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## XIth Symposium on Cationic Polymerization and Related Ionic Processes

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Conference Report

## XIth Symposium On Cationic Polymerization And Related Ionic Processes



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Over 110 scientists participated at the XIth Symposium on Cationic Polymerization and Related Ionic Processes which was held from July 5 to 8, 1993, in Borovets, Bulgaria. The Symposium was organized under the auspices of the Institute of Polymers of the Bulgarian Academy of Sciences and the IUPAC and was sponsored by the Bulgarian Academy of Sciences, the National Science Foundation of the U.S. and a number of industrial companies.

The meeting consisted of 27 invited lectures, 13 short communications and 24 communications which were presented in poster form. The chairman was Professor Ivan M. Panayotov and the Secretary was Dr. R. V. Berlinova, assisted by an International Scientific Committee. The Local Organizing and Program Committee was in the hands of Professor Christo B. Tsvetanov.

The meeting was opened by the Chairman of the meeting, Professor Panayotov, and by the Chairman of the Institute of Polymers, Professor Schopov. The greetings from the IUPAC was presented by Professor Pierre Sigwalt, a long-term active member of the Macromolecular Division of IUPAC.

Peter H. Plesch of New Castle, Staffordshire, U.K. discussed the "Development in Cationic Polymerization - a Personal View" which described the early discoveries and the discoverers of cationic polymerization from the early forties, when cationic polymerization was first properly recognized and the cocatalysis for Friedel-Craft catalysts was discovered - to few theoretical ideas which originated either in response to new facts, like pseudocationic polymerization and its relation to living polymerization.

Mitsuo Sawamoto of Kyoto, Japan presented his work of "The Nature of the Growing Species in Living Cationic Polymerization". He discussed the total analysis of growing ends by multinuclear NMR spectroscopy including proton, carbon, fluorine and tin NMR spectroscopy covering living and non-living polymers. The structures of the polymers obtained by this technique, involves initiation with tin tetrachloride with some phosphoric acids.

Stanislav Penczek, of Lodz, Poland, now of Paris, France discussed "Determination of Structure and Concentration of Active Species in Ionic Polymerizations - the <sup>31</sup>P Method". He showed that it is now possible by introducing phosphorous atoms as end groups and determine by <sup>31</sup>P NMR spectroscopy their structures and concentrations down to 10<sup>-6</sup> which allows this method to be used also for molecular weight determinations of rather large molecular weight polymers. (The <sup>31</sup>P NMR chemical shift changes with the degree of polymerization).



*Sofia, St. Alexander Nevski Cathedral*

Krzysztof Matyjaszewski of Pittsburgh, U.S.A. presented his work of "Salt and Solvent Effects in Living Cationic Polymerizations". Recent progress in cationic polymerizations of alkenes enables us to make well defined polymers, with control of molecular weight and functionalities. Salt and solvent effects play important roles in these polymerizations by shifting equilibria and by controlling the dynamics of the exchange reactions. The effects were particularly emphasized for the living polymerization of styrene,  $\alpha$ -methyl styrene and vinyl ethers.

"Studies of Ligand-Interactions with Ions and Ion Pairs" was the subject of the talk by Johannes Smid of Syracuse, NY, U.S.A. Ligands have been used to influence the course of ionic polymerization processes especially of anionic polymerizations for some time. It has now been shown that the techniques concentrating on chromophores can be utilized to probe ligand-ion and ligand-ion pair interactions.

"Active Center Structures in Anionic Polymerization" was the subject of Stanley Bywater of Ottawa, Canada. Spectroscopic determination of anionic active centers give valuable insight into polymerization mechanism. Use of  $^{13}\text{C}$  enriches models allowed to study concentrations down to the millimolar range. Aggregation has been demonstrated to occur at high concentrations; its effect on charge distribution could be measured.

A. A. Arest-Yakubovich of Moscow, Russia described the "Role of Bimetallic Active Centers in Anionic Polymerization of Hydrocarbon Monomers". The active centers of anionic polymerization of hydrocarbon monomers are normally considered individual metal-carbon bonds; a kind of insertion mechanism is concluded as the process of the polymerization reaction. Some kinetic and stereochemical processes can only be explained by simultaneous participation of two of more metals in



*Sofia, Bulgarian Academy of Sciences*



*Sofia, St. George Rotunda, (4th Century)*

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the complex active centers. These are two types of metals such as alkali metals and aluminum or zinc. Some bridging mechanisms have been proposed for the polymerization of these monomers.

