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8th Bratislava International Conference on Modified Polymers: ModPol2003

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Conference Report

18th Bratislava International Conference on Modified Polymers: ModPol2003

Stará Lesná, The High Tatras, October 6–9, 2003

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The 18th Bratislava International Conference on Modified Polymers: ModPol2003 was held in Stara Lesna, The High Tatras, from October 6–9, 2003. This is the 18th in a sequence of "Bratislava Conferences" that started about 35 years ago in Bratislava. This conference also coincided with the 40th anniversary of the founding of the Polymer Institute in Bratislava.

The conference was held in the Conference Center of the Hotel Academia, which is used by the Slovak Academy of Sciences for a number of their symposia and seminars.

The conference was organized by the Organizing Committee, consisting of Peter Cifra (Chairman), Jozef Rychly (Director of the Polymer Institute), Maria Omastova, Katarina Csomorova, Zuzana Hlouskova, Sidonia Kalinova, and Nadja Kulickova. To recognize the most prominent members of the Institute an Honorary Presidium was established consisting of Jaroslav Barton, Dusan Berek, Tomas Bleha, Eberhard Borsig, Ignac Capek, Ivan

Hotel Academia

Maria Omastova

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The High Tatras

Pavol Hrdlovič and Michal Ilavsky

Chodak, Dieter Lath, Milan Lazar, Pavol Hrdlovič, and Lyda Rychla.

The High Tatras is part of the Carpathian mountain chain that provides the mountainous spine of Slovakia and ends in the northeast of Romania. The Tatra Massif rises abruptly in east central Slovakia and is the most renowned of the mountains in Slovakia. The mountain range is compact, only about 20 miles across. Geologically the Tatras are young. There are more than 25 peaks rising over 2500 m in the Tatras National Forest (800 km^2)with Mount Gerlach standing 2654 m. The Tatras National Park has over 50 mountain lakes and dense forests below 1600 m. At the foot of the mountain range is a string of resort villages that started about 150 years ago. They provide spas and other types of sports activities and entertainments. An upper road connects these prominent spas and resorts—Stary Smokovec (990 m), Tatranska Lomnica (850 m), and Strbske Pleso (1350 m). Stara Lesna and the Hotel Academia are part of this chain of resort towns.

The conference consisted of five main lectures, 12 special lectures, 25 oral presentations, and 65 presentations in poster form. About 80 participants came from abroad—from 20 countries—and about 40 from Slovakia. The conference started on Sunday afternoon with the registration, dinner, and a welcoming party. This traditional affair allowed attendees to see old friends and to meet new and younger colleagues.

Miroslav Raab and Lyda Rychla at the welcoming reception.

The opening was held on Monday morning. We heard comments from Eli M. Pearce, Past-President of the American Chemical Society; Greame George, former President of the Australian Institute of Chemists; and Otto Vogl, former Chairman of the Division of Polymer Chemistry of the American Chemical Society and first President of the Pacific Polymer Federation.

The scientific part of the conference was opened by Otto Vogl (University of Massachusetts, Amherst, MA, and Polytechnic University, Brooklyn, NY, USA) with a lecture entitled, "Spacer Groups in Macromolecular Structures."

Both flexible and rigid spacer groups play an important role in macromolecular structures. Nature has carefully developed spacers in proteins and important amino acids (lysine, arginine, threonine, glutamic acid) that have their functional groups separated from the α-amino acid polymer chain by 2 or 3 methylene units.

In synthetic polymers, the different behavior and reactivity of functional groups attached directly to polymer chains were often referred to as the "polymer effect." Such effects are related to the structure of the polymer chain and to individual functional groups.

The research group undertook an extensive and systematic investigation to determine the effect of the flexible methylene side groups on the reactivity of the functional group at the end of the spacer group. They investigated the epoxidation of ω-alkenoates, and the polymerization and copolymerization of ω-alkenoates and ω-epoxyalkanoates. The group also investigated reactions on these polymers with polyethylene and polyoxyethylene chains.

They also recognized double melting points in crystalline iso-

The opening of the conference. Left to right: Peter Cifra, Jozef Rychly, Eli M. Pearce, Graeme A. George, and Otto Vogl.

tactic aliphatic polyaldehydes. The first "melting point" was the melting point of the polymer main chain and the second that of the paraffinic side chain. In all cases the required spacer length was 3–4 methylene groups.

