International Symposium on Ionic Polymerization, Istanbul, Turkey

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**Conference Report**

**International Symposium on Ionic Polymerization, Istanbul**

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The meeting was held at the Macka Campus of the Istanbul Technical University. It was attended by about 100 people from Turkey and abroad including participants from 22 countries. During the Symposium 68 invited and contributed papers were presented and 50 papers were presented in poster form.

The Symposium was opened by Professor Yusuf Yagci of the Technical University, the Chairman of the Conference.

The conference participants were then addressed by the President (Rector) of the Istanbul Technical University, Professor Resat Baykal. In his opening address Dr. Baykal said:

It gives me great pleasure to welcome the esteemed participants and guests of the International Symposium on Ionic Polymerization being conducted September 4–8, 1995 and organized by the Istanbul Technical University.

I am proud to be here this morning as the rector of Istanbul University.

I would like to take this opportunity to give you a brief background into the beginning of engineering education in Turkey. The first scientific and up-to-date engineering education in Turkey started in 1773, 222 years ago at the Technical University which was at that time under the name of “Müendislik-i İhtimâl” (which means Imperial Naval Engineers’ School) established to provide education in shipbuilding, and cartography with maritime sector roots.

Istanbul Technical University (ITU) is one of the oldest surviving engineering schools.

It has played the leadership role in the modernization movement during the time of the Ottoman Empire and the Republic of Turkey.

Today, ITU proudly has 11 faculties, 3 graduate Institutes, 12 graduate Institutes, a Turkish music conservatory and provides over 21,000 graduate and undergraduate students with a quality education. Your meetings are being conducted on one of the 5 campuses of the Istanbul Technical University.

As an engineering and scientific school of higher education of tradition and prestige, ITU attaches great importance to scientific research. Polymer research is one of the areas of the University that has received a great deal of recognition and support.

I would like to thank the organizing committee, the scientific committee, the authors, the supporting institutions and all the participants for the efforts to make this Symposium one of the high scientific standards and trust that it will be a very successful, beneficial and pleasurable symposium.

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I especially want to thank Professor Yusuf Yagci, the chairman of the international scientific committee of this symposium for his huge energy and efforts.

We are proud to be the hosts for this symposium and wish all participants a pleasant week during this symposium, and for our international guests, I wish you a favorable stay in Istanbul.

I hope that you spend a memorable time in the next few days and that this symposium will produce fruitful results for all of you.

J. P. Kennedy gave a brief "History of Ionic Polymerization", followed by the traditional greeting by IUPAC, the sponsoring organization offered by S. Penczek. M. Szware spoke on "Problems in Ionic Polymerization"; he discussed the asymmetry between cationic and anionic polymerization, the character of the bond forming process, including the transition states, the nature and reactivity of ion pairs, triple ions and higher associates. Finally he outlined living cationic polymerization, the crucial role of dormant polymer species and the advantage resulting from the dormant to active polymer equilibrium.

Influence of Reaction Medium Polarity on the Solvation of Carbocations on Reactivity Ratios". Radiation initiated copolymerization of p-methylstyrene, styrene and p-chlorostyrene in methylene solution showed that the behavior of all monomer pairs is perfectly ideal ($r_{ij} = 1$) but it strongly deviates from ideality in bulk or in non-polar solvents such as methylecyclohexane or benzene. The results were explained by competitive inter or intramolecular complexation of the unpaired carbocations with the monomers and with the penultimate aromatic ring.

T. E. Hogen-Esch of Los Angeles, CA, USA presented his work on "Anionic Synthesis of Narrow Molecular Weight Distribution Poly(methyl methacrylate) at Ambient Temperature in the Presence of Tetraphenyolphosphonium Cation." The anionic polymerization of methyl methacrylate in THF at ambient temperature initiated by the tetraphenyolphosphonium salt of triphenylmethyl anion gave poly(methyl methacrylate) in quantitative yield and with narrow molecular weight distribution. Polymerizations were complete in less than two seconds and gave polymers of a DP of about 300 and a molecular weight distribution of about 1.4. The initiator efficiency was about 50-70% and the lack of chain termination relative to termination at ambient temperatures was attributed to a decrease in the rate of termination relative to the propagation in the presence of large bulky cations.

The scientific part of the meeting was opened by J. P. Kennedy of Akron OH, USA on "Macromolecular Design by Cationic Techniques: Multi-Arm Polyisobutylene Stars". The author described mechanistic details of cationic polymerization that has led to the rational design of numerous well-defined complex polymeric systems. Among them are novel multi-star polymers comprising a large number (up to 100) of uniform molecular weight distribution polyisobutylene arms linked to the central polydivinylbenzene core. As expected in spite of the substantial increase of the molecular weight, the inherent viscosity remains low.

