University of Massachusetts Amherst

From the SelectedWorks of Otto Vogl

December, 1995

Croatian Symposium of Chemistry and Macromolecular Chemistry

Otto Vogl, University of Massachusetts - Amherst
Zvonimir Janovic

Available at: https://works.bepress.com/otto_vogl/135/
Conference Report

Croatian Symposium of Chemistry and Macromolecular Chemistry

Zvonimir Janović, University of Zagreb, Zagreb, Croatia and Otto Vogl
Polytechnic University, Brooklyn, NY 11201, U.S.A

A joint Meeting, the XIV Symposium of the Croatian Chemical Society and the IV Croatian Symposium of the Chemical and Technological Macromolecular Society was held in Zagreb, Croatia from February 6 to February 8, 1995. It was the first joint meeting of the two Societies and was attended by more than 500 participants. They came primarily from Croatia but participants from 12 other countries attended. The organization of the Meeting consisted of 17 plenary lectures and 370 papers that were presented in poster form. The plenary lectures represented the major subject area of chemistry and macromolecular chemistry and the poster session was also divided into several categories: a) Inorganic Chemistry and Solid State Chemistry, b) Organic Chemistry—this section was by far the largest section and included synthesis, reaction mechanisms and natural compounds; c) Physical Chemistry—thermodynamics, kinetics and structure; d) Theoretical Chemistry, e) Chemistry and Instrumentation f) Chemical and Biochemical Engineering, g) Industrial Processes and Quality Control, h) Environmental Protection and i) Chemical Education.

The sessions of the IV. Croatian Symposium on Chemistry and Technology of Macromolecules included, synthesis, processes characterization and application.

In this article we will comment specifically only on the plenary lectures and on the poster sessions of the IV. Symposium on Chemistry and Technology of Macromolecules.

The Symposium was under the Chairmanship of Professor Zvonimir Janović of the University of Zagreb, who was the chairman of the entire Symposium and of the organizing committee. The meeting was opened by the Minister of Science, Mr. B. Jeren, the rector of the University of Zagreb, Professor M. Sunjić, representatives of the Ministry of Education, the Ministry of Industry, the Croatian Chemical Society and of the Croatian Academy of Arts and Sciences.

After the Opening Ceremony, the Symposium was opened with a plenary lecture by Otto Vogl of Brooklyn, NY USA entitled Macromolecular Architecture and Design. He emphasized that polymer science and technology will have a continuing and increasing impact on the well being of mankind. Many needs that are essential for our existence and for the improvement of human life will be influenced by polymer science and technology. Specifically mentioned were clothing,
In the Old City

food and nutrition, shelter and housing, health care and medicine, construction, transportation, energy and communication.

Commodity plastics have reached a level of maturity in industrialized countries as can be seen from the drop or their relative growth rate. A number of important global companies have shifted their thrust of involvement from commodity plastics into more profitable ventures, such as products that serve health care, communication and transportation.

The speaker discussed selected areas that are now receiving considerable attention and pointed out that the economic synthesis of monomers and polymers will require more and efficient catalytic processes. In technical polymer synthesis, the importance of the production of polymeric materials with narrow and broad molecular weight distribution “on demand” for both homo- and copolymers are needed as is the concern of polymer production vs. the disposal. Living cationic, anionic and now even radical polymerizations (at least in some important cases) still show new avenues of development. Important examples are the methacrylate polymerization by group transfer techniques, macromolecular engineering by controlled carboxylation polymerization and methacrylate polymerization by cobalt complexes. We have learned and are still learning how to make star copolymers, hyperbranched polymers and dendrimers.

Fiber reinforced plastic materials play an important part in many polymer applications using ultrahigh molecular weight highly drawn polyethylene, carbon and aramid fibers. Reinforced epoxy laminates are starting to be used in construction, for repair and for the salvation of bridges and buildings.

