1984

Centers of Polymer Research; Polymer Science in Czechoslovakia: Slovakia I: Polymer Institute, Slovak Academy of Sciences, Bratislava

Otto Vogl
University of Massachusetts - Amherst, vogl@polysci.umass.edu

A. Romanov

E. Borsig

A. Romanov, E. Borsig and O. Vogl, *Centers of Polymer Research; Polymer Science in Czechoslovakia: Slovakia I: Polymer Institute, Slovak Academy of Sciences, Bratislava*, Polymer News, 9(8), 251-154 (1984)

Centers of Polymer Research

Polymer Science in Czechoslovakia: Slovakia I: Polymer Institute, Slovak Academy of Sciences, Bratislava

Andrej Romanov, Eberhard Borsig and Otto Vogl*

Polymer Institute, Center of Chemical Research, Slovak Academy of Sciences, Dubravska Cesta, 84236 Bratislava, Czechoslovakia

The Czechoslovak Socialist Republic consists of two Federal Republics, the Czech Socialist Republic and the Slovak Socialist Republic. This article and the subsequent article are concerned with basic research in macromolecular science which is carried out in the territory of the Slovak Socialist Republic.

Czechoslovakia has two Institutes of their Academies of Sciences where research in polymer science is carried out: the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences in Prague and the Polymer Institute, Center of Chemical Research of the Slovak Academy of Sciences in Bratislava. Research on polymers is also done at the Technical Universities in Prague, Pardubice, Bratislava, Brno and in some departments of the Charles University in Prague. Some basic polymer research is also carried out in research institutes whose primary objective is applied polymer research.

View of Bratislava

*Herman F Mark Professor, Polytechnic Institute of New York, 333 Jay Street, Brooklyn, NY 11201 (To whom all correspondence should be addressed)

Andrej Romanov

Most of the polymer research in Slovakia is done in Bratislava, the capital of the Slovak Socialist Republic. Other research centers are the Research Institute for Petrochemistry Novaky, the Research Institute of Evaluation and Application of Plastic Materials in Nitra and the Research Institute of Man Made Fibers in Svit.

Bratislava, a city of about 350,000 inhabitants, is the political and cultural center of Slovakia. The city is located on the Danube at the foot of the Carpathian Mountains, close to the borders of both Austria and Hungary. The historical roots of Bratislava go back to Roman times; over the centuries the city was ruled by many different nations all of whom left their imprints. Bratislava is the seat of the Slovak Academy of Sciences, a University and the Technical University.

Polymer Institute, Center of Chemical Research of the Slovak Academy of Sciences, Bratislava

The Polymer Institute, established in 1967 and based on the activities of the Laboratory of Polymers (since 1963), is an Institute of the Slovak Academy of Sciences and is devoted to basic research. In 1981 the Polymer Institute became one of three chemistry oriented Institutes of the Center of Chemical Research of the Slovak Academy of Sciences.

The Polymer Institute, with its Director, Andrej Romanov, is concerned with basic research of chemistry and physics of macromolecular substances. It involves the study of mechanisms and kinetics of reactions of macromolecular systems and the study of modification and stabilization of polymers.

Polymer News, 1984, Vol. 9, pp. 251–254
0032-3918/84/0908-0255$18.50

Eberhard Borsig

Methods of quantum chemistry and conformational analysis are also used for the study of synthetic polymers and biopolymers. A considerable amount of research is devoted to the investigation of the relationship between chemical structure and polymer properties, especially of modified polymers, and to the study of polymer flammability.

The Polymer Institute has 70 permanent employees and 15 research students. It is divided into two divisions: (a) chemistry of polymers, and (b) physics of polymers. These divisions are further divided into six departments. Laboratories are subdivisions of the departments and are responsible for solving individual research problems.

One of the missions of the Polymer Institute is the continued technical updating of scientists and the education of students. These activities are coordinated in close cooperation with Comenius University and the Slovak Technical University of Bratislava. The Polymer Institute also has close cooperation with industry. It is assisting in solving specific problems, is helping in the necessary training of researchers, and is keeping the scientists up to date with modern experimental methods.

