

1994

9th Bratislava Conference on Modification of Thermoplastic Polymers

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Vogl, Otto and Matisova-Rychla, Lyda, "9th Bratislava Conference on Modification of Thermoplastic Polymers" (1994). *Polymer News*. 133.

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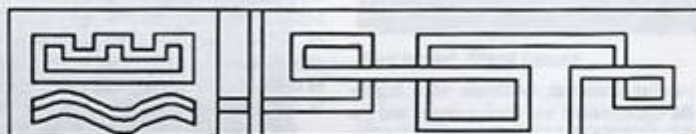
Lyda Matisova-Rychla and Otto Vogl, *9th Bratislava Conference on Modification of Thermoplastic Polymers*, *Polymer News*, **19(3)**, 89-94 (1994)

Conference Report

9th Bratislava Conference On Modification Of Thermoplastic Polymers

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Lyda Matisová-Rychlá



Otto Vogl

The Conference on "Modification of Thermoplastic Polymers" which was the 9th Bratislava Conference was held from June 14 to 18, 1993 in the House of the Scientists (SAV), in Stará Lesná near Tatranská Lomnica, in the High Tatras, Slovak Republic. The Conference was organized by the Polymer Institute of the Slovak Academy of Sciences and the Slovak Chemical Society on the occasion of the 30th anniversary of the foundation of the Polymer Institute of the Slovak Academy of Sciences.

The Conference was sponsored by the European Research Office, United States Army, London office, England, the Ciba-Geigy, Ltd., Basel Switzerland, the Eastman Chemical Company, Middle East and Africa, Ltd., The Hague, The Netherlands, Nestle Chemicals, Prague, Czech Republic and Slovnaft, Bratislava, Slovak Republic.

The Conference consisted of 9 main lectures, 24 short lectures and 60 presentations in poster form. About 130 scientists from 18 countries participated at the meeting. The Bratislava Conferences have become a tradition in the scientific communication in polymer science in Central Europe and have been known for the high technical quality and the great interest that have been attached by the

scientists to these conferences. They also underline and establish the importance of the Polymer Institute of the Slovak Academy of Science in Bratislava as one of the major Centers of polymer research and application.

The conference was opened by the director of the Polymer Institute, Professor Milan Lazár and the president of the Slovak Chemical Society, Professor Eberhard Borsig. Dr. Tomáš Bleha, the Vice President of the Slovak Academy of Sciences, responsible for life sciences and chemistry also greeted the participants of the meeting.

The opening lecture was presented by Daniel Belluš of Ciba-Geigy, Basel, Switzerland. His talk was entitled "How do Speciality Polymers Modify Chemical and Pharmaceutical Industry?" Speciality polymers play an increasingly important role in all stages of the enormous complex development processes of new biologically active products. They widen and facilitate the discovery phase by using polymer support for automatic peptide and oligonucleotide synthesis. Application of novel technology enables light directed



Milan Lazár, Director,
Polymer Institute
Bratislava



Eberhard Borsig,
President, Slovakia
Chemical Society



Slovakia

spatially addressable parallel chemical syntheses of a highly diverse set of peptides, the optimization and testing stages and the search for better application methods. Smart polymer patches often provide excellent ways of deliveries of many drugs. Water soluble bags and encapsulations greatly improve the environmental safety of agricultural chemicals. The market itself i.e. "user needs" create quasi-infinite opportunities for new monomers, photoinitiators, crosslinkings and stabilizings.

The next lecture was presented by Nicolai A. Platé of the A.V. Topchiev Institute of Chemical Synthesis of Moscow, Russia entitled "Polymeric Hydrogels Modified with Biologically Active Species and Living Cells". The chemical strategy and experimental approach has been developed to synthesize polymeric hydrogels based on vinyl pyrrolidone and derivatives which contain chemically immobilized enzymes, inhibitors, anticoagulants, living cells of microorganisms and some other species. Hydrogel preparations and chemically modified polyolefins and polyesters with these hydrogels can be interesting and promising materials for prosthetic devices, affinic absorbents for microbiology, detoxicants for haemoperfusion and active catalysts for some biotechnological processes.