S. Penczek of Lodz, Poland discussed "Selectivity in Polymerization of Cyclic Ethers". A reactivity/selectivity principle has been introduced, where the selectivity parameter $\beta = k_A / k_B$ describes the relationship between the parameters. It had been shown that $\beta$ (ions, ion pairs) < $\beta$ (covalent species). Several non-ionic (coordinative-covalent) initiators were compared.

F. Sigwart of Paris, France talked on "Cationic Copolymerization of Styrene Derivatives Initiated by $\gamma$-Rays: S. Kobayashi, Sendai, Japan discussed "Anionic Polymerization of Spiro Monomers Derived from Germynes". Anionic ring-opening polymerization of cyclic monomers from germylene having spiro structure were examined. The spiro germylene enolate monomer, was obtained from a five-membered cyclic germylene and an $\alpha,\beta$-unsaturated carbonyl compound, e.g. methyl vinyl ketone and was polymerized with anionic catalysts via ring-opening polymerization.

M. Footanile of Toulouse, France spoke on "Control of Reactivity in Anionic Polymerization of Polar Monomers". Among the problems which remain to be satisfactorily settled in anionic polymerization is the "livingness" of (meth)acrylic monomers because of the economic and commercial importance of these monomers. The authors used organolithium type initiators complexed with chelating tertiary amines to achieve the steric crowding of the large counterion that seems to, by necessity, decrease the intrinsic reactivity of the active anionic propagating species and avoid termination.
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M. Sawamoto of Kyoto, Japan presented his work on "Design and Mechanism of Living Cationic and Radical Polymerizations". The author believes his group has achieved a system of controlled radical polymerization of methyl methacrylate using CCl4/RuCl3/PPh3/methyl aluminum bis(2,6-di-tert-butyphenoxide) in toluene. There seems to be a similarity to the known "complexed radical system that has in the past been studied with cobalt as the central atom, also for methyl methacrylate polymerization. Sawamoto studied for these new initiating systems, other initiators (chlorine compounds), metal alkoxides as activators and block copolymerization of acrylic monomers.

K. Matyaszewski of Pittsburgh, PA, USA, discussed the "Role of Lewis Acids, Nucleophiles, Salts and Other Components in the Controlled/Living Carbocationic Polymerization". New "living" carbocationic polymerizations provide control of polymerization rates, molecular weights and lead to well-defined homopolymers and block copolymers. The various constituents of these multi-component systems were critically discussed.

R. Faust of Lowell, MA, USA, presented: "Synthetic Applications of Non-Polymerizable Monomers in Living Cationic Polymerization". A recently introduced foundation and methodology of using highly reactive but non-polymerizable monomers in living cationic polymerization for the synthesis of functional polymers and block copolymers was discussed. In situ functionalization of the living ends of a variety of nucleophiles (using diphenyl ether) was realized followed by end-quenching. Monomers studied were: isobutylene, p-methylstyrene, α-methylstyrene and vinyl ethers.

O. Vogl of Brooklyn, NY, USA presented his work on "Similarities in Stereospecific Chiral Polymerization and Chiral Crystalization". Configurationally and conformationally specific polymerization leads to helical macromolecules. This type of polymerization can be successfully carried out when monomer structure, polymerization mechanism and especially the spatial restrictions for monomer addition are carefully considered. Optically active polymers, having single helical screw sense could be prepared either by using a chiral initiating anion or a chiral counter-cation for chiral polymerization and a chiral counterpart for the polymerization of triaryltethyl methacrylates.

Surprisingly, the chiral crystallization of certain inorganic salts have much in common with the chiral stereospecific polymerization mentioned above. Sodium chlorate, which are achiral and completely ionized in aqueous solution, can crystallize spontaneously to give a mixture of pure levorotatory or pure dextrorotatory crystals. Nucleation of the crystallization with the pure enantiomer of the crystal furnishes new crystals of quantitative chiral purity.

R. Lenz of Amherst, MA, USA talked on "Anionic and Coordination Polymerization Reactions of β-Butyrolactone and Related Monomers". Aluminoxane and ionic initiation can polymerize β-butyrolactone and larger ring lactones to high molecular weight polymers. With the racemic monomer [R,S]-β-butyrolactone, anionic and cationic initiators yield only atactic polymers, but the aluminoxane catalysts can form either highly isotactic, highly syndiotactic or atactic depending on the composition and method of preparation of the aluminoxane and the condition of polymerization, as initially reported by Tsuruta for the polymerization of propylene oxide.