Five Main Lectures were presented. They are listed as follows:

K. Levon, (Polytechnic University, Brooklyn, NY, USA): Multifunctional Polymers for Detection of Biological Agents

Sensors for chemical and biological agents are based on cooperation of the recognition and transduction components, which are integrated together in nature. The function of ion channel proteins in bilayer membranes is an excellent example of a synergistic amplification as a result of the recognition process by the surface antibodies.

The surface imprinting method was applied on functional electrodes of the chemical sensors to produce cavities that selectively invite the template molecules. Thus the electrodes responded only when the template entered the imprinted cavity. The lecturer demonstrated the validity of the surface imprinted polymers with chiral anilino acids and with methyl phosphonic acid, the degradation product of Sarin and dipicolinic acid, a compound released from the spores of *B. anthracis*. The immobilization of specific ligand molecules such as antibodies, lectins, heptapeptides and sugars on the electrode surfaces provided the desired selectivity for *B. anthracis* in these stable and sensitive electrochemical sensors.

Kalle Levon, Eli M. Pearce, and Otto Vogl

B. Voit, D. Schmaljohann, Th. Huber, A. Ziemer, C. Clausnitzer, P. Pötschke, K. Grundke and K. Eichhorn (Institute of Polymer Research Dresden, Dresden, Germany): Hyperbranched Polymers and Their Interaction with Linear Polymers

Hyperbranched polymers exhibit special properties that differ from those of conventional linear or only slightly branched polymers due to their dense, globular structure and the high number of functional groups. They are much more soluble than comparable linear polymers, have low solution viscosities, and their functional groups are easily accessible for further modification reactions. They resemble perfectly branched dendrimers but with broad molar mass distribution.

Hyperbranched polyesters and poly(ether amide)s can be designed for specific applications (e.g., as blend components in combination with linear polymers, as additives, or as dye carriers). Phenol and acid functional hyperbranched polyesters have also been used as reactive compatibilizers.

Hyperbranched polymers influence the bulk viscosity of linear polymers in various ways. Hyperbranched polyesters modified with long alkyl chains into polyolefins have a lubricating effect on linear polymers.

Hyperbranched poly(ether amide)s reduce the melt viscosity of linear polyamide but without changing the mechanical properties and the crystallinity of the matrix polymer. They are also fully miscible but are only incorporated into the amorphous phase of Nylon 6. Hyperbranched polyesters interact in a complicated way in formulations for polyurethane foams.

E. M. Pearce (Polymer Research Institute, Polytechnic University, Brooklyn, NY, USA) Miscible Polymer Blends through Hydrogen Bonding: Designing Properties

Miscible polymer blends through hydrogen bonding are an alternative route to designing and controlling polymer properties

compared to synthesizing new polymers and copolymers. They have developed systems that are examples in which physical properties such as single glass transition temperature, water absorption, modulus and surface modification can be varied. In addition, and changes in chemical reactivity as shown by improved thermal and thermooxidative stability were discussed.

Model systems were developed by modifying polystyrene with H-bond donating functions and these were interacted with a number of H-bond accepting polymers. Glass transition temperatures varied as a function of the strength of the H-bond interaction. A crystalline polymer, nylon-6, was modified with small amounts of an H-bond donor that did not affect its crystallization but decreased its water adsorption and increased its modulus.

Silanol-modified polystyrene as well as a modified silicone version were shown to give IPN system precursors. An H-bond donating modified silicone was shown to be miscible with several H-bond accepting polymers and the surfaces of the blends were shown to be enriched with silicone as compared to the bulk.

K. Ulbrich, V. Subr, J. Strohalm, T. Etrych, M. Jelinkova , M. Kovar B. Rihova, and L.W. Seymour (Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic): N-(2-hydroxypropyl)methacrylamide Copolymer Carriers for Targeted Delivery of Biologically Active Compounds

Water-soluble conjugates of synthetic copolymers of N-(2-hydroxypropyl)methacrylamide with anti-cancer drugs and antibodies provide a potential drug delivery system, facilitating specific delivery of cytotoxic drugs to model tumors in mice. Conjugates result in efficient inhibition of tumor growth and a substantial increase in survival time.