Wolfram Schnabel of the Hahn-Meitner Institute, Berlin, Germany discussed "Light-Induced Synthesis of Block and Graft Copolymers". Block and graft polymerization has attracted and revitalized interest because of the growing demand for novel polymeric materials that can be synthesized from easily and cheaply available monomers. Commonly, processes based on free radical mechanisms are employed because they can be performed more readily than polymerization processes based on ionic polymerizations. Free radical light induced initiation has the advantage of being applicable at low temperature especially at room temperature. Moreover, because of absorptivity of certain groups, the chromophores, it is possible to produce sites at definite positions in the macromolecules.

The author discussed two major methods of block copolymerization both starting with the homopolymer A_n containing n repeating units of type A per macromolecule: a) Addition of monomer B to A_n and b) Coupling of homopolymer A_n with homopolymer B_m . Graft copolymerization can also conveniently be used by two methods: a) Direct grafting and b) Indirect grafting. The prerequisite for these two methods are that reactive sites are located

at the chain backbone or at pendant groups but not at the chain ends.

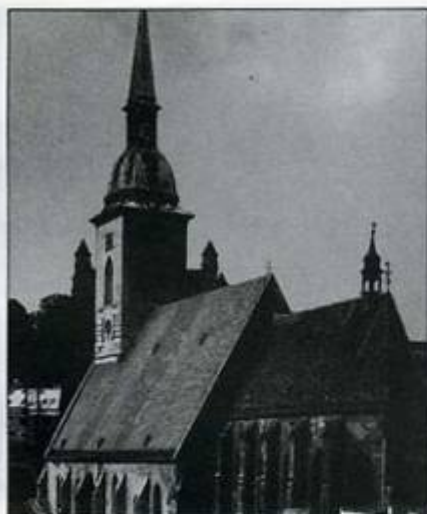
"Molecular Architecture of Polymers" was presented by Otto Vogl of the Polytechnic University, Brooklyn, NY, U.S.A. in cooperation with Ján Bartus. Scientific and technological success in the development and application of new materials has helped significantly the overall improvement of life in this world. Essential contribution came from the rapid progress of new and more adaptable materials. Specific materials belong to the categories of high strength long lasting materials and those whose properties cannot be matched or even approached with anything we know today. High strength materials such as polyimides, polyether imides and polyether ketones are some examples. New imaginative stabilization systems for traditional and commodity polymers allow a significant extension of the life times of these polymers. New thrusts in polymer science are developing in liquid crystalline polymer systems, especially in chiral and cholesteric liquid crystalline polymers, the full understanding of the behavior of helical polymers and in the understanding and use of photochemistry in polymeric systems. Thin films, surface properties of polymers and adhesion are also significant areas of development in this field.

P.J. Lemstra of Eindhoven University of Technology, Eindhoven, The Netherlands presented his work on "Polymer Blending using Reactive Diluents". A new route for blending high Tg polymers was developed involving reactive diluents which may be epoxy resins. Polymers like polycarbonates, polysulfones, polyetherketones and poly(phenylene ether) can be dissolved in epoxy 'monomers' at elevated temperatures. The presence of epoxy reduces the viscosity and the processing temperature, for example of poly(2,6-dimethylphenylene ether). Upon curing of the epoxy resin, phase separation may be initiated followed by phase inversion. The epoxy solvent will be converted into a high Tg epoxy thermoset filler while the other polymers becomes the continuous matrix. The author discussed various advantages in the preparation of fabrics, glass and carbon fiber impregnation of such mixtures and advantages in the polymer systems obtained by curing.

Aubrey D. Jenkins of the University of Sussex, Brighton, Sussex, U.K. discussed the "Synthesis of Graft, Block and Star Polymers using Enolate-Initiated Anionic Polymerization". Initiation of the polymerization of methacrylate monomers by enolate ions affords broad opportunities for the design of several types of