J. V. Crivello of Troy, NY, USA gave his talk on "Synthesis and Cationic Polymerization of Novel Monomers from Renewable Resources". He pointed out that interest has arisen in the use of materials and chemicals from renewable resources including the preparation and utilization of monomers. The design of monomers from three classes of ubiquitous biorenewable substrates has been undertaken in Crivello's laboratory: lipids, carbohydrates and terpenes. They have explored the synthesis of cationically polymerizable monomers that could be polymerized using photochemical techniques to polymers with a minimum consumption of energy.

V. Percec of Cleveland OH, USA, spoke on "Supramolecular Architectures via Molecular Recognition and Ionic Polymerization Processes".

E. J. Goethals of Ghent, Belgium, presented the work of his group on "New Materials Based on Polycetals". Cationic (co)polymerization of cyclic acetals in the presence of suitable transfer agents leads to the corresponding (co)polymers with functional end groups originating from the transfer agents. Hydroxyl terminated teleimers could be crosslinked with isocyanates to polyurethane networks or capped with (meth)acrylates that could further be polymerized.
O. Nuyken of Munich, Germany spoke on "Macromonomers from 2-Phenyl- and 2-Nonyl-2-Oxazoline". The two monomers could be polymerized with triflic acid and the polymeric cations terminated to prepare macromonomer with well-defined end groups, for possible further reaction or polymerization.

A. Ledwith, of Lancashire, U.K. talked about "Ionic Polymerizations and Materials Development". Ionic polymerizations as defined in the broadest sense, have been invaluable in development of commercially important elastomers, adhesives and sealants, in addition to polyether block components of polyester and polyurethane systems. Not so well known are the products of both chain reaction and step reaction ionic polymerization processes which are important in lithography, electrophotography, electroluminescence, liquid crystal variable transmission windows, abrasion resistant coatings and fire retardant systems. The lecture reviewed the progress and prospects in these fields.

P. Kubisa of Lodz, Poland, discussed the “Kinetic and Thermodynamic Control in the Cationic Copolymerization of Cyclic Ethers”. Polymerization of THF cannot be induced at the typical conditions of Activated Monomer polymerization of oxiranes. In the presence of oxirane, however, copolymerization of THF with oxirane proceeds as long as there is unreacted oxirane in the system. The process involves the following steps: a.) protonation of ethylene oxide forming a secondary oxonium ion; b.) n-THF propagation steps proceeding on the tertiary oxonium ions; c.) reaction of the tertiary oxonium ions (active species of THF propagation), with hydroxyl groups, reforming the proton (secondary oxonium ion).

M. Van Beylen of Leuven, Belgium, presented "Anionic Propagation of Symmetrical and Non-symmetrical Poly(diphenylmethyl Magnesium Bromide)". THF as a solvent for the symmetrical dipropyloxyl magnesium salt PS,Mg is slightly dissociated into ions. The free PST anion however forms triple ions with the non-dissociated ion pairs. Addition of MgBr₂ to the solution of PS,Mg transforms the latter into the non-symmetrical PS2MgBr₂. These equilibria were measured by conductance measurements and interpreted accordingly.

H. Cheradame of Thiais, France gave his talk on "Cationic Polymerization of 1,3-Pentadiene". Polymerization of 1,3-pentadiene with Lewis Acids, including Al(OTf), gave polymers that have less than one double bond per monomer unit suggesting that some cyclization had occurred during the polymerization.

J. Smid of Syracuse, NY, USA talked about "The Role of Ion Binding Ligands in Anionic Polymerization". Ion binding ligands, especially crown ether, but also linear cyclic polyethers and polyamines, are known to play a prominent role in the formation of polymers by anionic polymerization. They not only modify the initiation and propagation reactions, but also extend a profound effect on the stereochemical structure and tacticity or the sequence distribution of monomer units in copolymerization processes.
R. P. Quirk of Akron, OH, USA presented the "Anionic Synthesis of Well-Defined Polymers by Controlled Chain-Transfer Reactions". Chain transfer reactions have been used in anionic polymerizations to prepare low molecular weight polymers, i.e. oligomers. The random nature of the chain transfer events result in loss of control of molecular weight and molecular weight distribution. Attempts with limited success have been made to develop transfer methodology. Selected hydrocarbons and amines have been tried with limited success.