Interpolyelectrolyte complexes, formed by self-assembly of various polycations and DNA plasmids were coated with N-(2-hydroxypropyl)methacrylamide copolymers. This system provided an efficient gene delivery system. Semitelechelic N-(2-hydroxypropyl)methacrylamide polymers and multivalent N-(2-hydroxypropyl)methacrylamide copolymers with reactive succidimidyl, 4-nitrophenoxy, thiazolidine-2-thione, maleimidyl, and 2-pyridyldisulfanyl groups (polymer precursors) were also synthesized. They could react with drug models, cytotoxic drugs, antibodies, and anilino group-containing polycations. Their complexes with DNA were also studied. Each conjugate structure imparts specific physico-chemical and biological properties to the polymer drug conjugate.

G. A. George, I. Blakey and B. G. S. Goss (Queensland University of Technology, Brisbane, Australia): Infectious Spreading of Degradation in Polyolefins: Modeling and Experimental Evidence

The oxidative degradation of polyolefins and, in particular, polypropylene, show features such as the evolution of volatiles and the appearance of microcracks within the "oxidation induction period" that cannot be rationalized within a simple homogeneous kinetic scheme. An alternative model for the oxidation of the solid polymer has been developed in which the oxidation is highly heterogeneous and the oxidation product-time curve is viewed as a statistical accumulation.

Josef Rychly

Ziegler-Natta catalyst residues have been implicated in the initiation of oxidation through catalysis of the decomposition of hydroperoxides, the main reactive intermediate in oxidation. In the heterogeneous model, the catalyst provides sites for the initiation of rapid oxidation that is initially confined to zones in the immediate vicinity of the residual catalyst and is therefore undetectable by analytical methods. This localized oxidation generates species such as the hydroperoxy radical that are able to increase the volume of the oxidizing zones and gradually consume the polymer.

The authors modeled this using an epidemiological model involving three populations. This has been replaced by stochastic modeling of the spreading of oxidation for a range of volume fractions of infectious sites that assumes no mixing of the populations.

M. Strlic, D. Kocar, J. Kolar and J. Malesic (University of Ljubljana, Slovenia): The role of Carbonyl Groups in the Oxidation of Polysaccharides

Atmospheric oxidation of polysaccharides is a topic of great interest in the pulp and paper industry, production of biodegradable materials, and preservation of archival materials. The degradation of pullulan (polymaltotriose) and cellulose samples was studied under various conditions of temperature and humidity.

A. S. Luyt (University of the Free State, Phuthaditjhaba, South Africa): The Influence of Wax on the Morphology and Properties of Polymer Blends and Composites

Wax has a considerable influence in polyolefin/wax blends based on the type of polyethylene used. It effects the lamellae thickness and crystal perfection. It also plays a significant role in the properties of polyethylene/wax sisal fiber compositions.

G. Ruggeri and A. Pucci (University of Pisa, Pisa, Italy): Effect of Compatibilization on the Optical Performances of Linear Polarizers Based on Polyethylene Films

Linear optical absorbing polarizers have been produced by dispersing low molecular weight organic terthiophene-based dyes in ultrahigh molecular weight polyethylene and successive orientation by uniaxial stretching. The persistence existed between the phase separated absorbing organic guest molecules and the apolar polymer matrix

R. Demadrille, B. Dufour, P. Rannou, and A. Pron (University J. Fourier-Grenoble, Grenoble, France): New Comb-Shaped π-Conjugated Architectures Containing Polyaniline or its Oligomers-Preparation of Polymeric Systems with Tunable Electronic and Optical Properties via Chain Engineering and Dopant-Induced Self-Assembly

A large variety of ordered supramolecular aggregations could be obtained by self-organization of comb-shaped macromolecules. The authors demonstrate that polyaniline doped with new dopants, namely diesters of sulfophthalic or sulfosuccinic acids containing alkyl or alkoxy substituents, can be considered as comb-shaped polymer. These structurally ordered polyanilines combine high stretchability with high electrical conductivity and excellent thermal stability.