"Influence of Magnesium Bromide on the Conductance and the Anionic Propagation of Dipolystyryl Magnesium in Tetrahydrofuran" by P. Jappens, M van Beylen and P. Huysken of Heverlee, Belgium was presented by Marcel van Beylen. Conductance measurements showed that in THF as the solvent the symmetrical distyryl magnesium salt  $(PSt)_2Mg$  is slightly dissociated in single ions. From these conductance measurements it can be concluded that the unsymmetrical salt is less dissociated than the symmetrical one and that the  $(PSt)_2Mg$  trip ion becomes progressively transformed to  $PStMgBr^-$  and  $PStMgBr^-$  ion upon further addition of  $MgBr_2$ , triple anions  $MgBr_3^-$  and aggregation of  $(PSt)_2Mg$  ion pairs being negligible. Polymerization under these conditions were chiefly ruled by the remaining free polystyryl anions.

R. P. Quirk of Akron, U.S.A. discussed "Anionic Synthesis of Chain-End and In-Chain Functionalized Polymers". Anionic polymerization produces living carbanionic polymers which react with a variety of electrophilic agents to form chain-end functionalized polymers. Non-homopolymerizable monomers and low ceiling temperature monomers provide a methodology for the synthesis of functionalized polymers via living copolymerization. The anionic system of in-chain, amine-functionalized polymers was described. The extension of this

methodology to other living polymerizations was illustrated with examples of the use of low ceiling temperature monomers in group transfer polymerization.

The Tuesday morning session was opened by a lecture on "Stereoregular and Conformationally Regular Oligomers and Polymers" by O. Vogl, J. Bartus, K. Ute and K. Hatada. The talk was presented by Otto Vogl of Brooklyn, NY, U.S.A. For a long time it was believed that the regularity of a stereoregular polymer depended exclusively on the coordination of the end of the growing polymer chain with the incoming monomer guided by very specific interactions with a coordination initiating system. As more information was obtained it became clear that the side group size of the monomer became the predominating factor for the configurational and conformational specificity of the polymer chain. With larger side group size, the polymer conformation became locked in a rigid helical conformation. Specific examples were described with polychloral as the example.

"Synthetic Strategies to Well-Defined Polymers by Ionic Polymerization" was the subject of R. Faust of Lowell, MA, U.S.A. During the past decade considerable advances have been made in carbocationic polymerization toward the synthesis of well-defined polymers. Living cationic polymerization and sequential copolymerization of isobutylene and styrene has been achieved. Poly(methyl methacrylate)-*g*-polyisobutylene graft copolymers have been prepared by the combination of living cationic and group transfer polymerization with an initiator-coinitiator pair leading to counterions strongly interacting with the growing center. The modulation of the ionicity of the growing species by the addition of a Lewis base or by salt have given new impetus to the understanding of living polymerization of such monomers as vinyl ethers, isobutylene, styrene and styrene derivatives.



Sofia, The Russian Church



Sofia, Mosque



**St. Petra from Epivat Church (15 Century)**



**Rila Mountains, Borovets**

A very interesting talk was presented by J. P. Vairon of Paris, France. The title was "The Ionic Polymerization of Methyl Glyoxalate" coauthored by J. P. Vairon, E. Muller and C. Bunel. Methyl Glyoxalate can be polymerized in methylenechloride solution either cationically or anionically to the corresponding polyacetal. The polymerization has a ceiling temperature of 26°C and the polymer has a glass transition temperature of 37°C. Stop flow techniques have been used to follow the polymerization.

P. Kubisa of Lodz, Poland presented his work on "Vinyl and Ring-opening Cationic Polymerization Leading to Ionic Networks". The presence of ions in polymers is an additional structural parameters available for modification of macromolecular systems through aggregation of ionic groups. Well known are ionomers where the ionic groups are statistically distributed along the polymer chains. Less studied are polymers having ionic groups located specifically at the chain ends. Cationic polymerization provides a convenient route for the synthesis of polymers terminated at both ends with stable ionic groups. The synthesis method based on termination of bifunctional living polymers with suitable capping agents such as tertiary amines or phosphines or employing bifunctional chain transfer agents with the subsequent transformation of the appropriate end group was described.