Otto Vogl

One of the laboratories of the Polymer Institute is the Stabilization Laboratory (Zdenek Manasek). In this laboratory the stabilization of polymers against photooxidation which consists of the synthesis of high molecular weight light stabilizers and the study of the mobility of lower molecular weight stabilizers in polymer matrixes is being investigated. The effectiveness of photostabilization and the increased permanence (decreased extractability) of the ultraviolet stabilizers in polyolefins is being investigated with new polymerizable and polymeric ultraviolet absorbers of the 2-hydroxybenzophenone type; among these stabilizers are glycidyl derivatives of 2-hydroxybenzophenone. The kinetics and mechanisms of the ionic polymerization of epoxy monomers in the presence of these polymerizable 2-hydroxybenzophenone derivatives are being studied. Oligomeric stabilizers based on sterically hindered amines and their compatibility in plastic materials are also being investigated.

The Laboratory of Photochemistry (Pavol Hrdlovic) is concerned with polymer reactions initiated by light from two points of view: (a) utilization of photochemical reactions for the modifications of polymers, and (b) inhibition of photochemical reactions in order to prepare highly stable poly-

Polymer Institute, Center of Chemical Research, Bratislava

Bridge over the Danube, Bratislava

macromolecules with concentration are also of interest, (b) preparation and the study of properties of new types of column packings for liquid chromatography on the basis of silica gel and organic polymers with special emphasis on gels with large pore size and their application, (c) new unconventional applications of gel chromatography, e.g. determination of preferential solvation of low- and high-molecular solutes in mixed solvents, the study of interactions solute/solvent, solute/solute and solute/gel.

Part of the activity of the laboratory is devoted to the comparison of spatial structure of small molcules and macromolecules including biological macromolecules and their properties in solution, in the solid polymer phase and in the polymer network when crosslinked. On the basis of theoretical calculations, the molecular interactions of macromolecules and small molecules are established. Special attention is being given to molecular and macromolecular compounds which have oxygen atoms in 1,3 position as, for example, in acetals, phosphates and siloxanes. Linear hydrocarbons, lipides and some structures derived from them, such as membrane bilayers on liquid crystals are being studied with emphasis on their biological functions. Again, conformational and relaxation processes in the hydrocarbon chains, particularly in the solid state, are being investigated. A thermodynamic study of the influence of solvent on the properties of macromolecules on the molecular basis is being undertaken.

The activity of the Laboratory of Polymer Solutions (Dieter Lath) involves the characterization of polymeric materials near their theta temperature and in thermodynamically good solvents. Influence of temperature and polymer composition in mixed solvents on the unperturbed dimensions and the conformation of macromolecules is being studied, with special emphasis on ethylene and propylene copolymers having various termonomers in the polymer structure. The properties of solid polymers blended with some oligomers are also the subject of these studies; these blends are of practical interest as adhesives. Polymer mixtures that have rapidly increasing solution viscosities in mixed solvents are also investigated with the objective to increase the viscosity of mineral oils. Research is also underway to characterize derivatives of cellulose in solution and to prepare membranes and fibers from cellulose and its derivatives.

In the Laboratory of Radiospectroscopy (Frantisek Szocs) structure and reactivity of free radicals in solid polymer matrices are being investigated. Methods which make it possible to study the influence of the high pressures (up to 1500 MPa) on the radical reactions are being evaluated; the work consists of generating free radicals by ionizing radiation or by mechanical work under high pressure; at these pressures molecular motions are generally supressed which cause, because of the bimolecular nature of radical termination reaction, retardation of radical transfer and termination reactions.

The effect of pressure on generating free radicals in the systems polymer - monomer - peroxide is also being investigated; retardation of radical generation is always observed. Peroxides decompose into radicals, i.e. with an activation volume which is much smaller than the activation volume of the disappearance of macroradicals. Consequently the peroxide decomposition to generate radicals is little effected by pressure but the combination of macroradicals is strongly retarded. These differences of the activation volumes make it possible under high pressure to generate and accumulate a relatively high concentration of free radicals and also makes it possible to follow the course of the polymerization reactions by ESR.