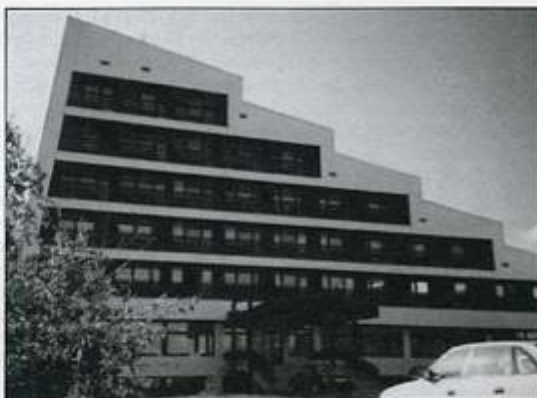
Bratislava, Castle



Beatislava, St. Martins Cathedral

macromolecules. Alone, or in combination with other techniques, enolate-initiation provides routes for the preparation of well-characterized graft copolymers, block copolymers, star polymers and other types of polymers. The general mechanism of polymerization initiated by lithiated esters and silyl ketene acetals was discussed and examples were presented of each of the kind of polymer molecules mentioned above. Jenkins as well as one of us (OV) believes that the so-called group transfer polymerization of methacrylates is, in actual fact, a true anionic polymerization. Its living nature, even at the technologically feasible temperature of 80°C in tetrahydrofuran is guaranteed by the equilibrium of ionic and covalent growing species, which is almost entirely on the side of the covalent species but with a small but significant amount of ionic species present.

Jacques Verdu of ENSAM-Paris, France discussed the "Effect of Ageing on the Mechanical Properties of Polymeric Materials".



Sav Hotel, Stará Lesná

He concluded that ageing can modify the polymer structure of the molecular, macromolecular and/or morphological scale and thus induces changes in the mechanical properties. Stiffness is generally not modified for non rubbery materials, except for important mass transfer in amorphous polymers, or phase transfer in semicrystalline polymers. The most important modulus changes were observed in the case of radiochemical ageing of semicrystalline polymers having their amorphous phase in the rubbery state.

Ferenc Tüdös of the Central Research Institute for Chemistry of the Hungarian Academy of Sciences in Budapest, Hungary presented his talk on "Isodisperse Telechelic Polymerization", a work that was carried out in cooperation with E. Földes and T. Bereznich. In order to produce a polymer with optimal physical and mechanical properties from a reactive oligomer, it must fulfill several requirements: 1) The oligomers should have end-groups for further reactions in order to build up the desired molecule. 2) Since the oligomer is always a mixture of polymer homologues, the number average degree of polymerization should be kept constant. 3) The polymer dispersity of the oligomer should be kept at a minimum and at a constant value as well. 4) The functionality of the oligomer should also be kept constant, usually at about 2. For economic



Meeting Participants

Conference Report

consideration radical polymerization is always most advantageous for the production of polymers and reactive oligomers. A so-called 'isodisperse' polymerization can be realized by radical mechanisms. There are conditions that are feasible in 'good approximation' under isothermal conditions at certain combination of initial concentrations; it requires, however, inacceptably long reaction times in practice. In an anisothermal regime, conditions can be exactly fulfilled at any reaction time because of heat transfer.

Manfred Rätzsch of PCD Polymere Ges.m.b.H., Linz, Austria presented his talk on "Synthesis of New IPNs and Reactive Coupling of Polymers in the Interface". Rätzsch concluded that at the present time the opportunities for the development of polymer blends made up of two polymers are largely defined. The aim for new blends is to combine the properties of the single components in one material. Precondition for obtaining desirable properties is the construction of heterophase blends, i.e. the range of partial thermodynamic miscibility of the components. To avoid a decrease of the mechanical properties of the blends due to interfacial failure, block and graft copolymers are used as compatibilizers.

Considerations of a further increase of properties in systems of two high modulus and crystalline polymers lead to polymer alloys with fibrous and lamellar structures on the submicron scale which can be done basically by two ways. 1) Building up a polymer starting from a monomer which is dissolved in the other polymer. To prevent phase separation during polymerization, the polymer has to be crosslinked which may lead to semi IPN structure or the polymerization has to take place below the melting point of the other polymer. Simultaneous graft reactions result in *in-situ* interlayers which stabilize compatibility. 2) Polymer blends of the submicron scale could only be produced by separation of the mixtures with partial compatibility of the blend components due to the lowering of temperature. For the alloys of polyesters it was shown that the solubility of polyesters in TPU is good because stable interlayers were formed. Many answers in the blending problems still need to



Dobrosiava, Small Wooden Church.



Bojnice Castle, Slovakia.

be answered but an enormous effort is being undertaken to utilize well known and easily modified polymers for the utilization and the design of the ideal polymer blends and alloys.

