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CONFERENCE REPORT

INTERNATIONAL SYMPOSIUM ON IONIC POLYMERIZATION, ISTANBUL, SEPTEMBER 4-8, 1995

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Yusuf Yagci

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Emblem of Istanbul



Emblem of Istanbul Technical University

The International Symposium on Ionic Polymerization, the First Symposium of its kind, was held from September 4–8, 1995 in Istanbul, Turkey. It was held at the Istanbul Technical University and was under the sponsorship of IUPAC. The following organizations contributed to the Symposium: The Scientific and Technical Research Council of Turkey, the Union of Chamber of Commerce and Industry of Turkey, KORDSA, POLINAS, The Istanbul Technical University Foundation, the German General Consulate, Turk Henkel, GEMSAN, Bogazici Kimya Ltd., ANAMED, KUTAY Dis Tic A.S., Hüthig and Wepf Verlag, Pilkingtons, Terra A.S., Kermanlar and Cantaylar Fotocopi.

The meeting was held at the Macka Campus of the Istanbul Technical University. It was attended by about 160 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 for September 4-8, 1995 and organized by the Istanbul Technical University.

I am proud to be here this morning as the Rector of Istanbul Technical 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 'Mühendishane-i Hümayun' (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, a Turkish music conservatory and provides over 21,000 graduate and undergraduate student 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 very successful, beneficial and pleasurable symposium.

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 greetings by IUPAC, the sponsoring organization offered by **S. Penczek**. **M. Szwarc** 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.



Old City, Istanbul.

The scientific part on the meeting was opened by **J.P. Kennedy** of Akron OH, U.S.A. on 'Macromolecular Design by Cationic Techniques: Multi-Arm Polyisobutylene Stars' The author described mechanistic details of carbocationic 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 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 $\beta = k_p/k_{tr}$ describes the relationship between the parameters; It had been shown that β (ions, ion pairs) $< \beta$ (covalent species). Several non-ionic (coordinative-covalent) initiators were compared.

P. Sigwalt of Paris, France talked on 'Cationic Copolymerization of Styrene Derivatives Initiated by γ -Rays: 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 ($r_1r_2 = 1$) but it strongly deviates from ideality in bulk or in non-polar solvents such as methylcyclohexane 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, U.S.A. presented his work on 'Anionic Synthesis of Narrow Molecular Weight Distribution Poly(methyl methacrylate) at Ambient Temperature in the Presence of Tetraphenylphosphonium Cation'. The anionic polymerization of methyl methacrylate in THF at ambient temperature initiated by the tetraphenylphosphonium 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 30–70% 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.



S. Penczek and A. Müller.

S. Kobayashi, Sendai, Japan discussed 'Anionic Polymerization of Spiro Monomers Derived from Germylenes'. 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 α , β -unsaturated carbonyl compound, e.g. methyl vinyl ketone and was polymerized with anionic catalysts via ring-opening polymerization.

M. Fontanille of Talance, 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 organo-

lithium type initiators complexed with chelating tertiary diamines to achieve the steric crowding of the large countercation that seems to by necessary the decrease the intrinsic reactivity of the active anionic propagating species and avoid termination.

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 $CCl_4/RuCl_2(PPh_3)_3/$ methyl aluminum bis(2,6-di-butylphenoxide)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 system, other initiators (chlorine compounds), metal alkoxides as activators and block copolymerization of acrylic monomers.

K. Matyjaszewski of Pittsburgh, PA, U.S.A., 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.



K. Matyjaszewski, M. Sawamoto, O. Nuyken and Mrs Nuyken.

R. Faust of Lowell, MA, U.S.A., 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, U.S.A. presented his work on 'Similarities in Stereospecific Chiral Polymerization and Chiral Crystallization'. 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 be using a chiral initiating anion or a chiral counter-cation for chloral polymerization and a chiral counterion for the polymerization of triarylethyl methacrylates.

Surprisingly, the chiral crystallization of certain inorganic salts have much in common with the chiral stereospecific polymerization mentioned above. Sodium chlorate which is 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 chiroptical purity.

R. Lenz of Amherst, MA, U.S.A. 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 polyesters. 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 polymer 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, U.S.A. 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, U.S.A., spoke on 'Supramolecular Architechtures via Molecular Recognition and Ionic Polymerization Processes'.

