymerization with an oxocarbenium growing center on the polymer has been designed for the synthesis of N-substituted polyamides. The effect of structural heterogeneities on the thermo-oxidation of lactam polymers is being investigated and sensitive analytical methods have been developed for the determination of end groups and irregular structures (weak links) incorporated into the polymer chain.

The Department of Bioanalogous Polymers, under Jaroslav Kálal, Deputy Director of the Institute, is developing synthetic polymers and systems containing biopolymers for special purposes including biomedical applications.

Scientists in the Laboratory of Membranes and Medical Aids (Jiří Vacík) are designing heterogeneous and homogeneous membranes for electro dialysis, dialysis ultrafiltration and catalysis, and are also preparing a variety of medical aids based on synthetic polymers. Besides traditional hydrophilic gels based on hydroxyethyl methacrylate, other hydrophilic polymers are being synthesized from new monomers and macromers. These are designed for their use as soft contact lenses, synthetic emboli, surgery, otolaryngology and gynecology. Protein sorption on polymer surfaces is being studied by infrared spectroscopy and ESCA from the point of view of hemocompatibility. Selectivity and porosity of membranes from hydrophilic polymers, polyolefins, fluorinated polymers, polyphenyleneoxide and cellulose derivatives are being investigated by conventional methods in this laboratory.

Research in the Laboratory of Polymer Dispersions (Eva Žůrková) is concerned with the synthesis and investigation of the properties of polymer particles of submicron size. Particles of a chosen size are prepared by emulsifier-free micro-suspension polymerization of styrene and reactive monomers such as glycidyl methacrylate and methacrolein. The work includes the preparation of latexes with functional groups resuspendible in water, reactions for obtaining complex

Centers of Polymer Research

forming groups capable of binding heavy metal ions onto the polymer matrix as well as bearing radioactive or fluorescent labels. Most of these polymers are intended for medical diagnostics and application in the pharmaceutical industry, e.g., soluble polymers of very high hydrophilicity or their aqueous dispersions which are used to develop drugs with long-lasting effectiveness. Specialty polymers based on new fluorinated monomers are also under development.

The Laboratory of Biodegradable Polymers, under the direction of Jindřich Kopeček, is studying the relationship between structure and biodegradability of polymers designed as novel drug carriers. Most of the polymers investigated are based on water-soluble copolymers of N-(2-hydroxypropyl)-methacrylamide or on N-methacryloylated oligopeptides on which the drug is attached covalently to the side chain. The rate of drug release by enzymes is determined and correlated with the composition of the oligopeptide. In addition to drugs, molecules are attached to the copolymers which can assist in targeting polymeric drugs to particular body tissues. Sustained and controlled drug release is also being studied on hydrophilic gels with enzymatically degradable bonds.

Work in the Laboratory of Particular Polymers (František Švec) is concerned with the synthesis and the properties of insoluble porous polymers which have functional groups for binding biologically active compounds or which have groups that can assist in the sorption of ions or gases and can act as support for functional groups with catalytic activity. Classical or modified suspension polymerization techniques are used for the preparation of spherical porous particles, the size of which can be varied over a wide range. Starting monomers and materials include 2,3-epoxypropyl methacrylate, vinylpyridine, cellulose, and other polysaccharides. After

modification, the well-characterized particles are being used as carriers for the immobilization of enzymes and other proteins, as chromatographic or selective sorption materials for affinity, pseudoaffinity, or covalent chromatography or as selective sorption materials for metal ions or gases. Hydrophilic porous beads have been designed for their use for medical purposes like biologically active powders for wounds, synthetic emboli, or as packing materials in hemoperfusion and plasmapheresis devices for detoxification.

The Department of Polymer Modification and Analysis, headed by Pavel Čefelín, is dealing with modifications, functionalization, and stabilization of polymers, processing of polymers, and analysis of polymers.

The Laboratory of Reactive Polymers and Polymer Mixtures, also under Pavel Čefelín, is involved in the preparation of multicomponent polymer materials and with the synthesis of polymers with functional groups in the main chain or as side chains. Among these are polymers containing biodegradable segments with controlled lifetime in the living organism, functionalized polymers or copolymers acting as catalysts or reagents for protection and deprotection of functional groups; comblike copolymers of semicrystalline domain structure are also being investigated. Rheology, thermodynamics, and morphology of polymer mixtures are being investigated and related to the compositions and processing conditions with the aim of elucidating processes occurring during the stirring of components and optimizing polymer properties.

The Laboratory of Analytical Chemistry (Jaromír Petránek) is responsible for the microanalyses of organic compounds and the determination of selected functional groups. The staff cooperates closely with other laboratories in developing new analytical methods and procedures. Gas chromatography and some electrochemical methods are used for the determination of trace impurities in monomers and model compounds. The synthesis and electrochemical characterization of permselective polymeric membranes is being investigated from the point of view of developing ion-selective electrodes.