M. M. Chehimi, S. Bousalemi, C. Mangeney, A. Azioune, Y. Alcote, T. Basinska, and S. Slomkowski (Université Paris 7, Paris, France): Interfacial Chemistry and Potential Biomedical Applications of Reactive, Functionalized Conducting Polypyrrole Collodial Particles

Polypyrrole-coated polystyrene latex particles and polypyrrole-silica nanocomposites bearing reactive N-succininidyl ester functional groups were prepared by in-situ copolymerization of pyrrole and the active ester functionalized.

Ivan Chodak

These novel N-succininidyl ester functionalized polypyrrole colloidal particles can attach appropriate proteins and have biomedical potentials.

J. Pionteck, G. Dlubek, G. Pompe, A. Janke, V. Bondarenko and R. Krause-Rehberg (Institute of Polymer Research Dresden, Dresden, Germany): Characterization of Interfacial Diffusion by DSC, PALS, and AFM

Polymer blends with different interphases have been prepared. PALS (positron/positronium annihilation lifetime spectroscopy) was used for the characterization of interdiffusing polymer systems. The results agreed well with data already obtained by DSC spectroscopy.

N. Moszner (Ivoclar Vivadent AG, Schaan, Liechtenstein): Development of New Monomers for Dental Applications

Dental filling materials are an interesting field of application for new monomers. On the one hand they can improve important properties, such as reduction of polymerization shrinkage in the case of restorative composites or enhancement of the stability and adhesive properties of dentin adhesives. On the other hand, the high price of new monomers is not an important criterion for their use in dental filling materials.

X. Colin, L. Audouin and J. Verdu (Laboratoire de Transformation et de Vieillissement des Polymères, Paris, France): Inverse Methods in Polymer Oxidation Kinetics

Kinetic modeling of polymer oxidation kinetics required fitting experimentally obtained kinetic curves. Kinetic models take into account the hydroperoxide decomposition based on initiation rate, long kinetic chain length, and interrelationship between termination rate constants. The reaction constant between peroxy radical and polymer radical is difficult to estimate. Inverse methods appear to be convenient approaches for the determination of this constant.

J. Lacoste, S. Commereuc, M. Baba, A. Kumar and F. Jestin (Université Blaise Pascal, Aubière, France): Crosslinking Reactions, Another Consequence of Polymer Aging

The photo, thermal, and radiochemical aging of synthetic polymers involve well known radical oxidations that result in the formation of polar groups, such as acids, ketones, and alcohols accompanied by a decrease of the average molecular weight by chain scissions. Recombination of macro-radicals results in the crosslinked polymer insoluble networks. Several analytical techniques were especially useful for the evaluation of these phenomena.

W.D. Habicher, I. Bauer, B. Pawelke, G. Theumer, S. Chmela, J. Mosnacek, Cs. Kosa, P. Hrdlovic, and J. Pospisil (Dresden University of Technology, Dresden, Germany): Multifunctional Stabilizers for Polymers

To protect polymers against different damaging influences during their production, processing, and application it is important to use effective stabilizers. The lecturers were able to prevent or reduce the different degradation and aging processes. Mul-

Magdalena Kulickova and Anton Mancinein at the reception.

Jozef Rychly and Graeme A. George at the medal presentation.

tifunctional stabilizers have been conceived and synthesized. They provide even distribution in the polymer matrix and synergistic effects of their individual activities. Conventional classes of stabilizers, such as sterically hindered phenols or amines were lined with diisocyanates with inorganic acid derivatives, such as phosphites or borates.

B. V. Kokta (University of Quebec, Trois-Rivières, Quebec, Canada): Polypropylene Composites Reinforced with Cellulosic Fibers

Polypropylene was compounded with various natural fibers and grass in various compositions. In several cases a substantial increase in the tensile properties increased while preserving very high initial impact strength of polypropylene.

The high point of the conference was the symposium banquet on Tuesday evening. The special entree at the dinner was suckling pig. For those of us that have a special appreciation for suckling pig, it was a rare treat. The head was presented to a carefully selected and appreciative person to emphasize the uniqueness of the occasion.

Eberhard Borsig and Otto Vogl at the banquet.

At the end of the banquet Honorary Medals of the SAS Polymer Institutes were presented to persons for their continued commitment, cooperation, and dedication to the SAS Polymer Institute. All recipients presented lectures at the conference.

After the farewell party, the participants left with a feeling of accomplishment. We all look forward to future cooperation and interaction with the Polymer Institute and the Bratislava Conferences.