E.J. Goethals of Ghent, Belgium, presented the work of his group on 'New Materials Based on Polyacetals'. 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. Hydroxy terminated telemers could be crosslinked with isocyanates to polyurethane networks or capped with (meth)acrylates that could further be polymerized.



Sight-seeing: T. E. Hogen-Esch, J. Smid and Mrs Smid.

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 Polystyryl Magnesium Salts'. THF as a solvent for the symmetrical dipolystyryl magnesium salt PSt_2Mg is slightly dissociated into ions. The free PSt^- anion however forms triple ions with the non-dissociated ion pairs. Addition of $MgBr_2$ to the solution of PSt_2Mg transforms the latter into the non symmetrical PStMgBr. These equilibria were measured by conductance measurements and interpreted accordingly.



Sultanahmet Mosque, Istanbul "The Blue Mosque".

A.H.E. Mueller of Mainz, Germany discussed the 'Kinetic Investigation and Mechanism of Methyl Methacrylate in the Presence of Aluminum Alkyls'. Living polymerization and 'livingness' of methyl methacrylate of methyl methacrylate has been a focal point of anionic polymerization because of the importance of (meth)acrylic polymers in the coatings industry. The polymerization of methacrylates in the presence of aluminum alkyls or aluminum alkoxides was of particular interest because they can be carried out at or around room temperature. and in the presence of non-polar solvents without losing its 'living' character. At low temperatures highly syndiotactic polymers are formed in aluminum-free polymerization. These results are consistent with the formation of complexes that might involve the carboxylate of the growing polymer anion.

J.M. DeSimone of Chapel Hill, NC, U.S.A. spoke on 'Cationic Polymerizations in Liquid and Supercritical Carbon Dioxide'. He carried out cationic polymerizations both in supercritical and liquid carbon dioxide. He had followed the earlier work of Plesch, using this solvent for the polymerization of isobutyl vinyl ether with ethylaluminum dichloride and oxetanes with BF_{3} .



Hagia, Sophia.

B. Ivan of Mainz, Germany, presented 'Synthesis, Principles and Strategies for New Microphase Separated Polymer Systems by the Combination of Ionic Polymerizations'. Isobutylene polymers with unique polymer ends have been used as precursors for macroinitiators to induce living anionic polymerizations of selected monomers leading to block copolymers Silyl protected HEMA was used for the preparation of hydrophobic PIB blocks and hydrophilic HEMA blocks.

H. Cheradame of Thiais, France gave his talk on 'Cationic Polymerization of



Grand Bazaar, Istanbul.

1,3-Pentadiene'. Polymerization of 1,3 pentadiene with Lewis Acids, including $Al(OTf)_3$ gave polymers that have less than one double bond per monomer units suggesting that some cyclization had occurred during the polymerization.

J. Smid of Syracuse, NY, U.S.A. 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, U.S.A. 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. Reetz of Muehlheim, Germany, gave his talk an the most interesting subject on '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 1500–25,000. Advantages include: (a) Cheap initiators; (b) high conversion; polymerization temperature of 20°C to 50°C; (d) fairly narrow molecular distribution (1.1 to 1.4). Backbiting and Hoffmann elimination still occurs. 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 Poly(1,3-Dioxolane) Blocks'. Cationically polymerized 1,3-dioxolane in the presence of perfluoroisopropanol favors propagation through the activated monomer mechanism. Some surfactants are needed to carry out the polymerization effectively.

R. Stadler 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. A 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) functionalized 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 Catalysis in the Controlled Synthesis of Polymers and Block Copolymers'. Electron transfer processes are playing an increasingly important role in organic synthesis and anionic polymerization of vinyl and heterocyclic monomers. The utility of supramolecular

catalysts for synthesis of polymers, functional polymers, and biomedical polymers was presented.

F. Sanda of Tokyo, Japan spoke on the 'Design of Latent Catalysts 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) benzylsulfonium salts; (b) benzyl ammonium salts; (c) benzyl phosphonium salts and (d) benzyl pyridinium salts. Their activity depended to a great extent on the counteranion.

The subject of the talk be **M. Zsuga** of Debrecen, Hungary was 'Investigation of the Mechanism of Crossover Reaction of *p*-Dicumylchloride/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 cation were recognized but the species are produced at very low concentrations, the concentration decreases with increasing temperature and level off at coinitiator to initiator concentrations of 1:20.