The Laboratory of Polymer Stability under Jan Pospíšil is investigating the processes involved in degradation and aging of polymers. The polymers studied include many commercial polymers such as polyolefins, polystyrene, modified polystyrenes and elastomers based on dienes. The main thrust of this work is the elucidation of the mechanisms that are involved in the stabilization of polymers against oxidative degradation influenced by heat, radiation, impurities, and fillers. The complicated scheme of reactions involved in the stabilization of polymers is also studied with respect to synergistic or antagonistic effects caused by mixtures of stabilizers or by mixtures of stabilizers and their reaction products. For these purposes, reaction products of various types of stabilizers are being isolated and identified. Attention is being given to the impact of stabilized polymers and composite materials and their service life on their technical applications.

The Laboratory of Instrumental Analytical Methods, headed by Svatopluk Pokorný, is interacting with a number of laboratories of the Institute. Its responsibility is analysis and characterization of polymeric systems, oligomers, and monomers by HPLC, GPC, membrane osmometry, vapor-phase osmometry, light scattering, IR, UV, and mass spectrometry. Typical polymers and copolymers investigated are based on vinyl chloride, styrene, isobutylene, methacrylates



Institute of Macromolecular Chemistry, Prague

and acrylates as well as on lactams. A number of other technically important polymeric materials are being investigated, e.g., liquid rubbers and block copolymers. For cellulose, MWD measurements were developed which were the basis of an original method which allows cellulose to be handled without any chemical modification. In addition to molecular parameters like MW, MWD, and dimensions of macromolecular particles, data on specific properties are determined, e.g., distribution of functional groups, branching, supermolecular structure, and polymer-solvent interaction.

The Department of Physical Chemistry of Polymers (headed by Pavel Kratochvíl) is concerned with the investigation of structure, molecular weight, and molecular dimensions of macromolecules and interactions involving macromolecular systems by a variety of physicochemical methods.

The Laboratory of Molecular Parameters, led by Pavel Kratochvíl, is engaged in the determination of the basic molecular parameters of polymers and the relationship to the conditions of the polymer synthesis. Molecular weight, macromolecular dimensions, degrees of branching, and the distribution of these characteristics in polydisperse systems are being studied. Supermolecular structures in polymer solutions are also determined by light scattering, differential refractometry, fractionation, ultracentrifugation, and equilibrium dialysis. The studies are being carried out on chemically heterogeneous random copolymers, block and graft copolymers, polymer solutions in multicomponent solvents, and polymers that are not completely soluble on a molecular level. Industrially important polymers, such as poly(vinyl chloride), polyamides, polyolefins, and block copolymers of styrene and butadiene are of primary interest.

In the Laboratory of Hydrodynamics under Miloš Bohdanecký, hydrodynamic and rheological properties of macromolecular systems are being investigated by viscometry, sedimentation analysis, and flow birefringence in order to understand such properties as conformation and flexibility of polymer chains, branching of polymer chains, heterogeneity of comonomer compositions, and molecular weight. Attention is being paid to the interactions between macromolecules and solvents as well as between macromolecules of identical and different chemical composition. Investigated also are melts and aqueous suspensions of polymers.

The Laboratory of Spectroscopic Methods (Jiří Spěváček) is involved in the development of spectroscopic methods and their use in the determination of the chemical and of the dynamic structure of polymeric systems. Raman and IR spectroscopy as well as liquid and solid-state NMR spectroscopy are used for the investigation of polymers; great emphasis is being given to the study of the conformation of polymer chains; it includes the investigation of the formation of ordered structures in liquid and solid polymer systems. The effect of the medium on intermolecular interactions of macromolecules and on the structure and stability of ordered structures of polymers is also being studied.

In the Laboratory of Thermodynamics, headed by Julius Pouchlý, work is being carried out on the development of thermodynamic methods and other theoretical treatments for polymer systems based on poly(ethylene oxide), other hydrophilic polymers and on polyamides. Such properties as swelling, solubility, sorption capacity, and thermal properties of polymer systems are being determined and correlated with macromolecular structure, association, and solvation of polymers. A number of experimental methods are used, for ex-

ample, calorimetry, osmometry, densitometry, and sorption. Particular emphasis is being placed on the effect of polymer structure and the history of individual polymers, on phase transitions, particularly glass transition, crystallization, and melting behavior.

The Laboratory of Separation Methods (Miroslav Kubín) is concerned with the analysis and characterization of polymeric systems of lower molecular weight compounds by HPLC, high-speed GPC, and by diffusion methods. Research is being done on some theoretical problems of chromatography of polymers and on the optimization of separation efficiency. The effect of the structure of macromolecules and the character of the sorbent on the mechanism of the separation and retention parameters is being studied and used for the determination of the hydrodynamical characteristics and molecular parameters, statistical distribution of relative molecular weights of homopolymers and copolymers, and the chemical composition of copolymers.