26 short lectures and 60 posters have also been presented which show the immediate development and advances in the individual areas. We can only briefly mention the short lectures. The following short lectures were presented: "Modified Atelocollagen Matrices for Implants", "Preparation of Crosslinked Poly(acrylamide) Nanoparticles", "Use of Reactive Processing to Make Compatibilizers for Multiple Phase Polymeric Systems", "Polymer Analysis by Combining Size Exclusion and Interactive Liquid Chromatography", "Preparation and Properties of an Interpenetrating Polymer Network-Like System Consisting of Polystyrene-Polyethylene", "Solution Properties of Polyimides as a Function of Composition and Molecular Weight", "Surface Tension and Interfacial Profile of Polymer Surface and Polymer/Polymer Interface", "Annealing Studies on Toughening Polyamide I. Dependence on Rubber Grafting", "Annealing Studies on Toughening Polyamide II. Influence of Rubber Grafting", "Phase Separation in SAN-Modified Segmented Polyurethane", "The Influence of Polymer Matrix on Triplet Probes; Monoketones of Benzophenone Type; 9,10-Anthraquinones and Derivatives of 1,2-Diketones", "Crosslinked Polyolefins as Matrices for Two-Phase Materials", "Reactions of Hydroxy (HO.) and Hydroperoxy (HOO.) Radicals with Polymers", "Modifications of Recycled Polymers", "Photooxidation of the Composite Lignin/Polypropylene Films", "Dynamic Vulcanization on the Basis of Multiphase-Systems", "The Effect of Carboxylic and Basic End Groups Modification on the Thermooxidation of Hydrolytic Poly(12-Dodecanelactams)", "Preparation and Photochemical Properties of 4-Propenylbenzil Polymers", "Microporous Polymer Membranes for Electrolysis", "The Application of Nonisothermal Chemiluminescence for Studying Oxidative Stability of Modified Epoxy Resins", "Worm-Like Chain Model Applied on the Solution Properties of Polymethacrylates with Pendant Side Chain Groups", "Crystallization of Poly(Butylene Terephthalate) and Polycarbonate

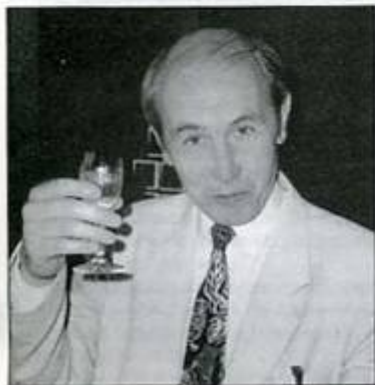


Polymer Institute of the Slovak Academy of Sciences

in the Polymer System Poly(Butylene Terephthalate)/Polycarbonate", "Modification of Macroporous Membranes Based on Methyl Methacrylate and Ethylene Glycol Dimethacrylate Copolymers with Polypyrrol" and "Monte Carlo Study of the Effect of Molecular Motion on Free-Radical Decay in Amorphous Polymers".

The Polymer Institute, Slovak Academy of Sciences: The Polymer Institute was founded thirty years ago by Milan Lazár who became its first director. After the 1968 upheaval, the Institute was redirected by Andrej Romanov. Now, after 1989, Dr. Lazár became again its director. He is assisted by the Deputy Director Pavel Hrdliovic and the scientific secretary Lyda Matisová-Rychlá. The scientific activity of the Polymer Institute is focused on the study of the changes of the structures of macromolecules related to the properties of polymer systems.

The research staff has a great deal of experience in the study of free radical reactions



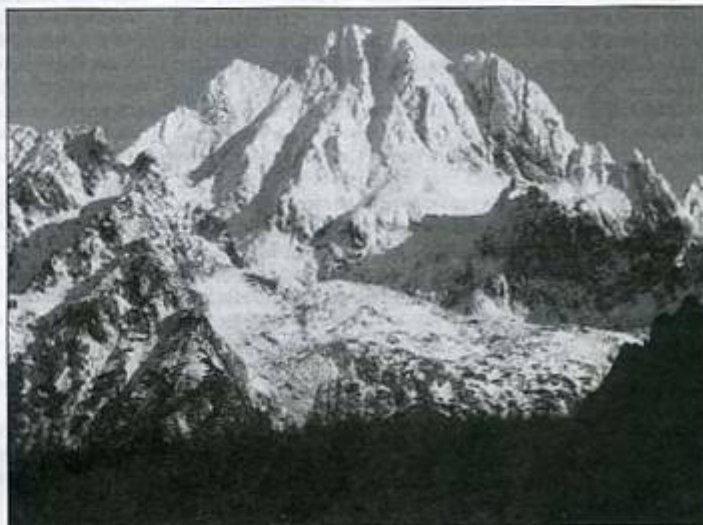
Ivan Chodák



At the welcoming reception.