M. T. Retz of Muelheim, Germany, gave his talk on the most interesting subject of "Synthetic and Mechanistic Aspects of Metal-Free Polymerizations of Acrylates". Metal-free anionic polymerization of acrylates based on tetraalkylammonium salts of CH- and NH- compounds may well constitute an industrially viable process for obtaining polyacrylates in the molecular weight range of 1,500-25,000. Advantages include: a.) Cheap initiators; b.) High conversion; c.) Polymerization temperature of 20°C to 50°C; d.) Fairly narrow molecular weight distribution (1.1 to 1.4). Backbiting and Hoffmann elimination still occur. Initiators are not "naked" anions but primarily supramolecular dimeric ion pairs.

E. Franta of Strasbourg, France spoke about the "Synthesis of Triblock Copolymers Containing a Fluorinated Central Block and Two Outside Pdyl(1,3-Dioxolane) Blocks". Cationically polymerized 1,3-dioxolane in the presence of perfluoroisopropyl alcohol favors propagation through the activated monomer mechanism. Some surfactants are needed to carry out the polymerization effectively.

R. Studler of Mainz, Germany discussed the "Morphological Engineering in ABC Triblock Copolymers". Sequential anionic polymerization produces ABC triblock copolymers of various compositions and chemical stereochemistry. This technique allows the creation of new multi-phase morphologies based on the thermodynamic incompatibility between the blocks. As expected, the morphology of the triblock is very sensitive to the block sequences.

G. Riess of Mulhouse, France presented the "Synthesis of Block Copolymers by Anionic Polymerization, their Colloidal Properties and Application Possibilities". Block copolymers are still of great interest in solution and in the solid state (microphase separation). They derive their molecular structure from tailoring their macromolecular architecture. The authors studied block copolymers made by anionic polymerization, such as a.) "all-acrylic copolymers"; b.) functionalyzed and fluorescent labeled copolymers; c.) Copolymers having an A-B-C structure.

Z. J. Jedlinski of Zabrze, Poland gave an interesting talk on "Novel Supramolecular Catalysats and their Application to Polymer Synthesis". Control of polymerization or curing is an issue of great importance in polymer science. Latent initiators are very useful, since they can show their initiating activity in polymerization or curing by certain external stimulation such as heating and photo irradiation. The following types of initiators were explored: a.) benzylsulphonium salts; b.) benzyl ammonium salts; c.) benzyl phosphonium salts and d.) benzyl pyridinium salts. Their activity depended to a great extent on the counterion.

The subject of the talk by M. Zsuga of Debrecen, Hungary was "Investigation of the Mechanism of Crosslinking Reaction of p-Diisocyanate/Lewis Acid/Isobutylene Systems by Glass Fiber Optic Photometry". The ion generation plays a fundamental role in the kinetics of ionic polymerization reactions. The formation of cations were recognized but the species are produced at very low concentrations, the concentration decreases with increasing temperature and level off at a constant concentration at 1.20.

C. Tsetanov of Sofia, Bulgaria discussed "Quaternary Onium Salts as Additives in Anionic Polymerization of Methyl Methacrylate". Anionic polymerization of methyl methacrylate was carried out with triethylsilane and potassium t-butoxide in the presence of different ammonium and phosphonium salts. The tacticity of the polymers depended strongly on the size and shape of the onium salt additive. It increases the initiator efficiency and usually also the syndiotactic content of the polymer.

S. Bywater of Ottawa, Canada discussed "Association Effects in Anionic Polymerization, their Effect on the Polymerization Mechanism". In hydrocarbon solvents the degree
of association of the active centers is an important parameter in the chain propagation mechanism and trace amounts of polar impurities in the solvents can alter significantly the rate of polymerization and the stereocomposition of the final polymer.

M. Moller of Ulm, Germany presented his work on "Polyim)nophosphazenes, an Efficient Cominitator/Activator for the Anionic Ring Opening Polymerization of Oxiranes, Cyclicsloxanes and Cyclic EsterS. Different -OH and -CH compounds have been deactivated by inimophosphonate bases P₂₃₁₈. The usually high base strength in combination with low nucleophilicity and excellent solubility of the protonated iminophosphonate allowed the efficient polymerization of oxiranes, cyclicsloxanes and lactones with high polymerization rates. In addition, the iminophosphazenes are good receptor and cryptands for lithium ions.

T. Kitayama of Osaka, Japan presented the work of Hata's group on "Highly Heterotactic Polymerization of Methyl Methacrylates: Isotactic and syndiotactic polymers are typical stereoregular polymers, which consist of repetition of meso- or racemo-units. Heterotactic polymers are stereoregular polymers of alternating sequences of meso- and racemo-units. The group in Osaka has recently found that a combination of butyllithium and bis(2,6-di-t-butylphenoxymethyl)aluminum gave heterotactic polymers with narrow molecular weight distribution in the polymerization of alkyl methacrylates in toluene at low temperatures. The heterotacticity depended somewhat on the ester group of the monomer, the highest value was found for the ethyl ester."