A program was developed which makes it possible to analyze multicomponent ESR spectra, and interpret ESR spectra of polymeric radicals. The experimental technique is complemented by quantum-chemical calculations.

The Laboratory of Theoretic Chemistry (Ondrej Kysel) has developed theoretic methods to describe the properties of molecules which are important for the light stabilization of synthetic polymers and molecules which are used as monomers, solvents or additives in anionic polymerization.

Quantum-chemical methods and experimental physicochemical methods are being used to evaluate the influence of the electronic structure on the properties of photostabilizers (2-hydroxybenzophenone type ultraviolet absorbers). One research group in this laboratory is studying the character of the electronic excited states of these molecules, the influence of position and character of the substituents on the acidity of the hydroxyl and on the basicity of the carbonyl group of 2-hydroxybenzophenones in their lowest excited states. The group is also investigating the influence of substituents on the energy of the intramolecular hydrogen bond. On the basis of these results a mechanism of the radiation-free dissipation of ultraviolet energy absorbed by 2-hydroxybenzophenones, has been proposed which is consistent with the intramolecular transfer of the proton from 2-hydroxy group to the carbonyl group.

Theoretical studies are also being done on chemical reactions and on the effect of physical factors (migration of stabilizer, influence of the oxidized domains) on the course of the chemical reactions. A qualitative description of the mechanism of the inhibition of the photooxidation of the synthetic polymers by light stabilizers of the sterically hindered amines type (HALS) has been developed. New knowledge about the mechanism of the inhibition of photooxidation is being accumulated.

In anionic polymerization of styrene, the influence of the electronic structure of a polar environment on the initiation and propagation step is carried out with semi-empirical quantum-chemical methods. The theoretical results make possible a more detailed explanation of the effect of polarity of solvent and the influence of the structure of the ion pairs on the kinetics of the propagation reaction of anionic polymerization of styrene.

The Laboratory of Chemical Reactivity (Jozef Tino) is involved in the study of the theory and application of flame initiation and flame propagation. Reactions that might be responsible for the carbene cycle of burning are being considered. Macroradicals formed by the effect of ionizing radiation on polymers, or formed by mechanochemical reactions of polymers are being studied to estimate the lifetimes of the radicals in solid polymers and evaluate the disappearance of the macroradicals. Activation energies of the decay of macroradicals and possible mobility of macroradicals are also the object of this investigation. A simple method for calculating the activation barrier is being developed which involves physical migration of the macroradicals followed by chemical reactions. Application of these methods to polyethylene and isotactic polypropylene provided calculated energetic barriers of motions, values for the stability of the polymer radicals, and an understanding of the disappearance of the radicals as a function of temperature.

mers (for plastics and fiber use), with main emphasis on polypropylene.

The following photochemical reactions on polymers and low molecular model compounds are being studied: Photo-Fries rearrangement, Norrish II reaction, photoaddition of maleic anhydride and maleimide derivatives onto polystyrene and photooxidation (initiated or inhibited) of polystyrene and polypropylene. Ivan Lukac of this laboratory is preparing new types of phenyl vinyl ketones and is studying their homopolymerization and copolymerization. The emission spectra and photolysis products of these polymers show similarities and differences between the Norrish II reaction of low molecular compounds and of polymers; this work has the potential of developing ways of inhibiting the polymer photodegradation by using a built-in triplet quencher.

New types of monomers and polymers with 1,2-dicarbonyl groups are also prepared and their emission properties are being studied. Considerable attention is given to the evaluation of light stabilizers which belong partly to the ultraviolet absorbers type (2-hydroxybenzophenones) and partly to the hindered amine light stabilizer type.

The scientific activity in the Laboratory of Polymerization Reactions (Jaroslav Barton) is involved with the influence of metal salts and complexes of metals or organic donor-acceptor systems in their basic or excited state on the kinetics and the mechanism of radical polymerization. Regular or activated redox initiator systems for radical polymerization as well as donor-acceptor interaction between monomer and photosensitizers are being investigated. Additional knowledge about reactivity of the monomer – Lewis Acid complexes and bound ligands on the radical chain transfer reaction is giving more insight into regulated radical polymerization and copolymerization, into new initiation methods for radical polymerization and ultimately into syntheses of new and desired modifications of known polymers.

