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## IUPAC 6th International Symposium on Cationic Polymerization and Related Processes

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Conference Reports

# IUPAC 6TH International Symposium on Cationic Polymerization and Related Processes

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The 6th Symposium on Cationic Polymerization and Related Processes was held in Ghent, Belgium from August 30 to September 2, 1983, in the Faculty of Sciences of the University of Ghent; Professor Eric Goethals was the Chairman and Dr. Etienne Schacht the Secretary. A total of 16 invited lectures were presented and 35 contributed shorter communications were given. Many important problems of cationic reactions and polymerizations were discussed, and many advances were reported.

Probably the single most important problem is the control of cationic polymerization which ultimately leads to living cationic polymerization. The demonstrations of clearcut examples of living cationic polymerization have long been elusive because of the intrinsic instability of carbocationic species. Higashimura and his group have found that  $\text{HI/I}_2$  as initiating systems are effective examples of living polymerization of isobutylvinyl ether when the polymerization is carried out at  $-15^\circ\text{C}$  and in *n*-hexane. The polymers formed under "pseudoliving" conditions are nearly monodisperse ( $M_w/M_n \approx 1.1$ ) and have  $M_n$  in direct relation to monomer conversion and initiator used. Under optimal conditions living polymer systems were also found where *p*-methoxystyrene and *N*-vinylcarbazoles were used as the monomers and  $\text{HI/I}_2$  as the initiating system. These living polymer systems could be used for the preparation of block copolymers and functional polymers.

J. P. Kennedy described new telechelic prepolymers and

networks therefrom. These cationic inifer systems have recently been explored further; they were very effective for the controlled synthesis of various linear and star shaped telechelic polymers. Polyisobutylene based polyurethanes have been synthesized and new polyurethane networks were prepared using three and higher star polyisobutylene polyols with diisocyanates.

Progress has also been made in the synthesis of polystyrene/polyisobutylene block copolymers to obtain polystyrene/polyisobutylene tri- or penta block polymers.

A new technique for the polymerization of isobutylene was discovered which involves what Kennedy calls "quasiliving" cationic polymerization. It involves the constant "starve feeding" of the polymerizing system with the monomer with  $\text{TiCl}_4$  as the coinitiator and cumylchloride as the initiator.

Structures and reactivities in ring opening and vinyl cationic polymerization were discussed by St. Penczek in the opening lecture. It was shown in the polymerization of 1,3-dioxolane or 1,3-dioxepane that the active species exist in dynamic equilibrium and only the oxonium ion contributes to the chain growth. Also in cationic  $\beta$ -lactone polymerizations, the oxonium ion and not the acylium ( $-\text{C}^+=\text{O}$ ) ion contributes to the polymerization. Penczek also showed that, in the formally called "pseudocationic" polymerization no propagation of the ester species has been demonstrated but only in the ionized form.

As mentioned by Conrad Schuerch, polysaccharides can be prepared by cationic ring opening polymerization of bicyclic acetals and protected sugar derivatives. The polymers, when deprotected can be used as model polysaccharides to investigate enzyme, antibody and lectin reactions, and to investi-

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gate the relation between structure, conformation, and physical or physiological properties. Triflic anhydride, silver triflate and trityl perchlorate at room temperature and below have been the best initiators. Sumitomo studied polymerization of the racemic mixture of the individual enantiomers of bicyclic acetals, particularly 6,8-dioxabicyclo[3.2.1] octane and their 4-bromo derivatives, as simple models for the synthesis of dextran, a naturally occurring (1→6) linked polysaccharide. Living cationic polymerization for the preparation of block copolymers was demonstrated by using N-tertiarybutyl aziridine (Goethals, Van de Velde).

The first day of the symposium was actually devoted to carbocation polymerization: It introduced such subjects as functionalized oligo- and polyisobutylenes (Cheradame), cationic polymerization of pentamethylstyrene (Bywater), the determination of the propagation rate content of the cationic polymerization of alkenes (Plesch), new facts about the polymerization of isobutylene with Lewis acids (Marek), cationic polymerization of tetramethylindene (Sanchez) and detailed observations on the inifer technique and equilibria in cationic polymerization (Pask).

The recent understanding of the propagation mechanism in cationic vinyl polymerization (Heublein), led to novel approaches toward the controlled cationic polymer synthesis (Wondraczek).

