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## Tenth International Symposium on Cationic Polymerization and Related Processes

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Conference Reports

# Tenth International Symposium on "Cationic Polymerizations and Related Ionic Processes"



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The Tenth International Symposium on Cationic Polymerization and Related Processes was held from August 26-29, 1991 in Balatonfüred, Hungary. The Symposium was organized under the auspices of the Kossuth Lajos University of Debrecen, the Debrecen Group of the Hungarian Academy of Sciences, the National Committee for Technical Development of Hungary, the National Science Foundation of the U.S.A. and several companies. The meeting was chaired by Professors Tibor Kelen and Ferenc Tudos with Dr. Miklos Zsuga acting as secretary.

The conference was opened by the Chairman, Professor Tibor Kelen, Dr. Frigyes Geleji, vice-president, National Committee for the National Committee of the Hungarian Government, and Professor Gyorgy Bazsa, prorector of the Kossuth Lajos University of Debrecen. The meeting consisted of 28 invited lectures, 19 short communications and 18 communications which were presented in

poster form. It was attended by more than 120 participants and was held at the Hotel Fured in the town of Balatonfüred. The last Cationic Symposium was held in Strasbourg, France in June of 1989, with Professor Paul Rempp as Chairman. The previous Cationic Symposium was held in Munich, Germany in 1986; Professor Oskar Nuyken was the Chairman.

The 10th Cationic Symposium opened with a lecture by Joseph P. Kennedy of Akron entitled "Tailored Macromolecules by Living Carbocationic Techniques." The most significant advance that has occurred in the last decade in the field of cationic polymerization is undoubtedly the discovery and follow-up development of living cationic polymerization, specifically the discovery of living isobutylene polymerization in 1984. The early developments concerned tertiary esters and ether/boron trichloride combinations as initiating systems and, principally, isobutylene as the monomer. A large amount of systematic follow-up research led to a number of titanium tetrachloride based living initiating systems. The latter, particularly in the presence of certain electron-donors such as esters, amides and amines, yielded new well-defined polyisobutylenes and polystyrenes. More recently the focus shifted to the preparation of new and useful block copolymers and networks.

Peter H. Plesch of Keele, England discussed "Cationoid Living Polymerizations." The cationoid polymerizations consisted of two well defined subcategories: a.) Cationic polymerization in which the propagating species is an organic cation and b.) pseudo-cationic polymerization in which an alkene is inserted between the positive C-atom and a negative hetero-atom of a polar bond at the growing end of a polymer chain. The living cationoid polymerizations have the characteristics of pseudo-cationic polymerization and show none of the features of cationic polymerizations; therefore they are pseudo-cationic. This realization provides a useful basis from which numerous questions arising from the recently accumulated plethora of information on living type polymerization can be



Miklós Zsuga, Secretary, and Tibor Kelen, Chairman, of the symposium.





The Hotel Füred, Balatonfüred, Hungary, the site of the symposium.

approached. Answers to these questions were examined critically.