C. Tsvetanov of Sofia, Bulgaria discussed 'Quarternary Onium Salts as Additives in Anionic Polymerization of Methyl Methacrylate'. Anionic polymerization of methyl methacrylate was carried out with α -lithioethylisobutyrate 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 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 rate of polymerization and the stereochemistry of the final polymer.

M. Müller of Ulm, Germany presented his work on 'Polyiminophosphazenes, an Efficient Coinitiator/Activator for the Anionic Ring Opening Polymerization of Oxiranes, Cyclosiloxanes and Cyclic Esters'. Different -OH and -CH compounds have been deprotonated by iminophosphazene bases P_{4} -t-Bu. The unusually high base strength in combination with low nucleophilicity and excellent solubility of the protonated iminophosphazene allowed the efficient polymerization of oxiranes, cyclosiloxanes and lactones with high polymerization rate. In addition, the iminophosphazenes are good receptors and cryptands for lithium ions.

T. Kitayama of Osaka, Japan presented the work of Hatada'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 *t*-butyllithium and bis(2,6-*t*-butylphenoxy)methyl aluminum have heterotactic polymers with narrow molecular weight distribution in the polymerization of certain alkyl methacrylates in toluene at low temperatures. The heterotacticity depended to some extent 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 Dimers: A Stop-Flow Approach of the Kinetics and Mechanisms of the Reaction with Triflic Acid in Methylene Dichloride'. Rapid kinetics of styrene polymerization was found when the polymerization was initiated with triflic 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-butenes), 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'.

M. Kamigaito, Kyoto, Japan: 'Living Cationic Polymerization with Titanium(IV) Complexes'.

N. Haucourt, Ghent, Belgium: 'Amphiphilic Block Copolymers Based on Poly(vinyl Ether)Segments'.

G. Maier, Munich, Germany: 'New Polyindanes by Cationic Polymerization'.

N. Spassky, Paris, France: 'Ring-Opening Polymerization: Controlled Polymer Synthesis of Polylactides'.

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

C. Decker, Mulhouse, France: 'Laser induced Cationic Polymerization of Multi-functional Monomers'.

H. Mayr, Darmstadt, Germany: 'Modeling Cationic Polymerizations: Kinetics of Ion Molecule Reactions'.

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

A.F. Johnson, Bradford, U.K.: 'Modeling and Control of Ionic Polymerization Processes'.

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

D.M. Haddleton, Coventry, U.K.: 'Polymerization of Methacrylates by Trialkylaluminum Alkyl/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 Chloroformates'.

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

R. Velickova, Sofia, Bulgaria: 'Amphiphilic Copolymers Based on Heterocyclic Monomers'.

J. Kops, Lyngby, Denmark: 'Functionalization of Polyisobutylene by Reaction with Isobutyltrimethlsilane'.

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

S. Boileau, Paris, France: 'Anionic Polymerization of Cyclosiloxanes with Various Substituents'.

B. Ryan, Dublin, Ireland: 'Ionic Depolymerization Processes of Alkylcyanoacrylate Polymers'.

A.A.B. Sobrinho, Rio de Janeiro, Brazil: 'Synthesis of Poly- β -amide and its Block Copolymers with Polyethers using Alumino-Alkaline Catalyst'.

F.M. Cabelo, Enschede, The Netherlands: 'Complexes of Diethylzinc and Trimethylsilyl Methyllithum as Initiators for the Anionic Polymerization of Styrene in Toluene Solution'.

B. Belenkaya, Moscow, Russia: 'Cationic Copolymerization of ε -Caprolactone and L,L-Lactide in the Presence of Hydroxyl-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. Kowalczuk, Zabrze, Poland: 'Chemistry of 2-Oxetanone Polymerization'.

J. Penelle, Louvain-La-Neuve, Belgium: 'Anionic Ring-Opening Polymerization of Substituted Cyclopropanes'.

S.C. Kim, Taejon, 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 Mehter Band, the world's oldest military band in the afternoon and the evening dinner, buffet style was during a Bosporus Cruise on a yacht.



R. Stadler, Y. Yagci and Mrs Yagci on the yacht.

The Symposium Banquet was held Thursday night at the Historical Galata Tower and the farewell reception was offered on Friday evening in the form of a Cocktail Party in the garden of the German General Consulate.