Radiation initiation, both by high energy or by photoinitiation played a substantial part of this symposium. Cationic polymerization and grafting initiated by high energy radiation (Stannett) plays an important role. New aspects of the mechanisms of photoinitiated cationic polymerization (Ledwith), recent progress in the design of new photoinitiators for cationic polymerization (Crivello), and new photopolymerization catalysts for epoxides (Hayase) were also presented.

Thermally induced cationic initiators for cationic polymerizations (Crivello) and latent catalysis for thermally induced cationic polymerization (Pappas) were an important part of this symposium.

Copolymerization involving carbocations was discussed by Cesca with the polymerization of isobutylene with conjugated dienes; block copolymerization of styrene and  $\alpha$ -methylstyrene in liquid sulfur dioxide (Gomes), cationic polymerizations and electrophilic reactions promoted by metal salts of strong acids (Gandini), kinetics of cationic oligomerization of styrene using poly(styrenesulfonic acid) resin as catalyst (Showan Chen) and the cationic cyclocodimerization of 1,3-bis(p-vinylphenyl)propane (Nishimura) were also discussed.

New intriguing cationic rearrangement reactions have been discovered and were presented in this symposium: Repeating unit isomerization via onium ion intermediates (Tirrell) and 2,5-polytetrahydrofuran diyls via cationic transformation of fully epoxidized 1,4-polybutadiene (Smith).

Cationic ring-opening polymerization played an important role at the 6th Cationic Symposium. Especially important was the discussion of the effect of ring size and substitution on the cationic lactam polymerization (Sebenda), and the

stability of active centers of cationic polymerization of heterocyclics (Ponomarenko).

Numerous aspects of homopolymerization of heterocyclics were discussed: The cationic ring-opening polymerization with dioxolane salts (Jedlinski), the cationic polymerization of spiro-orthoesters (Matyjaszewski), the polymerization of cis- and trans-2,4-dimethyloxacyclohexane (Kops), the polymerization of racemic and optically active 2-methyloxetane (Leborgne), and some new sequential copolymers by cationic ring-opening polymerization (Percec).

Cationic polymerization of cyclic acetals were presented by a number of authors: Steric control in the cationic ring-opening polymerization of cyclic acetals (Sumitomo), influence of the medium on the polymerization of cyclic acetals (Rozenberg); the initiation of the polymerization of 1,3-dioxolane by 2,4,5-trisubstituted 1,3-dioxolan-2-ylidinium salts (Lukaszczyk), and the especially good work of the sequential polymerization of cyclic ethers and acetals (Kubisa).

Cyclic co-oligomerization was observed during the polymerization of chloromethyloxepane (Tezuka), and spontaneous copolymerization to form cyclic oligomers of N-alkylaziridines and  $\beta$ -lactones (Bouquet).

Various other cationic ring-opening polymerization were presented: Some new aspects of cationic polymerization of cyclohexanones (Sauvet), the role of hydrogen bonding in the ring-opening cationic polymerization (Chojnowski), the ring-opening oligomerization of oxdranes by fatty alcohols (Sebag) and the cationic polymerization of N-tertiarybutyl-2-phenyl-aziridine (LeMoigne).

Polymers of tetrahydrofuran were the subject of a number of papers: New routes to telechelic and multifunctionally terminated polymers by cationic ring-opening polymerization of tetrahydrofuran (Matsumoto), the synthesis of polytetrahydrofuran with positively charged functional end groups (Tezuka), Elastomeric ionenes containing poly(oxytetramethylene) units (Kohjya) and tentatives to graft polytetrahydrofuran onto poly(vinyl chloride) (Franta).

The 6th Cationic Symposium, attended by about 120 participants, was a great success. It was refreshing to see that younger scientists played an important role. Much of the overall collegiality and friendship was contributed by the evening programs: on Tuesday evening a reception of the participants at the medieval Town Hall of the City of Ghent by the mayor, on Wednesday evening a harpsichord recital at the Bijloke Museum, and on Thursday the Symposium dinner at the Faculty Club "Het Pand". The atmosphere of the city of Ghent, the medieval capital of Flanders certainly contributed significantly to the success of the Symposium.

The 7th Symposium on Cationic Polymerization and Related Processes will be held August 12 to August 15, 1985 in Jena, the German Democratic Republic. The Sektion Chemie of the University of Jena assisted by the Institute of Macromolecular Chemistry, Prague (Czechoslovakia) will jointly organize this Symposium with G. Heublein and M. Marek as Co-chairmen.

The 8th Symposium has been tentatively scheduled in the Federal Republic of Germany.