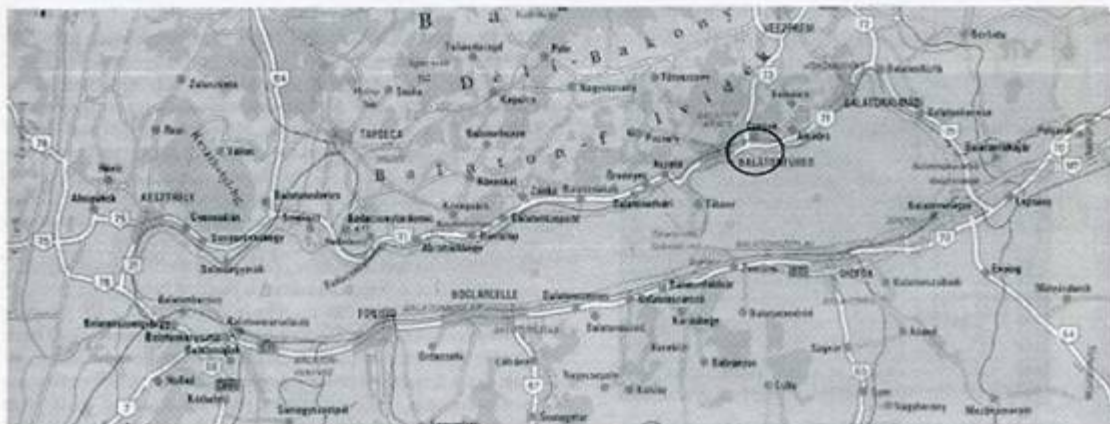
"Effect of the Mixture Tertiary-Butyl Chloride/Stannic Chloride on the Cationic Polymerization of Isobutylene" was discussed by Ludek Tomann and Rudolf Lukas of Prague. In the polymerization of isobutylene, carried out in the presence of stannic chloride, aliphatic chlorides with a chlorine atom bound at the tertiary carbon atom are generally regarded as non-reactive. It was, however, found that tertiary-butyl chloride combined with stannic chloride effects the cationic polymerization of isobutylene. The investigation of the effect of tertiary-butyl chloride on the polymerization of isobutylene carried out in dichloromethane was analysed. It was found that isobutylene of a molecular weight of about 2,000 was formed with a monomodal molecular weight distribution with a polydispersity of 2.5. In the presence of tertiary-butyl chloride, a polymer with a bimodal molecular weight distribution was ob-

served indicating the existence of two characteristic polymer fractions. With increasing concentration of tertiary-butyl chloride the number average molecular weight remains unchanged. Only the weight ratio of both fractions changed.

Mitsuo Sawamoto and T. Higashimura of Kyoto discussed "Living Cationic Polymerization of Vinyl Ethers and Styrene Derivatives: Design of Initiating Systems and Controlled Polymer Synthesis". Sawamoto discussed particularly: a) Initiating systems based on hydrogen chloride ( $\text{HCl}/\text{MXn}$ ) and b.) Amphiphilic multi-armed polymers. In the first examples, in addition to hydrogen iodide, trifluoroacetic acid and other protonic acid, hydrogen chloride was also capable of initiating living cationic polymerization of vinyl ethers in toluene at  $0^\circ\text{C}$  in the presence of Lewis acid activators such as zinc chloride and stannic chloride. Depending on the Lewis acidity of the metal chloride, living polymers could be obtained in the case of a hydrogen chloride/stannic chloride system when an excess of 1,4-dioxane as a cation-stabilizing base was used. In the second case, a series of multi-armed amphiphilic polymers of vinyl ethers have been synthesized where a hydrophilic polyalcohol chain can be placed either in the inner or the outer segment. The syntheses are based either on sequential living polymerization with a multi-functional initiator or on a linking reaction of a living block polymer with a bifunctional vinyl ether (3-60 arms per molecule).

O. Nuyken, G. Maier, M.B. Leitner and D. Yang of Bayreuth presented their work on "Polymers with Indane Units by Cationic Polymerization: Cationic polymerization of 1,4-2-Diisopropenylbenzene to Soluble Polymers". The mechanism of the formation of these polyindanes which exhibit high glass transition temperature and very high decomposition temperatures was discussed.

St. Penczek of Lodz presented his work on "The Carbenium-Oxonium Equilibria in Cationic Polymerization." In both ring-opening and vinyl cationic polymerization, the carbenium-oxonium equilibria can be involved in the interconversion of the reactive species. Both or only one of the species might contribute to the actual propagation of the polymerization. Equilibria and their equilibrium constants could be determined and the distribution of



A geographical map of Lake Balaton, Hungary (site of meeting circled).



The scenic view of Lake Balaton.

the carbenium and oxonium ions in the chain growth of cyclic acetals was finally established. Surprisingly the carbenium ions are only 100 times more reactive at  $-78^{\circ}\text{C}$  than their oxonium counterparts. These findings have been used in analyzing the roles played by ligands in the polymerization of vinyl ethers. The nucleophilic centers are then located in both monomer molecules and polymer repeating units when external ligands are not added.