The International Symposium on Ionic Polymerization was the First Symposium on Ionic Polymerization and is the successor of the Symposia on 'Cationic Polymerization' in their various forms, on 'Ring-Opening Polymerization' and on 'Anionic Polymerization'. It was a great scientific but also a great social success. The participants of the Symposium were looking forward to the next Ionic Symposium in Paris in 1997.



Bridge to Asia.

The History of International Symposia on Ionic Polymerizations (Cationic, Anionic and Ring-Opening) [Otto Vogl]

This summary is a brief history of Symposia on Ionic Polymerization, Cationic, Anionic and Ring-Opening Polymerizations.

The modern era of cationic polymerization began in 1973 with the Cationic Symposium in Rouen, France with Pierre Sigwalt and Ernest Maréchal as the co-chairmen; it was later called the 3rd Symposium on Cationic Polymerization. This Symposium was soon followed by the first Symposium on Ring-Opening Polymerization organized by Stanislaw Penczek. This Symposium was called: Symposium on Heterocyclics (Ring-Opening) and was held in Warsaw-Jablona in 1975. For both types of Symposia, the series of symposia on cationic polymerization and on ring-opening polymerization, steering committees were formed that guided the successions of the meetings, accepted the proposals for the locations and leadership of the next Symposia and influenced their contents.

By the mid-1980s it was felt that a combination of the three recognized categories of cationic, anionic and ring-opening polymerizations into one single Ionic Symposium was found to be desirable. At the Balatonfured meeting in 1992, the 10th cationic Symposium, this action was first formally proposed. At the next cationic Symposium, the Borovets Meeting, the steering committee met under the chairmanship of Otto Vogl and considered a official proposal by Stanislaw Penczek, representing the interests of the 'Ring-Opening Polymerization' and Axel Mueller, representing the interests of the 'Anionic Polymerization'. The decision was made to assign the next Cationic Symposium that had just been approved for Paris in 1997 under the chairmanship of Jean-Pierre Vairon and Pierre Sigwalt for Paris, the title 'Ionic Symposium'. At the same time the next Symposium was confirmed for the projected 10th Cationic Symposium in Istanbul under the chairmanship of Yusuf Yagci. It was left to Yagci to choose the specific title, to call it the '12th Symposium on Cationic Polymerization' or to call it the 'Symposium on Ionic Polymerization'. Yagci opted for 'Symposium on Ionic Polymerization' as the title for the Symposium in Istanbul in September 1995. Based on this decision, this Symposium became the First Symposium on Ionic Polymerization.

The following officially recognized Symposia related to **Ionic Polymerization** have been held previously: **Symposia on:**

Cationic polymerization:

- I. 1949 Discussions in Friedel-Crafts Polymerization Dublin, Ireland: D.C. Pepper, Chairman
- II. 1952 Conference on Cationic Polymerization Keele, U.K.: P.H. Plesch, Chairman
- III. 1973 International Symposium on Cationic Polymerization Rouen, France: P. Sigwalt and E. Maréchal, Cochairmen
- IV. 1976 4th International Symposium on Cationic Polymerization Akron, U.S.A.: J.P. Kennedy, Chairman
- V. 1980 5th International Symposium on Cationic and other Ionic Polymerizations Kyoto, Japan: J. Furukawa and T. Saegusa, Co-chairmen
- VI. August 30 to September 2, 1983 6th International Symposium on Cationic Polymerization and Related Processes (IUPAC) Ghent, Belgium: E.J. Goethals, Chairman
- VII. August 12–15, 1985 7th International Symposium on Cationic Polymerization and Related Processes (IUPAC) Jena, East Germany: G. Heublein, Chairman
- VIII. August 15 to 17, 1987 8th International Symposium on Cationic Polymerization and Related Processes (IUPAC) Munich, West Germany: O. Nuyken, Chairman
- IX June 5 to 9, 1989 9th International Symposium on Cationic Polymerization and Related Ionic Processes (IUPAC) Strasbourg, France: E. Franta and P. Rempp, Co-chairmen
- X. August 26 to 29, 1991 10th International Symposium on Cationic Polymerization and Related Processes (IUPAC) Balatonfüred, Hungary: T. Kelen and F. Tüdös, Co-chairmen
- XI. 1993 11th International Symposium on Cationic Polymerization and Related Processes (IUPAC) Borovets, Bulgaria: I.M. Panayotov and Ch.B. Tsvetanov, Co-chairmen