More efficient antioxidants and ultraviolet stabilizers for polymers and better ways of applying them are being developed. Most prominent are stabilizers bound to the polymers; they are compatible, non-fugitive and capable of surface assembly of the polymer chains, now sometimes called morphology engineering.

Stable and Persistent Bis(ketenes): Novel Chemical Intermediates of Theoretical and Practical Importance were the subject of Thomas T. Tidwell, Toronto, Canada. The study of ketene chemistry has become of renewed interest worldwide. The effect of substituents on the ketene structure and reactivity and the origin of the extraordinary stabilizing effect of silyl substituents on ketenes has been recently elucidated by ab initio molecular orbital calculations. The authors have prepared silylated cyclobutenediones where the substituents are trialkyldiyl groups. Thermolysis of these compounds gives the more stable 1,2-bis(ketene) as the only observable product. 1,2 Bis(ketenes) are reactive toward a variety of reagents, including oxygen, water, alcohols, and electrophiles.

Opera, Zagreb

Cycodextrins as Tools in Scientific Research and Industrial Applications was discussed by Wolfram Saenger, Berlin, Germany. Cycodextrins are obtained by enzymatic degradation of starch. They are cyclic oligosaccharides consisting of 6 to 10 glucose units with α(1→4) linkages. Due to their angular structure, they, like common crown ethers, are able to form inclusion complexes even in solution. Cycodextrins are used as excellent models for a number of biological processes where nonequivalent intramolecular interactions are desired. The formation of these inclusion compounds has been followed by different spectroscopic techniques.

Bernard Schröder, Essen, Germany presented his recent work on New Applications of NIR FT Raman Spectroscopy. Since its discovery in 1928, Raman spectroscopy, a valuable tool in science, has never become a method for routine analysis in the industrial environment. This is caused by the fact that most samples contain impurities that are inherent in the samples or products of oxidation. Of special importance are the products of photochemical and thermal reactions which fluoresce after excitation with the usual exciting radiation for Raman spectroscopy at 488 or 515 nm. It has now become possible to
strength, the ultimate toughness of polymeric materials, another important engineering property, is poorly understood as demonstrated by the numerous papers with conflicting views. Toughness is in first approximation proportional to the total energy involved in deformation up to fracture, i.e. the area under the stress-strain curve. On a microscopic level (i.e. inside deformation zones) a satisfying correlation has been established between the local strain and the strain-to-break based on stretching the molecular network to its full extension.

Increasingly stringent water quality regulations lead to the need for treating all of the various waste streams containing pollutants. Waste waters originating from industrial activities contain organic pollutants which are either toxic or biodegradable, consequently direct biological treatment is not feasible.

**Computer Integrated Plant Operations** in Chemical & Refining Industry was presented by V. Mahalec, Cambridge, MA. Plant models throughout plant life cycle (from design to plant operation to revamp), including decision making in process control, on-line optimization, production scheduling and production planning were examined. Such models become the basis for models used in all aspects of the plant decision making: a) Design modifications; b) Design of Advanced Process Control Strategies; c) On-line Optimization and d) Production Planning and Scheduling.

Advances In Polymer Blends, was the subject of the talk by Roberto Greco, Napoli, Italy representing E. Martuscelli. Syntheses of new polymers are still being developed in order to meet the growing demand of materials tailored for specific technological needs. In recent years and, specifically, in the last decade, multicomponent polymeric systems became the subject of intensive study. New properties could be achieved by the proper matching of the properties of already existing polymers.

Multicomponent polymer systems are made from a thermoplastic or thermosetting matrix intimately mixed to one or more minor polymer phases. The influence of the molecular structure of components (tactility and constitution), composition, procedures of blending and processing and crystallization conditions on the kinetic and thermodynamic factors of the crystallization process, phase structure in the melt and the condensed state and morphology has been investigated for different type of polymer blends containing crystallizable and amorphous components.