The afternoon session was opened with a talk by Ph. Hubert, A. Soum, M. Fontanille and T. E. Hogen-Esch on "Kinetics and Mechanism of Syndiospecific Polymerization of 2-Vinylpyridine". The paper was presented by M. Fontanille of Talence, France. The living anionic polymerization of methyl methacrylate proceeds with a syndiotactic placement when the polymerization was performed by alkyl lithium/trialkylaluminum in nonpolar solvents. A similar behavior was observed when 2-vinyl pyridine was polymerized under similar conditions. The authors concluded that the syndiotactic placement which is favored under these conditions involved the hindrance of the active centers which favored the syndiotactic placement.

A most interesting talk was presented by K. Hatada of Osaka, Japan; it was entitled "Preparation of Isotactic and Syndiotactic

Poly(methyl methacrylate)s without Molecular Weight Distribution and their Properties". Synthetic polymers usually have distribution of molecular weight; the properties of the polymers are always described having average values. Hatada's group has synthesized highly isotactic and syndiotactic methyl methacrylate polymers of narrow molecular weight distribution using methods that had been developed in Hatada's laboratory. The polymer mixtures were subjected to supercritical fluid chromatography using liquified carbon dioxide as the mobile phase and methanol or ethanol as the modifier on silica gel. Individual fractions of oligomers could be obtained up to a DP of 100. The 100 mer stereospecific with a molecular weight of 10,000 was isolated and characterized. Hatada also discussed the stereocomplex formation of these uniform polymers of isotactic and syndiotactic poly(methyl methacrylate) of uniform molecular weight, uniform because they have characteristics typical for proteins, nucleic acids and enzymes.

The next talk was presented by Thico E. Hogen-Esch of Los Angeles, CA, U.S.A. on "Synthesis and Characterization of Macrocylic Block Copolymers". The formation of monodisperse macrocylic block copolymers was indicated by the lower (15-30%) hydrodynamic value of the rings compared to that of the linear block copolymers. The preparation of polystyrene-*b*-poly(2-vinyl-pyridine) and polystyrene-*b*-polydimethylsiloxane was carried out by initiation of polystyrene with lithium naphthalide followed by addition of 2-vinylpyridine or hexamethyl cyclotrisiloxane (D3). The polymers were terminated, or coupled with bromomethylbenzene or dimethyldichlorosilane.

V. N. Sgonnik of St. Petersburg, Russia described the "Anionic Polymerization of Non-Polar Monomers by Organolithium Compounds". The influence of the solvent nature, the concentration of the living chains and monomers on the microstructure of the polymer formed, the rate and the dependence of the reaction order with respect to initiator and living chains were discussed. Stoichiometry of living chain complexes with electron donors and the interpretation of the experimental results related to this complexation reflects on the parameters of the monomers and polymers of dienes and styrenes. The interpretation of the experimental results were related to this complexation, mixed- and homogeneous associates of the living chains and the initiating systems.

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"Controlled Copolymer Structures via Anionic/Insertion Polymerization of Cyclic Carbonates" was presented by H. Hoecker of Aachen, Germany. Cyclic carbonates were polymerized by ring-opening fashion by means of anionic and insertion type of initiators. Different hexacyclic carbonates were randomly copolymerized when both monomers were added simultaneously to the initiator. Block copolymers were obtained when the monomers were added in a sequential way. Various procedures were used for the preparation of copolymers with lactams. The polycarbonate was first formed and lactams and lactones were then inserted into the carbonate bond to form urethane and ester bonds. Eventually alternating polyesterurethane bonds are formed.

The Wednesday morning session was opened by a talk of Emile Franta of Strasbourg, France. The title was "Functionalization of poly(1,3-dioxolane)" by E. Franta, P. Lutz and L. Reibel and of M. Belbachir, N. Sahli and S. Ould Kada of Oran, Algeria. It was found possible to prepare poly(1,3-dioxolane) of controlled molecular weight. It has also possible to use these hydroxy-terminated poly(1,3-dioxolane)s of a molecular weight range of 1,000 to 20,000 to form networks with polyisocyanates. Often metalated  $\alpha,\omega$ -dihydroxylated poly(1,3-dioxolanes) had to be used to carry out the reaction in a quantitative way.