Jean-Pierre Vairon of Paris discussed "The Stability of Carbocationic Species in the Polymerization of Styrene and Homologues." Fundamental aspects of cationic polymerization have advanced rapidly. The major problem concerning the polymerization of ethylenic monomers still remains the identification of the active species and the determination of their concentrations. Vinyl aromatics with UV absorbing cations were investigated by stopped-flow methods. The presence of low concentrations of large acid aggregates was observed, the reactivity of which increased with size.

Krzysztof Matyjaszewski of Pittsburgh presented his work on "Carbenium Ions, Onium Ions and Covalent Species in the Cationic Polymerization of Alkenes." Rate constants for the addition of carbenium ions to alkenes are very high. The monomer is very rapidly consumed in polymerizations proceeding exclusively in the presence of carbenium ions. Contributions of undesired transfer and termination processes increases strongly after the monomer conversion was completed. Few systems are known in which carbenium ions coexist with onium ions and covalent species. Other problems have to be considered, such as deactivation of salts

with complex anions which reversibly decompose and accelerate the exchange between active and dormant species, or termination reactivation by nucleophiles to form inactive onium ions.

"Mechanism and Kinetics of the Ring Opening Polymerization of 1,5-Dioxepan-2-One" was presented by Ann Christine Albertsson and Ronnie Palmgren of Stockholm. The polymerization of 1,5-dioxepan-2-one gives polymers whose interesting characteristics are due to the hydrolytical degradability and in vivo absorption of the materials. The polymers resemble the human tissue with respect to tensile strength and elasticity. Ring opening apparently proceeded by acyl cleavage; cross linked degradable elastomers with interesting properties for drug release applications have been synthesized.

"Cationic Polymerization of Cyclocarbonates" was discussed by H.R. Kricheldorf, J. Janssen and B. Weegen-Schulz of Hamburg. The cationic polymerization of cyclocarbonates is limited to six and higher membered aliphatic cyclocarbonates. It is initiated by protons, carbenium ions and strong Lewis acids. The chain growth proceeds by alkylation of the carbonyl oxygen and cleavage of the alkyl-oxygen bond in analogy to the cationic polymerization of lactones. Weak and strong Lewis acids form complexes with cyclocarbonates that mainly involve the carbonyl oxygen. However, weak Lewis acids initiate an insertion mechanism for this polymerization which involves cleavage of the acyl-oxygen bonds and yielded polycarbonates free of ether groups.

Y. Yagci of Istanbul presented his work on "New Aspects on the Photo Initiated Free Radical-Promoted Cationic Polymerization". Free radical promoted cationic polymerization of vinyl heterocyclic monomers has been the object of considerable investigation. Absorption sensitivity of photo-initiators such as diaryl iodonium salts extended to longer wave lengths of mercury lamps and provided substantial emission. Photo initiation of cationic polymerization was carried out via oxidation of electron-donor radicals which formed upon irradiation of the onium salts. Efficient photodegradation of polysilanes suggested that these polymers were useful as free radical sources that ultimately promoted cationic polymerization.

E. Franta, P. Kubisa, S. Ould-Kada and L. Reibel of Strasbourg discussed "The Polymerization of Cyclic Acetal Via Cationic Processes." Classical initiation induces polymerization through cyclic tertiary oxonium ions. The activated monomer mechanism, the polymerization in the presence of a diol, has been successfully studied in cases of some substituted oxiranes such as epichlorohydrin and propylene oxide. Transacetalization led to complications at the onset of the reaction in the case of the attempted preparation



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## Conference Reports



F. Tüdös, Z. Jedlinski, A.C. Albertsson and H. Tüdös in a Csarda, Hungarian Wine House.

of triblock copolymers. When *p*-isopropenylbenzyl alcohol was used it was possible to prepare macromonomers.