Additional research in the Laboratory of Polymerization Reactions is concerned with the kinetics and mechanism of polymerization and copolymerization of unsaturated hydrophobic and hydrophilic monomers in aqueous and organic dispersion; new photoinitiations for radical polymerization are also being sought.

The Laboratory of the Changes of Polymers (Ivan Chodak) has research underway to develop new processes which might give modified properties of polyolefins and vinyl polymers, for example, radical reactions on polyolefins which might lead to change in molecular weight, or highly effective crosslinking techniques to effect facile network formation especially for polypropylene. Possibilities of modifying polymer properties by attaching functional groups on the polymer chain are also being studied.

New initiator systems for radical polymerization and low temperature polymer modification reactions are being investigated with emphais on the catalysis of the oxidative-reductive decomposition of peroxides and hydroperoxides; the main emphasis here is the development of light-sensitive polymer layers.

The Laboratory of Model Substances (Eberhard Borsig) is involved in the syntheses of compounds used for chemical modification of polymers, especially the properties of polyethylene, polypropylene and other vinyl polymers. Multifunctional monomers as reagents for polypropylene crosslinking of peroxides are being prepared; the objective is to maximize the properties of polyolefin products, especially polypropylene fibers. This investigation also involves work to increase the compatibility in polymer blends and composites.

Not only are modified polymer systems and blends being prepared but the mechanism of the action of low molecular compounds and monomers on polymer mixtures is being studied.

The Laboratory of Mechanometry (Andrej Romanov) is concerned with the study of structure-property relationship of modified polymers in the solid state. Attempts to improve the properties of polyolefins are carried out by studying copolymers, graft, block copolymers and composites of various polyolefins. The variation in polymer structure, especially that of copolymers, is being studied as a function of the properties that effect the T_g; furthermore, interaction parameters of polymers with fillers are determined by dynamic-mechanical measurements. Using model composite systems, internal deformation and thermodynamics of polymer matrices are being investigated. Compatibility of modified polymers such as graft and block copolymers with a number of conventional polymers is being evaluated. Improved adhesion of nonpolar polymers (polyethylene, polypropylene) to more polar polymers is being developed by modifying the nonpolar polymers.

The research program of the laboratory also includes interactions of polymers with low molecular substances. Calorimetric methods are being used to study these thermodynamic interaction properties and to obtain information about the influence of polymer tacticity and polymer molecular weight on the thermodynamic properties of polymer-low molecular weight compound interactions. This work is essential in order to understand the interaction of polymers with dyes; and is directed toward the improvement of the dying capacity of nonpolar polymers modified with small amounts of functional groups in the polymer chain, for example groups containing basic nitrogen atoms in the macromolecules.

In the Laboratory of Calorimetry (Konstantin Marcincin) is carried out research on the kinetics and mechanism of decomposition of labile peroxide and azo compounds and the study of the thermal degradation of polyolefins. Investigations are directed toward the influence of new types of antioxidants, zeolites and inorganic oxides on polymer stability and on the formation and identification of volatiles from polymers. Thermooxidation of polypropylene is being investigated in the absence and presence of various additives. The use of flame retardants as they effect the flammability of polyolefins is qualitatively evaluated by observing ignition delay and the rate of burning. Phosphorous and halogen containing compounds and some metallic oxides were found to retard the thermoxidation and burning of polyolefins. Differential scanning calorimetry, thermogravimetry, chemiluminescence, radiothermoluminescence and oxygen absorption are used to study the various phases of thermooxidation.

The Laboratory of Liquid Chromatography (Dusan Berek) of polymeric systems is involved in two areas of research: (a) gel chromatography and (b) thermodynamic-conformational analysis of macromolecular substances.

The studies of gel chromatography include the following areas of research: (a) mechanism of the separation processes especially from the point of view of secondary processes; adsorption, partition and the changes of dimensions of