The blend types may be assembled, according to the mutual miscibility of components in the melt and in the amorphous state as follows: a) Miscible, b) Phase separated, c) Immiscible. The speaker was particularly interested in: a) Melt miscible blends; b) Melt phase separated Blends; c) Melt immiscible blends and d) Reactive blending technologies. Interesting materials with improved properties were realized starting with the following types of polymer pairs.

Vol. 20, No. 11, POLYMER NEWS 367
Conference Report

Polymerization of p-Methylstyrene was presented by F. Tedos, Budapest, Hungary. Radical bulk polymerization of p-methylstyrene was investigated at 50°C with AIBN as initiator. The results of measurements were compared with relevant literature data. The overall rate constant of p-methylstyrene was practically equal to that of styrene, but vinyl toluene polymerizes at about a 20% higher rate. The inhibitive effect of p-nitroso aniline derivatives and other aromatic nitroso compounds (e.g., trinitrobenzene, 0- and p-dinitrobenzene) was studied on the bulk polymerization of p-methylstyrene. The inhibitive effects of p-benzoquinone and its derivatives (tobuquinone, o-xylenequinone) was also studied in bulk and solution polymerization. All these compounds were found to be effective inhibitors.

Ultimate Properties of Synthetic Polymer Systems was the subject of the plenary lecture of Peter J. Lemstra, Eindhoven, The Netherlands. Polymer Science and Technology is the paradigm of an integrated discipline in which Chemistry, Physics, Processing and Design constitute a "chain-of-knowledge." In order to exploit the intrinsic potential, aiming at ultimate properties of synthetic polymeric materials, the various elements in this "chain-of-knowledge" need to be linked and be of equal strength.

Creative chemistry requires creative processing and examples were presented concerning novel processing routes of intractable, high Tg polymers, using reactive solvents. Apart from sophisticated chemistry, substantial progress has been made in the past two decades concerning physical aspects of polymer science and technology. A striking example in this respect is the development of high-modulus and high-strength fibers based on the "primus inter pares" of simplicity in synthetic polymers, polyethylene. Besides the development of high-strength/high-modulus fibers based on flexible macromolecules, another important parallel line of research was the development of high performance fibers based on intrinsically rigid macromolecules, i.e. the aromatic polyamide fibers.

In contrast with the ultimate properties like stiffness and...
strength, the ultimate toughness of polymeric materials, another important engineering property, is poorly understood as demonstrated by the numerous papers with conflicting views. Toughness is in first approximation proportional to the total energy involved in deformation up to fracture, i.e. the area under the stress-strain curve. On a microscopic level (e.g. inside deformation zones) a satisfying correlation has been established between the local strain and the strain-to-break based on stretching the molecular network to its full extension.

Maria Ranogajec  Igor Čatić

increasingly stringent water quality regulations lead to the need for treating all of the various waste streams containing pollutants. Waste waters originating from industrial activities contain organic pollutants which are either toxic or biodegradable, consequently direct biological treatment is not feasible.

Computer Integrated Plant Operations in Chemical & Refining Industry was presented by V. Mahalec, Cambridge, MA. Plant models through the plant life cycle (from design to plant operation to revamp), including decision making in process control, on-line optimization, production scheduling and operation planning were examined. Such models became the basis for models used in all aspects of the plant decision making:

a) Design modifications; b) Design of Advanced Process Control Strategies; c) On-line Optimization and d) Production Planning and Scheduling.

Advances in Polymer Blends was the subject of the talk by Roberto Greco, Napoli, Italy representing E. Martuscelli. Syntheses of new polymers are still being developed in order to meet the growing demand of materials tailored for specific technological needs. In recent years and, specifically, in the last decade, multicomponent polymeric systems became the subject of intensive study. New properties could be achieved by the proper matching of the properties of already existing polymers.

Multicomponent polymer systems are made from a thermoplastic or thermosetting matrix intimately mixed to one or more minor polymer phases. The influence of the molecular structure of components (tacticity and constitution), composition, procedures of blending and processing and crystallization conditions on the kinetic and thermodynamic factors of the crystallization process, phase structure in the melt and the condensed state and morphology has been investigated for different type of polymer blends containing crystallizable and amorphous components.