Anionic polymerization:

No official listings or records exist on Symposia on Anionic Polymerization, although 'meetings on anionic polymerization' had been part of meetings of the American Chemical Society. Symposia on Cationic Polymerization have, since the 5th Symposium on Cationic Polymerization in Kyoto in 1980, frequently included in their title and contents the notions 'and Related Ionic Polymerizations' or 'and Related Processes'. Contributions on anionic polymerization, including coordinative anionic polymerization and group transfer polymerization (a special case of 'coordinative polymerization' specifically for methacrylate polymerization) have been formally recognized in the programs since the IX. Cationic Symposium in Strasbourg in 1989 and 'official' Symposia on Cationic Polymerization were to a substantial extent devoted to anionic polymerization.

Some recent meetings on Polymer Chemistry had substantial parts devoted to 'Anionic Polymerization'. The most important meeting was the so-called workshop which might have been the spawning ground for 'Symposia on Anionic Polymerization' which was recently held in Mainz:

July 1992, European Polymer Federation Workshop on Anionic Polymerization and Related Processes Mainz, Germany, Axel Mueller, Chairman.

Other meetings with contents of Anionic Polymerization were:

June 95 International Conference on 'Advanced Polymers via Macromolecular Engineering', Vassar Campus, Hudson Valley, NY, U.S.A.: Munmaya Mishra, Chairman.

December 1995 International Symposium on Controlled Polymer Synthesis, Pacifichem, Honolulu, Hawaii: Co-Chairmen Shohei Inoue and Kristof Matyjaszewski.

A much better record keeping exists for the Symposia on 'Ring-Opening Polmerization', in part because the Chaiman of the first Symposium, Stanislaw Penczek, maintained a continued interest in the succession of the Symposia on Ring-Opening Polymerization.

Ring-opening polymerization:

The first official Symposium on Ring-Opening Polymerization was held in 1975 in Warsaw-Jablona. The work and publications on the polymerization of heterocyclics, later called ring-opening polymerization, had intensified starting from the middle to late 1950s.

Over the years the commercialization of polymers from trioxane, ethylene and propylene oxide had greatly increased the interest in the subject and justified separate symposia devoted to ring-opening polymerization.

There was, however, a forerunner and a symposium on this subject which might be considered the first meeting on ring-opening polymerization. It was held at the IUPAC Meeting in Boston in 1971. The Symposium was called 'Polymerization of Heterocyclics', and in the preface of the book based on this symposium, it stated clearly that this title meant the ring-opening polymerization of hererocyclics. The contents of the one day symposium consisted of lectures of the experts in the field of ring-opening polymerization, each lecture representing the then known special subjects on ring-opening polymerization:

July 29, 1971 Polymerization of Heterocyclics, at the XXIIIth IUPAC Congress Boston, MA, U.S.A.: Otto Vogl and Junji Furukawa, Co-Chairmen.

Seven official Symposia on 'Ring-Opening Polymerization' were held until 1992, when it was decided to combine the three categories into one general subject: **Symposia on Ionic Polymerization:**

June 23 to 25, 1975 Symposium on Polymerization of Heterocyclics (Ring-Opening) Warsaw-Jablonna, Poland, Stanislaw Penczek, Chairman. Two 'Ring-Opening Symposia' were held at ACS Meetings involving E. Vandenberg, T. Saegusa and E.J. Goethals.

September 22 to 25, 1980 Symposium on Ring-Opening Polymerization of Heterocyclics (1980 Prague Meetings on Macromolecules, 21st Microsymposium) Karlovy Vary, Czechoslovakia, Jan Sebenda, Chairman.

June 22 to 26, 1986 5th International Symposium on Ring-Opening Polymerization Blois, France, Pierre Sigwalt, Chairman.

April 22 to 27, 1990 6th International Symposium on Ring-Opening and Cyclo-Polymerization Boston, MA, U.S.A. (at the ACS Meeting), Judith S. Riffle and Krystof Matyaszewski, Chairpersons.

July 7 to 11, 1992 7th Symposium on Ring-Opening Polymerization Warsaw, Poland, Zbigniew Jedlinski, Chairman.

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