"Block and Graft Copolymers of Oxazolines" was presented by R. C. Schulz of Mainz, Germany in cooperation with A. Dworak of Gliwice, Poland. The cationic ring-opening polymerization of 2-oxazolines was further studied. Chloroformates, prepared from alcohols and phosgene were

found to be exceptionally good initiators. This type of initiator allowed the preparation of two-block, three-block and graft copolymers as well as star shaped polymers.

"Tailor-Made Polymers and Copolymers from Aziridines and 1,3-Oxacyclanes" was the subject of the talk of R. S. Velichkova of Sofia, Bulgaria. This work was done in cooperation with D. C. Christova and V. B. Gancheva. Telechelic poly(tertiary-butyl aziridines and 1,3,6-trioxocane)s as well as their macromonomers were synthesized by living cationic techniques. These polymers were studied for their molecular weight and end-functionality distribution. Various tailor-made polymers based on uniform size telechelics and macromonomers were prepared.

"Some New Developments in Vinyl ether Polymerization" was presented by E. J. Goethals of Ghent, Belgium. The work was done in cooperation with Li-Bing Peng and N. Haucourt. Two aspects of the polymerization of vinyl ethers were reported. The first is the use of acetals in initiation and transfer reactions of the polymerization. The second described the use of polymerizable cyclic sulfides as carbenium ion stabilizers in the acid/sulfide initiated polymerization. Particularly studied were the acetals in vinyl polymerization and the polymerizable cyclic sulfides as carbenium ion stabilizers.

Y. Yagci of Istanbul, Turkey, presented the work on "Direct and Sensitized Photoinitiated Cationic Polymerization using Pyridinium Salts". The work was done in cooperation with W. Schnabel of Berlin, Germany. Certain N-alkoxy pyridinium and N-alkoxyquinolinium salts were found to be capable as photoinitiators for the cationic polymerization of cyclic ethers such as cyclohexene oxide and vinyl ethers such as n-butyl vinyl ether. Flash photolysis studies revealed that reactive nitrogen-centered radical cations were formed upon direct irradiation of these salts.

"New Living Cationic Polymerization Systems: Effect of Electron Donors and Salts on Inifer Mechanism" was the subject of the talk by M. Zsuga of Debrecen, Hungary, in cooperation with Gy. Deak and T. Kelen. The possibility of improving the living character of carbocationic systems is based on both externally added Lewis base or of the use of common ion effect to shift the Winstein spectrum of ionicities toward nonionic species. This way optimum conditions for living polymerization of isobutylene could be defined. Technological aspects of producing larger quantities of telechelics were also discussed.

The Thursday session started with a talk by S. K. Ying of Shanghai, China of "Some Aspects of the Anionic Copolymerization". The author discussed the relationship of ideal copolymerization and the nature of the active species in anionic polymerizations. Various aspects were also studied by NMR spectroscopy. The kinetics and the mechanism of anionic equilibrium copolymerization of  $\alpha$ -methylstyrene - butadiene and  $\alpha$ -methylstyrene - styrene were also investigated.

"Synthesis of Star-Branched Oligomers by Reaction of Oligobutadienyl Lithium with Diesters and Epoxidized Soja Oil" by F. Schue, J. Couve, R. Dobrev, J. Sledz and P. Nicol was presented by F. Schue of Montpellier, France. The polymerization of well defined forms of branching has posed a challenge to polymer chemistry for many years. Anionic polymerization can produce branches with low and narrow molecular weight distribution. By reacting an oligobutadienyllithium with a diester (dimethyl adipate, diethyl adipate, dimethyl phthalate) it is possible according to the ratio



Excursion to World Famous Boyana Church (8th Century)

of the living species to the reacting species, to obtain diketones corresponding to a degree of coupling of 2 or a mixture of the ketone and a tertiary alcohol (degree of coupling larger than 2). The reaction with an epoxidized soja oil produces a very rapid cleavage of the ester group, following by a slower rate of addition onto the epoxide group.

The last paper of the Symposium was by Rugang Zhuang and A. H. E. Muller of Mainz, Germany. It was entitled "Kinetics of Group Transfer Polymerization of n-Butyl Acrylate Catalyzed by Hg/Me<sub>2</sub>Si". Group Transfer Polymerization of n-butyl acrylate was carried out at room temperature in toluene with 1-methoxy-1-(trimethylsilyloxy)-2-methyl-1-propene as the initiator and with mercuric iodide as the catalyst. Molecular weight control was good and the polymer had narrow molecular weight distribution although a slight cyclization reaction leading to some termination of the living polymer chains was observed. The results were explained by exothermic formation by a 1:1 complex of trimethylsilyl iodide and mercuric iodide. The complex seems to work as a nucleophilic catalyst. A similar behavior was found in dichloromethane as the solvent although the rates were two orders of magnitude higher.