The blend types may be assembled, according to the mutual miscibility of components in the melt and in the amorphous state as follows: a) Miscible, b) Phase separated, c) Immiscible. The speaker was particularly interested in a) Melt miscible blends; b) Melt phase separated blends; c) Melt immiscible blends and d) Reactive blending technologies. Interesting materials with improved properties were realized starting with the following types of polymer pairs.
phases, plays a determining role in a transport of matter during membrane separation operations. Because the membranes for both the separation operations and for the physicochemical studies are usually built of polymeric materials, their properties depend greatly on the proper choice of the polymer. Asymmetric membranes are most often prepared by the phase inversion technique. The procedure for the proper addition in the membrane preparation and some new ideas on the formation of a “defect-free” skin was presented.

Polystyrene-Block-Poly(Methyl Methacrylate) Micelles By Size Exclusion Chromatography/Low Angle Laser Light Scattering was discussed by Z. Grubisic-Gallet, Strasbourg, France. Block copolymers in selective solvents (i.e. thermodynamically a good solvent for one block and at the same time a poor solvent for the other block) form multimolecular associates—called micelles—having a core formed by blocks of poor solubility and a protective shell formed by blocks of good solubility. Micelles are formed via so-called closed association, which is characterized by an equilibrium between micelles, with a narrow molecular-weight and size distribution and a molecularly dissolved copolymer—unimer. Size exclusion chromatography (SEC) is known to be a powerful method of characterizing polymer molecules in solution based on the separation of macromolecules according to the hydrodynamic volume.

An example of SEC results obtained for micellar system polystyrene-b-methyl methacrylate diblock copolymer in the mixed solvent system 1,4-dioxane/cyclohexane was reported. Good separation of peaks of micelles achieved for this system enabled a direct molecular-weight characterization of micelles by a low angle laser scattering detector. Experiments with changing flow rate and concentration of injected sample solutions showed moderately fast unimer-micelles re-equilibration in the course of separation.

The Mechanism of Singlet Photoreactions was presented by M. Klessinger, Munster, Germany. The reaction pathway of a nonadiabatic photochemical reaction begins on the excited-state potential energy surface at the Franck-Condon region or on a spectroscopic minimum of the reactant. It finishes at the product minimum on the ground-state surface. Conical intersections are a common feature in most nonadiabatic singlet photo reactions. Geometries at which conical intersections are likely to occur can now be predicted by means of simple models.

HPLC, NMR and Chiroptics in Stereochemistry: Axial Chirality of Hindered Amides was the subject of the lecture by A. Mansscheek, Regensburg, Germany. The following physical methods, essential for organic stereochemistry, particularly enantioselective H NMR, enantioselective HPLC, circular dichroism and polarimetry techniques were used to study silylated hindered amides. The demonstration of their axial chirality, the analytical and semipreparative separation of their enantiomers and/or diastereomers, the determination of their relative configuration and the measurement of their barriers to stereoisomerizations was discussed. The latter was found to occur by the following processes: rotation about the aryl-N and aryl-C bonds in dialklyaminobenzic and dialklyhalogeno acid amides and the rotation about the =C= and =C=N bonds in benzoic, naphthoic and acrylic thioureas. Acrylic thioureas represent a novel class of axially chiral compounds.

Recent Progress in the Investigation of Carbocations was
discussed by Hans-Ulrich Siehl, Tubingen, Germany. He pointed out that the award of the 1994 Nobel Prize in Chemistry to George Olah underscores the importance of carboxylation chemistry. The latest progress in this field can be characterized by the fruitful interplay of advanced experimental methods and quantum chemical methods for the characterization.