40th Anniversary of the SAS Polymer Institute (co-author Jozef Luston)

The Polymer Institute of the Slovak Academy of Sciences is located in Bratislava, the capital of Slovakia, and is the scientific arm of Slovak Polymer Science. It was originally founded in 1963 as the Laboratory of Polymers with Milan Lazar as the first director. At that time the Slovak Republic was part of Czechoslovakia. The laboratory was enlarged and renamed the Polymer Institute of the Slovak Academy of Sciences in 1967. In its 40 year history, the Institute provided the entire region of Europe with the scientific background and research activity of polymers science. It had a succession of directors: Milan Lazar, Andrej Romanov (during much of the communist regime) and later Jaroslav Barton. After the velvet revolution and the separation from the Czech Republic, Milan Lazar, Pavol Hrdlovič, and Jozef Rychly each became director.

A detailed account of the Polymer Institute was written 10 years ago and published in *Polymer News* [Otto Vogl, Polymer Institute Slovak Academy of Sciences Bratislava, Slovakia, *Polymer News, 19*(5), 151–157 (1994)]. Time goes by and the younger scientific generation of the Institute is learning from the established scientists. It would probably be appropriate to add and

The participants of the conference.

publish an account of the last 10 years and the present status of the Polymer Institute and what is planned for the future.

The Institute decided to hold a special 40th anniversary celebration before the 18th Bratislava Conference in Stara Lesna. On Friday, October 3 and Saturday, October 4, the entire scientific community and staff of the Institute assembled and exchanged memories and took pride in their accomplishments of the last few decades. The final celebration was the dinner on Saturday evening, with the leader of the Slovak Academy, Jan Knopp (Member of the Board), and the Dean of the Faculty of the Chemical and Food Technology of the Slovak University of Technology, Dusan Bakos, present. They recognized the accomplishments of the Institute and received the Honorary Medal of recognition from the Polymer Institute.

Otto Vogl presented the congratulatory document of the ACS Division of Polymer Chemistry for the Polymer Institute in recognition of their accomplishments in Polymer Science. It expressed the appreciation of the cooperation between the members and the Institute with the Division of Polymer Chemistry.

The presentation was followed with a celebration for the members of the Polymer Institute, expressing happiness for their accomplishments over the years.

The Slovak Academy of Sciences and the Polymer Institute have many responsibilities. Among them is the authority to have graduate students that lead to the PhD, and have the authority to grant a PhD in the subject of the study at the Institute, macromolecular chemistry and polymer technology.

The Polymer Institute has organized meetings and workshops in polymer science. Few events were organized during the dark times of the communist regime, but they have become more common in recent years. Most important are the Bratislava Interna-

The Polymer Institute

Jan Knopp and Dusan Bakos at the dinner.

tional Conferences on Polymers. The Polymer Institute started these conferences 35 years ago and the 18th conference has now been successfully concluded A list of these conferences and workshops follows.

Conferences and Meetings Organized by the Polymer Institute of the Slovak Academy of Sciences

Chemical Transformation of Polymers (1st Bratislava Conference). Bratislava, June 25–27, 1968. Chairman: Milan Lazar. Proceedings of the conference were published in *European Polymer Journal*, 1969, Supplement.

IUPAC International Conference: Chemical Transformation of Polymers (2nd Bratislava Conference). Bratislava, June 22–24, 1971. Chairman: Milan Lazar. Main lectures were published in a special issue of *Pure and Applied Chemistry*.

IUPAC International Conference on Advances and Future in Macromolecular Science (3rd Bratislava Conference). Strbske Pleso, High Tatras, May 15–17, 1973. Chairman: Andrej Romanov.

4th Bratislava IUPAC sponsored International Conference on Modified Polymers, Their Preparation and Properties. Bratislava, July 1–4, 1975. Chairman: Andrej Romanov. Main lectures were published as a special issue of *Pure and Applied Chemistry*.

5th Bratislava IUPAC sponsored International Conference on Modified Polymers. Bratislava, July 3–6, 1979. Chairman: Andrej Romanov. Main lectures were published as a special issue of *Pure and Applied Chemistry*.