"Reactive Oligomers by Addition of Oxiranes to Phosphoric Acid, Kinetics and Stereochemistry" was presented by Przemysław Kubisa and Tadeusz Piela of Lodz. Addition of oxiranes to the phosphorus or phosphoric acid leads to phosphorous containing di- or tri-functional hydroxyl terminated oligomers. The reaction was catalyzed by acids in the presence of "external" catalysts; in the case of tetrafluoroboric acid longer polymer chains are formed. The stereochemistry of addition of unsymmetrically substituted oxiranes was also studied. The direction of the ring opening at each step was established and related to both steric and electronic factors.

A. Gandini of Grenoble discussed "Furan Chemistry and Ionic Polymerization: A Novel Approach to Original Structures." The peculiarity of furan chemistry has been exploited to conduct oligomerizations and polymerizations in electrophilic and nucleophilic media in order to prepare specific structures. One of the studies was concerned with the origin of branching and finally crosslinking in the acid catalyzed polymerization of furfuryl alcohol. The synthesis of functional oligomers and block copolymers by cationic polymerization of conventional monomers in the presence of furane derivatives was also investigated.

B.A. Rozenberg of Moscow presented "Cationic Polymerization of Caprolactone in the Presence of Diols Via the Activated Monomer Mechanism." The kinetics of noncatalytic and catalytic interaction of caprolactone with a variety of diols in the presence of onium type catalysts as well as the structure of the resulting polymers were investigated. It was shown that oligocaprolactone with two hydroxyl end groups was formed.

"Structure, Stereochemistry and Conformation of Oligomers in Stereospecific Ionic Polymerization" was discussed by O. Vogl of New York. This work was done in collaboration with C. Kratky, C. Garner, W.J. Simonsick Jr. and K. Hatada. The oligomerization and the establishment of the structure of individual oligomers was found to be of great help for the understanding of the respective polymerization. It allowed the authors to draw conclusions as to how stereospecificity and (in some cases) even conformational specificity developed in polymerization that lead to stereoregular isotactic polymers. The embryonic state of the anionic oligomerization of three trihaloacetaldehydes, fluoral, chloral, bromal as well as the anionic oligomerization of methyl methacrylate was

studied. Achiral and chiral initiators were used for the oligomerization of the trihaloacetaldehydes followed by acetate end-capping. The oligomers were analyzed by GC, K+IDS mass spectrometry and NMR spectroscopy. Single crystal investigations of individual crystalline stereoisomers established their absolute configuration. The stereochemistry of the addition of the first monomer unit with the initiator used is random. Oligomers from the dimer to the octamer were separated on a chiral column into left handed and right handed helices which do not racemize by helix reversal. Bromal oligomerization was also successfully carried out. Oligomerization of methyl methacrylate and trihaloacetaldehydes gave a rich data base for the understanding of stereospecificity and in some cases conformational specificity necessary for the formation of helical isotactic polymers.

P. Rempp of Strasbourg discussed the "Synthesis of Model Macromolecules via Ionic Polymerization." Tailor-made macromolecules have attracted increasing interest; ionic living methods are among the most efficient ways to synthesize model macromolecules of various types. They include: a) functional polymers including macromonomers; b) cyclic polymers; c) star shaped polymer with "arm-first" and "core-first" techniques; d) block copolymers; e) star block copolymers and f) end-linking reactions.

"The Role of N-Acylactam in Ionic Lactam Polymerization" was discussed by R. Puffr, J. Stehlicek and J. Sebens of Prague. Solvolytic cleavages of the N-acylamide group proceed much faster than that of the amide group. The rates of acid and base catalyzed aminolysis and transacylations of model amides and imides were compared. In anionic polymerization of the N-acyllactam groups represent the centers of chain propagation which proceed by acylation of the lactam N-anion. In cationic polymerization of N-acyllactams, the propagation rate is several orders higher than that of the unsubstituted lactam. The copolymerization can be carried out even at low temperatures using carbenium initiators.