This had been particularly for disubstituted carboxylations (vinyl cations) and silyl substituted carboxylations which were up-to-now not accessible in solution. Using special experimental techniques to avoid cationic polymerization the authors successfully protonated suitably substituted alkenes and allenes.

Finally, an interesting work was presented by M. Eckert-Maksic, Zagreb, Croatia, entitled "Electronic Structure and Reactivity of Fused 7-Oxanorbornenes." 7-Oxanorbornenes, linked either via common carbon-carbon aromatic moieties, are of great interest as potential building blocks of highly interesting molecules such as polynuclear spacers and macromolecules with extended π-conjugation. They represent also a great challenge from both spectroscopic and theoretical points of view as they provide a unique framework for exploring transannular orbital interactions.

At the Banquet

Polymer Polyols” by J. Sadačinovic, V. Rek, and K. C. Frisch.
“Isothermal Degradation of Poly(Vinyl Chloride)/Methyl
Methacrylate-Butadiene-Styrene Blends” by B. Baric and T.
Kovacic.
“Study of Thermochemical Degradation System of
Copolymer/Butadiene-g-Styrene” by D. Pajc-Lipelin, D. Hace
and V. Kovacevic.
“Investigation of Thermo-oxidative
Degradation of PVC/ABS Blends by Infrared Spectroscopy” by
I. Klaric and U. Roje.
“The Effect of Molecular Weight of Polyols on Photosensitivity in Polyurethane Elastomers” by E.
Govoric-Bajic, V. Rek, A. Sendjarevic, V. Sendjarevic and
K. C. Frisch.
“Effect of Molar Volume of Solvent and
Vulcanization Structure on Interactions in the System Solvent-
Crosslinked Polymer” by Z. Hrjanak-Murgic, J. Jelencic, M.
Bravar and M. Marovic.
“Chemorheology of Unsaturated
Polyester Resin” by M. Opalski, M. M. Kenny and L.
Nicolais.
“Rheological Behaviour Comparison of PVC Plastics on the
Basis of Emulsion and Microsuspension PVC” by Z. Spehar and
V. Rek.
“Adsorption of Polyacrylic Acids on the Hydrophobic
Surface” by M. Pivacic and B. Cosovic.
“Water Absorption
Effects of PA 6 on DSC Measurements” by D. Spanicek and Z.
Smoljcic Zerdik.
“Standardization in the Fields of Plastics and
Rubber in Croatia” by I. Catic and D. Spanicek.
“Annealing
Process in Segmented Polyurethane” by V. Rek and E.
Govoric-Bajic.
“The Effect of Polymers in Formulations of
Engine Lubricant” by M. Orsic.
“Paraffin Wax-Polymer Blends”
by J. Jakopovic.
“Polymer Materials in Shipbuilding” by Z. Hell
and Z. Mršlic.
“Weathering of Polypropylene (PP) Fibers During
Usage” by E. Pezelj, R. Cancio and M. Andra。”
The Influence
of CaCO3-Filler on the Properties of Poly(Vinyl Acetate) Based
Polymers” by S. Lucic and V. Kovacevic.
“The Polymer
Painting Ground” by S. Horvat-Kurbegovic and D. Tarkal.
“Enzymatic Starch Hydrolysis Kinetics in Nutrition Media for
Oxysterolcycline Biosynthesis” by K. Mihaljevic, I. Markovic,
A. Stoj, and M. Halusek.

On Monday evening, February 6th, a very nice reception
was given which allowed the people to become acquainted. It
gave the participants, especially the foreign visitors the opportunity to
meet their Croatian colleagues and some of the many young
scientists and students who participated in the Symposium. A
banquet was held on Tuesday evening for the invited speakers
and a number of the key organizers and scientists of Croatia.

Zagreb as a City presented itself at its best with sunshine
during the entire meeting period. This allowed some of the
participants also to see the beautiful sights of this most
interesting city, the cultural center of this part of Europe.

Acknowledgements

We would like to thank Meifang Qin for her assistance during
the preparation of this manuscript.