The Department of Polymer Physics under the leadership of Karel Dušek is investigating the relationship between structure and properties of polymer systems with special emphasis of the behavior in the solid state.

The Laboratory of Structure and Mechanical Properties of Polymer Networks and Systems is also directed by Karel Dušek. Here, the investigation of the formation, the structure, and the properties of polymer networks both from the theoretical and practical aspects are being carried out. Network structures are being prepared and characterized; the changes of molecular weight, rheological, viscoelastic, rheo-optical properties, and the position of the gel point are being studied. Theories for polymer branching and network formation are being developed on the basis of statistical methods, kinetic theory, and computer simulation. Theoretical studies are also being carried out to evaluate the time-dependent viscoelastic behavior and the ultimate properties of crosslinked polymers. Networks based on epoxides, urethanes, and telechelic polymers as well as on composites are the primary objectives.

Work in the Laboratory of X-ray Structure Analysis of Polymers (Karel Huml) is being carried out by determining the molecular and supermolecular structure of polymers, of model compounds, of polymer solutions and of swollen polymers. High resolutions obtained with model compounds allows the determination of the precise positions of individual atoms. The structure of polyelectrolytes and their interaction in dilute solutions with the surrounding medium are being studied. For semicrystalline polymers, the work is focused on the structure of the amorphous phase and the interphase boundary between crystalline and amorphous phases. Small-angle scattering data are used to study the supermolecular structures. Computer programs are being devised for the profile analysis of diffraction intensities and the determination of molecular and supermolecular structures.

The Laboratory of Physics of Optical and Electronic Phenomena under Petr Štěpánek is investigating polymer systems by optical methods; electrical and photoelectrical properties of organic materials are also being studied. Quasielastic light scattering is used for the determination of the size and polydispersity of particles in solutions or dispersions. Conformational behavior of polymers is being studied by depolarization of scattered and fluorescent light as well as by circular dichroism. Static and dynamic properties of macromolecules are investigated primarily in the solid state, in con-

Centers of Polymer Research

centralized solution and in dispersion. Electronic structure, charge generation and transport, photoconductivity and related electronic processes are being studied both in polymers and in low molecular weight organic compounds.

In the Laboratory of Morphology under Zdeněk Paloušek, light and electron microscopy is used for the investigation of the supramolecular order of polymeric systems. The development of the morphology of polymers during polymerization and the changes occurring during crystallization, orientation, coagulation from solution, mixing, degradation, crosslinking, and fracture are being followed in order to establish the relationship between polymerization conditions, physical conditions of treatment, and macroscopic properties of polymeric materials. A wide range of different polymer samples are being investigated; they include oriented fibers and films, porous materials, separation membranes, foams, composites, and high-impact polymer. The laboratory uses high-resolution light microscopes, REM, TEM, as well as analytical electron microscopes that are capable of analyzing for different elements.

The Department of Special Polymers and Their Application is under the leadership of Professor Vladimír Kaldáček, Director of the Institute. It is concerned with the development of new polymeric materials with important optical, electrical, photoelectrical, and biological properties.

The Laboratory of Special Polymers and Model Compounds, also under Vladimír Kaldáček, is investigating the influence of composition and structure on the optical, physical, and mechanical properties of polymers which are being used as components of optical fibers, both as cores and as

optically active envelopes. These materials are based predominantly on fluorinated polymers, polystyrene, and polyacrylates. Materials with important electrical, photoelectrical, and magnetic properties are based on polymers and on model compounds like porphyrins, phthalocyanines, and ion-radical salts. New polymers with high halogens content, tertiary amine groups and amine groups are being synthesized with the objective of obtaining materials that have photoconductivity, show photochromism, and have low flammability.

The Laboratory of Polymer Biochemistry (Jaroslav Doušek) is involved in studies of interactions of synthetic polymers with biological milieus, e.g. chemical and physical changes, biodegradation, interactions with biopolymers, biocompatibility, and immunogenicity and their fate in the presence of living organisms. Special and model polymers are being synthesized and characterized, their biological behavior is being investigated in cooperation with other institutions involved in biological, pharmacological, and medical research in Czechoslovakia. Of special interest is the development of macromolecular diagnostics, macromolecular drugs, implants for drug application, immunostimulation, and specialty polymers for application in biotechnology.

A Center of Ophthalmological Research is now being set up for the coordination of research and development of soft contact lenses with improved biological tolerance. Several institutions of the CSAS are involved in these activities: the Institute of Macromolecular Chemistry of the CSAS, the Institute of Chemical Technology Fundamentals of the CSAS, the Institute of Experimental Medicine of the CSAS, the Faculty Hospital in Prague-Motol, and other medical institutions.