Z. Jedlinski of Zabrze presented his work on "Novel Ring-Opening Polymerization Induced by Alkali Metal Ions." Polyactones present useful types of polymeric materials exhibiting many interesting properties such as biodegradability and biocompatibility. Novel initiators for lactone polymerization involving sodium and potassium complexes with crown ethers have recently been investigated. The advantages of using alkali metal anions as initiators is that the result is very fast initiation and uncommon "living" type polymerization. The synthesis of several block polymers was accomplished using these initiating systems as well as using potassium/naphthalenide crown ether complexes.

"Anionic Polymerization of Styryl Bismuth Monomers" was presented by F. Ignatious, Y. Dalabiz, I. Cabasso and J. Smid of Syracuse, NY. Extensive application of plastics in dentistry and medical devices make radiopacity a highly desirable property for polymers. It permits the utilization of radiography as a nondestructive diagnostic tool for plastics. Most x-ray contrast additives such as barium or bismuth salts are incompatible with most common polymers. Triphenylbismuth is, however, biocompatible and provides an x-ray contrast additive miscible in large amounts with a wide range of polymers including polyacrylates, polystyrene, poly(vinyl chloride) and polyalkenes. Styryl and alpha-methylstyryl-diphenylbismuth were synthesized and polymerized.

K.S. Kuzanskii of St. Petersburg discussed "Functionalization During Anionic Polymerization of Heterocycles." The synthesis of nitroaromatic derivatives of poly(ethylene oxide) were prepared.



By alternative reactions of endgroups of commercial poly(ethylene glycol)-methyl methacrylate macromonomers and beta-propiolactone were synthesized and polymerized with functional initiators.

D. Pepper of Dublin discussed "Kinetics and Mechanisms of the Ionic Polymerization of Alkyl Cyanoacrylates." The polymerization of butyl and ethyl cyanoacrylate has been carried out from the point of view of general characteristics, initiating systems, initiation mechanism and overall kinetics. The overall kinetics approximate the classical "living anionic polymerization."

"Active Center Structures and the Stereoregulation Process of Anionic Polymerization" was presented by S. Bywater of Ottawa. <sup>13</sup>C NMR spectroscopy is an important tool for the study of active centers in anionic polymerization; low molecular models have to be used for higher concentrations. The polymerization of dienes was particularly investigated; it was found that the anionic polymerization produced mixed structures consisting of both cis and trans olefin structures in the polymers.

Owen W. Webster of the Du Pont Company, Wilmington, Delaware, presented his work on "A Comparison of Group Transfer and Anionic Polymerization of Acrylic Monomers." Large counterions as well as Lewis acid additives stabilize living polymerization of acrylates under ambient conditions. Trimethylsilyl capped enolates under nucleophilic catalysis provide a stable system for living polymerization of methacrylates. A mechanism for group transfer polymerization which accommodates data from a number of systems also takes into account the non-exchange of living end groups.

T.E. Hogen-Esch of Los Angeles discussed "Recent Developments on the Stereochemistry of Anionic Polymerization of Polar Vinyl Monomers." A recent resurgence of interest in the effect of complexing agents on the stereo-control of anionic vinyl polymerization, such as the presence of triethylaluminum or lithium alkoxide in the polymerization of methyl methacrylate, styrene and 2-vinylpyridene has been shown to lead to syndiotactic or isotactic polymers depending on the system. The dramatic increase in isotactic content of 2-vinylpyridene on an addition of one equivalent of lithium alkoxide to a polymerization mixture, as exemplified by tertiary butyl lithium/2-vinylpyridine system clearly demonstrated the occurrence of a 1:1 carbanion/lithium alkoxide complex. The nature of the alkoxy group has been shown to be of great importance in stereochemical controls. Tertiary alkoxides are shown to be generally superior to secondary and primary lithium alkoxide.