6th Bratislava IUPAC sponsored International Conference on Modified Polymers. Bratislava, July 2–5, 1984. Chairman: Andrej Romanov. Main lectures were published in *Die Makromolekulare Chemie, Macromolecular Symposium*.

7th Bratislava IUPAC sponsored International Conference on Modified Polymers. Bratislava, July 5–8, 1988. Chairman: Andrej Romanov. Main lectures were published in *Die Makromolekulare Chemie, Macromolecular Symposium*, 28, 1–304 (1989).

8th Bratislava IUPAC sponsored International Conference on Polymers: Solution Properties of Modified Polymers. Stara Lesna, High Tatras, June 10–14, 1991. Chairman: Dieter Lath. Main lectures were published in *Die Makromolekulare Chemie, Macromolecular Symposia*, 59 1–238 (1992).

9th Bratislava Conference on Modification of Thermoplastic Polymers. Stara Lesna, High Tatras, June 14–18, 1993. Chairman: Pavol Hrdlovic. Lyda Matisova-Rychla and Otto Vogl, 9th Bratislava Conference on Modification of Thermoplastic Polymers, *Polymer News*, 19(1), 89–94 (1994).

10th Bratislava International Conference on Macromolecules Chromatography of Polymers and Related Substances. Bratislava, September 18–22, 1995. Chairman: Dusan Berek.

11th Bratislava International Conference on Polymers. Thermal and Photo-Induced Oxidation of Polymers and Its Inhibition in the Upcoming 21th Century. Stara Lesna, High Tatras, June 24–28, 1996. Chairman: Lyda Rychla.

12th Bratislava International IUPAC/EPF Conference on Polymers. Modified Polyolefins for Advanced Polymeric Materials. Bratislava, August 25–28, 1997. Chairman: Eberhard Borsig. Otto Vogl and Pavol Hrdlovic, *Polymer News*, 23(8), 273–280 (1998). *Progress in Polymer Science*, 24(5), 777–791 (1999). Main lectures were published in *Macromolecular Symposia*, 129, 1–172, (1998). Eberhard Borsig and Otto Vogl eds, *Journal of Macromolecular Science—Pure and Applied Chemistry*, A35,(7&8), 1017–1432 (1998)

13th Bratislava International Conference on Polymers. Separation and Characterization of Macromolecules. Bratislava, July 4–9, 1999. Chairman: Dusan Berek.

14th Bratislava International Conference on Modified Polymers, Property Tailoring of Thermoplastics Based Blends and Composites. Bratislava, October 1–4, 2000. Chairman: Ivan Chodak. Main lectures were published in *Macromolecular Symposia*, 170, 1–357 (2001).

15th Bratislava International Conference on Polymers. Nonconventional Polymer Dispersions. Smolenice, June 25–28, 2001. Chairman: Ignac Chapek. Main lectures were published in *Macromolecular Symposia*, 179, 1–356 (2002).

16th International Bratislava Conference on Polymers. Bratislava, September 9–13, 2001. Chairman: Dusan Berek.

17th Bratislava International Conference on Macromolecules. Molecular Characterization of Polymers. Bratislava, August 24–28, 2003. Chairman: Dusan Berek.

18th Bratislava International Conference on Modified Polymers. ModPol 2003. Stara Lesna, High Tatras, October 8–9, 2003. Chairman: Peter Cifra. Otto Vogl and Maria Omastova, *Polymer News*, 29(4), 126–134 (2004).

Work Shops and Small Conferences

Microsymposium on Quantum Chemistry. Stary Smokovec, High Tatras, October 25–28, 1977.

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Microsymposium on Radical Polymerization in Heterogeneous Systems. Smolenice, April 10–14, 1989.

Microsymposium on Degradation, Stabilization and Combustion of Polymers. Stara Lesna, High Tatras, June 18–22, 1990.

International Workshop on Practical Applications of Chemiluminescence at the Oxidation of Chemical Systems. Smolenice, November 2–5, 1998

International Workshop on Environmentally Degradable Plastics. Smolenice, October 4–8, 1999.

1st Slovak-Czech Days on Polymers. Smolenice, October 23–25, 2000.

Michal Ilavsky, Eberhard Borsig, and Otto Vogl, 5th International Congress Aplichem. 85 International Chemistry Fair, Incheba, 1985, in Bratislava, *Polymer News*, 11(9), 248–286 (1986).