In addition to the invited papers the following short communications were presented: "Mechanism of Initiation in the System 2-Methylpropene-Ferric chloride in Non-polar Media"; "Living Polymerization of 2-Methylpropene without External Electron Donors"; "Kinetic Model for Active Chain-End Decomposition and Comparison with Real Living Carbocationic Polymerization Systems"; "Living Anionic-Coordination and Radical Polymerization of Alkenes with Organoaluminum Initiating Systems"; "The Nature of End-groups in the Polymerization of 2-Methylpropene Initiated by Di(1-azido-1-methylethyl)-1,4-benzene/Lewis Acid/dichloromethane Systems"; "The 'Flash' Polymerization of Styrene"; "Cationic Polymerization in Iodine/Liquid Sulfur Dioxide System"; "Control of the Kinetics of the Polymerization of Indene, an Approach to a Living System"; "Anionic Polymerization of Acrylic Esters by Complex Initiators"; "Living Anionic Polymerization of (Meth)Acrylates by Means of Ligated Processes"; "Poly(styrene-g-ethylene oxide) Through Anionic Graft Copolymerization of Ethylene Oxide"; "The Role of Complexation in Carbocationic Polymerization of Isobutylene in Lewis Acid/Ester Systems" and "Cationic Polymerization of Glycidol".



Samokov Hotel, Borovets



Registration

The XIth Cationic Symposium of the Bulgarian Academy of Sciences, Borovets, hosted by the Institute of Polymers was considered by the participants as a great success because the scientific discussions were of excellent quality. On Sunday night was a reception at the Hotel Samokov which brought together the scientists who had come from all over the world to this meeting, some of them brought their wives. This meeting brought together a world community of scientists interested in cationic polymerization and other ionic processes but was an even more important personal reunion of old and new scientific friends. On Wednesday there was an excursion to the world famous Rila Monastery which is one of the world's most renowned sightseeing places. During the week, excursions were also held to Plovdiv, a very ancient town about 100 km from Borovets.

Borovets is located at 1,350 m in the central mountain chain that crosses much of Bulgaria. A gondola took participant of the conference up to a 2,300 m elevation, which gave a beautiful panorama over the landscape of this region with the highest peaks of nearly 3,000 m of the Balkan peninsula.

The banquet was held on Tuesday evening, again to provide a forum for more scientific talks in a most congenial atmosphere among the scientists.

As it is tradition in those meetings, a steering committee met under the chairmanship of O. Vogl to decide on future meeting of cationic polymerization and related ionic processes. The 12th Symposium on Cationic Polymerization and Related Ionic Processes was given to Professor Yusuf Jagci, of the University of Istanbul, Istanbul, Turkey. The meeting will probably be held in September 1995.

A major deviation occurred also during this meeting. It was decided that the next meeting after Istanbul will be in Paris under the general chairmanship of Professors Pierre Sigwalt and Jean-Pierre Vairon. There was an essentially unanimous decision that this meeting should be organized somewhat differently from previous cationic meetings. Over the years the Symposia which had first been called "Cationic Polymerization" and then "Cationic Polymerization and Related Ionic Processes" have now

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*Welcoming Reception*

progressed into meetings where the cationic polymerization aspect is now less than 50% of the overall contributions of the meetings in addition to anionic contributions and contributions to "and related ionic processes". The committee concluded that it would only be practical to recognize this reality. The meeting in Paris will be called the meeting on "Ionic Polymerization". This decision made those scientists involved primarily in anionic polymerization very happy and this unifying concept was accepted



*At the banquet*

enthusiastically by the entire "ionic" community including those primarily interested in "ring-opening" polymerization.

Based on the decision of the committee which included also the leading members of the community of Anionic Polymerization and of Ring-Opening Polymerization, it appears that from 1997, the meeting in Paris, there will only be one meeting on "Ionic Polymerization", rather than three meetings that are now in existence, Cationic, Ring-Opening and Anionic Polymerization. It is believed that such a meeting will bring closer together scientists working in these areas and will benefit the progress of the entire field of "Ionic Polymerization" by a more active interaction of the scientists that are active in the forefront of these developments.