"Solvating Agents in Anionic Polymerization" were discussed by C.B. Tsvetanov, K.D. Dimov and E.B. Petrova of Sofia. Anionic polymerizations are strongly effected by additives with electron donor or electron acceptor properties. In the presence of solvating additives, the nature of the propagating species is changed due to the influence of association and anionic equilibria. The results of the influence of solvating agents of electron donor and electron acceptor capacity was reviewed.

"The Role of Associations/Complexation Equilibria in the Anionic Polymerization of (Meth)Acrylates" was presented by A.H.E. Muller of Mainz. Association equilibria governs the anionic polymerization of non-polar monomers such as styrene in non-polar solvents. A very small fraction of the non-associated ion pair is responsible for the propagation reaction. In polar solvents contact and solvent separated ion pairs as well as free ions are favored. Polar monomers such as acrylic monomers in polar

solvents associated and non-associated ion pairs coexist in comparable amounts (with some additional contributions from free anions). The position of the association equilibrium governs the kinetics of polymerization while its dynamics is responsible for the molecular weight distribution of the resulting polymers. Important complex forming additives are cryptands, alkali alkoxides and alkali halides which seem to break up associates by forming various complexes.

Other interesting contributions were given as oral presentations and included: "Polymers Containing Pseudo-Halide Groups by Cationic Polymerization," "Nature of Active Species and Reaction Mechanism of the Living Cationic Polymerization of Vinyl Ethers Initiated by Hydrogen Halides/Lewis Acid Systems," "Application of Chloroformate to Initiation of Oxazoline Polymerization," "Living Carbocationic Polymerization of Isobutylene with Blocked Bifunctional Initiators in the Presence of Proton Traps" and "Telechelic Polyisobutylene Based Amphiphilic Networks."

Of particular interest were papers on: "alpha-Halogenated Carboxylic Acids and their Corresponding Zinc Salts in the Living Polymerization of Isobutyl Vinyl Ether," "Synthesis, Characterization and Properties of a New Thermoplastic Elastomer," "Chain Carriers in Living Isobutylene Polymerization," "Transition from 'Conventional' to Apparently 'Living' Cationic Systems in the Polymerization of Indene," "Kinetics of the Anionic Polymerization of Lactones," "Cationic Interfacial Polymerization on Silica Surface" and "The Synthesis and Reactions of Uniform Size Telechelic Polymers via Ionic Processes."

Other presentations were concerned with "Anionic Polymerization of One-Ended Living Polystyrene with Calcium as the Counterion in Tetrahydrofuran," "Macromonomers and Telechelics via Cationic Polymerization of Heterocycles," "Anionic Polymerization of 2-Ethylhexyl Acrylate Initiated by Complex Base Lithium Esterenolate/Lithium Tertiary Butoxide," "Synthesis of Anhydride Telechelic Polyisobutylene," "Effect of the Initiator on the Cationic Oligomerization of Isoprene" and the "Polymerization with Reversible Aggregation of the Active Species."

The 10th Symposium on Cationic Polymerization was very successful. Excellent work was presented, and a pleasant group of people had decided to meet on Lake Balaton in Balatonfüred, one of the most important places on the lake. Lake Balaton and its surroundings are one of the most interesting tourist centers in Central Europe. The Balaton region comprises one of the oldest inhabited parts of Europe; it was already inhabited in the Stone Age and remnants of housing settlements and earth works from the Roman Age to the ruins of Roman buildings have been found. The Balaton is the largest lake in central Europe and is visited by many throughout the year. The participants of the 10th Cationic Symposium enjoyed the congenial atmosphere and the typical Hungarian hospitality, an important catalyst for the accomplishments of this most interesting and successful conference. The organizers and the entire team from the University of Debrecen are to be congratulated.

The next cationic meeting, the 11th Symposium on "Cationic Polymerization and Related Ionic Processes," is planned for Bulgaria with Professor Ivan Panayotov as the chairman. Interest has been expressed in combining, sometime in the future, the Symposium of Cationic Polymerization with the symposium on Ring-Opening Polymerization and the newly created Symposium on Anionic Polymerization to a joint and singular Symposium on "Ionic Polymerization."