Finally J. P. Vairon of Paris, France concluded the Symposium with his paper on "Protonation of Styrene Dimer: A Stop-Flow Approach to the Kinetics and Mechanism of the Reaction with Trimellitic Acid in Methylene Dichloride". Rapid kinetics of styrene protonation was found when the polymerization was initiated with trimellitic acid at low temperatures, in high vacuum using a UV detection stopped-flow device. In addition to the polystyryl cation, several more or less transitory peaks were also observed. To simplify the system, two ethylenic dimers of styrene (1,3-diphenyl-1-benzene), the cation of which is the correct model of polystyrene, were studied.

The following Contributed Papers were also presented:

A. Deffieux, Talence, France: "Nature and Concentration of Active α-Halogenoethers."

K. Kamigaito, Kyoto, Japan: "Living Cationic Polymerization with Titanium(IV) Complexes."

N. Haucourt, Ghent, Belgium: "Amphiphilic Block Copolymers Based on Polyvinyl Ether/Segments."

G. Maier, Munich, Germany: "New Polyanilines by Cationic Polymerization."

S. Spassky, Paris, France: "Ring-Opening Polymerization: Controlled Polymer Synthesis of Poly(α-lactides)."

W. Kuran, Warsaw, Poland: "Mechanism of the Coordination Polymerization of Oxiranes."

C. Dederer, Mulhouse, France: "Laser-induced Cationic Polymerization of Multi-functional Monomers."


E. Hadicke, Ludwigshafen, Germany: "Molecular Modeling of Chemical Reactions Illustrated by Anionically Initiated Polymerizations."


G. Litsynenko, Moscow, Russia: "Theory of Living Polymerization Proceeding with Slow Activity Exchange Between Active Species."

D. M. Hadfield, Coventry, U.K.: "Polymerization of Methacrylates by Trialkylaluminum Alkyl/Lithium Initiators."

A. A. Yakubovich, Moscow, Russia: "Chain Transfer Reactions in Anionic Polymerization of Non-Polar Monomers."

A. Dworak, Gliwice, Poland: "Polymerization of Oxazolines Initiated by Acid Chlorides and Chlorosilanes."

S. Sivaram, Pune, India: "Living Anionic Polymerization of Methyl Methacrylate using Lithium Perchlorate Ligated Alkyl Lithium Initiators."

R. Velckova, Sofia, Bulgaria: "Amphiphilic Copolymers Based on Heterocyclic Monomers."

J. Kops, Lyngby, Denmark: "Functionalization of Polyisobutylene by Reaction with Isobutylmethylethylsilane."

H. Keil, Aachen, Germany: "Well-Defined Polymer Structures by Ionic Ring Opening Polymerization of Cyclic Monomers Comprising the Respective Structure."


B. Ryan, Dublin, Ireland: "Ionic Depolymerization Processes of Alkylcyclohexylacrylate Polymers."

A. A. B. Sobrinho, Rio de Janeiro, Brazil: "Synthesis of Poly(β-amide) and its Block Copolymers with Polyether using Alumina-Alkaline Catalyst."


B. Belenkaya, Moscow, Russia: "Cationic Copolymerization of ε-Caprolactone and L.L-Lactide in the Presence of Hydroxy-containing Compounds."

F. R. Khalakov, Moscow, Russia: "Once Again About the Initiation Reactions of Cationic Polymerization of Olefins and Cationic Degradation of Polyolefins, Affected by Strong Lewis Acids."

M. Kowalczyk, Zabrze, Poland: "Chemistry of 2-Oxetanone Polymerization."


S. C. Kim, Taegon, Korea: "PPO-Nylon 6 graft Copolymers."

The Symposium was held in the Conference Hall of the Istanbul Technical University in the Macka district of Istanbul. The participants were housed at the guest House of the University and a number of Hotels in the proximity of the meeting place. The welcoming reception was held on Sunday night, September 3, 1995 at the Dining Hall of the Guest House offered by the Istanbul Technical University Foundation. On Monday evening the dinner, organized for lecturers and participants, at the Parksa Hilton was offered by KORDSA and on Tuesday by Polynas. Wednesday entertainment included a show of the Meher Band, the world's oldest military band in the afternoon and the evening dinner, buffet style was during a Iona Cruise on a yacht.