in polymers, in the reactivity of radicals in polymeric systems, matrices, polymerization in microemulsions, photooxidations, thermooxidations and combustion of polymers as well as the inhibition and retardation of radical processes in polymers. The Institute has now a staff of 94 members with 33 scientists and 34 with University degrees.

The following projects have been solved in the period 1992–1993: "Thermally initiated and photoinitiated radical reactions in microheterogeneous systems" by Jaroslav Barton, "Microparticulate porous polymer systems" by Dusan Běrek, "Molecular thermodynamics of polymers" by Tomáš Bleha, "Chemical modification of polyolefins for the preparation of polymer blends



High Tatras

Conference Report



At the banquet.



Otto
Vogl

Ferenc
Tüdös

Manfred
Rätzsch

and filled polymers" by Eberhard Borsig, "Preparation of composite polymer dispersions" by Ignác Capek, "Interactions in multicomponent systems of copolymers containing various polar groups" by Štefan Florián, "Photochemical, photophysical and photooxidation processes in polymers in the solid state" by Pavol Hrdlovic, "The effect of crosslinking on the properties of polyolefin-based blends and composites" by Ivan Chodák, "Additives to polymers with increased molecular mass" by Štefan Chmelá, "A theoretical study of reactive molecular collisions during polymer burning" by Viliam Klímo, "Multicomponent polymer systems in solution" by Dieter Lath, "Modern carbon solvents for analytical applications" by Ivan Novák, "Topology and composition of macromolecules and their influence on polymer properties" by Juraj Pavlinec, "Determination of conditions for the decomposition of polymer materials and their ignition in the presence of non-halogen flame retardant and antioxidants" by Jozef Rychlý and finally "Influence of molecular mobility on transport phenomena in solid polymers" by Jozef Tino.

The thirtieth anniversary celebration of the Institute was also the occasion to present for the first time to three foreign scientists the honorary membership of the Slovak Chemical Society. Even before the separation of the Czech and Slovak Republic from the original state of Czechoslovakia, the Slovak part of Czechoslovakia had its own Chemical Society and its own Academy of Sciences. In the past the honorary membership of the society, on rare occasions, was bestowed on prominent national figures in the chemical sciences.

This was the first year of the Slovak Republic with its own identity. The Slovak Chemical Society has chosen to bestow the honorary memberships of the Society to the three scientists for their contributions to International science and specifically to their contribution to Slovak chemistry and to the furthering of the Slovak

International activity and recognition in chemistry. The three scientists that were selected being awarded the first honorary memberships were Dr. Otto Vogl, Herman F. Mark Professor at the Polytechnic University, Brooklyn, NY, U.S.A., Dr. Ferenc Tüdös, Head of the Department of Polymer Chemistry of the Central Research Institute of Chemistry of the Hungarian Academy of Sciences and Professor of Chemistry at the University of Budapest, Hungary and Professor Manfred Rätzsch, Director of Research of PCD Polymere of the Austrian Oil Company (ÖMV) in Linz, Austria.

The meeting in the Tatra mountains, organized by the Polymer Research Institute of Bratislava has been a most important scientific and social event. It was the first time that Slovakia as an independent country has hosted a major meeting in polymer science. The Polymer Institute of the Slovak Academy of Sciences is an important institute of polymer science, well recognized for many years but an institution on its own and recognized for its established competence and for the high quality of their research scientists.

On Sunday evening, the participants of the meeting assembled for a welcoming reception, an excellent opportunity to meet each other and to get reacquainted with old friends. Wednesday afternoon was reserved for excursions and walking tours in the High Tatras, as well as for opportunities to see some of charming ancient towns and castles of Eastern Slovakia. It demonstrated the importance that this part of Europe has played already in the middle ages. The reception banquet on Wednesday evening was again a most delightful event.

The International community in polymer science is looking forward to further development in polymer science in this part of the world and expects Bratislava and the Polymer Institute to play an integral and leading part in global polymer science.