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### Preface

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## Preface

The Japan-U.S. Seminar on "Unsolved Problems in Ionic Polymerization" was held on October 15-19, 1974, in Fuji Hakone, Japan; it was sponsored by the Japan Society for the Promotion of Science and the U.S. National Science Foundation. This was the first seminar on Polymer Synthesis and 13 United States and 20 Japanese polymer chemists attended.

It has been recognized that ionic polymerization is more complicated than radical polymerization, but it is also more versatile for the preparation of new kinds of polymers. One of the reasons is that ionic polymerization is influenced by stereo and sequence regulation; isomerization and grafting may also occur during polymerization.

Vogl reviewed general aspects of ionic polymerization and the polymerization of chloral and related compounds. In cationic polymerization, P. Dreyfuss read the paper of Kennedy on cationic bigrafting of styrene,  $\alpha$ -methylstyrene, or isobutene polymers on bromide and chloride terminated hydrocarbons. Kunitake proposed a mechanism of syndiotactic polyaddition of  $\alpha$ -methylstyrene which takes into account the influence of radius of counteranion on the cationic polymerization.

In ring-opening polymerization, Saegusa described a new alternating copolymerization of oxazoline and acrylic monomer through their addition product which exists as a zwitterion. Litt reported on the polymerization of N-substituted oxazoline and pointed out the sharp increase in the molecular weight of this polymer due to chain branching. M. P. Dreyfus explained the polymerization and oligomerization of cyclic ethers by oxonium intermediates. The ring-opening polymerization of spiro acetals prepared from alkylene oxide and lactone was reported by Bailey, in which volume expansion accompanies the polymerization. Harwood found by careful NMR analysis that the polymerization of N-carboxylic acid anhydride proceeds through a carbamate anion.

In anionic polymerization, Ise described the importance of triple anions as active species for the polymerization of styrene in addition to free anions and ion pairs in mixed solvents such as dimethoxyethane and benzene. Stereoregulation of  $\alpha$ -phenyl as well as  $\alpha$ -methyl acrylate polymerizations were reported by Yuki. Modification of alkylmetal catalyst by ethers and amines was reported by Tsuruta and potassium-substituted compounds of pentadiene derivatives were discussed by Tani. Anionic polymerization of aromatic and heteroaromatic vinyl monomers was reported by Pearson and Iwakura (read by Toda), respectively. Ionic polymerization by radiation was investigated by Hayashi. Lenz reported the NMR study of poly- $\alpha$ -chloroacrylic ester prepared with Grignard reagent as an initiator and proposed a template polymerization.

The mechanism of alternating copolymerization of olefins or diolefins with acrylic monomer in the presence of Lewis acid was discussed by Hirai and Furukawa, emphasizing the importance of donor-acceptor complex intermediates. Stille reported the role of donor-acceptor complexes in the polymerization of vinyl ether or dioxene as donors and quinones or vinylidene cyanide as acceptors.

Polymerizations with transition metal catalysts, particularly alkyl nickel dipyrindyl, was investigated by Yamamoto, and ESR studies of a titanium alkoxide-metal alkyl system was discussed by Takeda. Otsu described the isomerization polymerization of  $\beta$ -olefins which yields polymers of  $\alpha$ -olefins. Calderon reviewed several hypotheses for the metathesis polymerization. Finally, an ionic condensation of aromatic amines with dicarboxylic acid by means of alkyl phosphite was reported by Yamazaki.

All problems discussed are of current interest. Some of them seem to have been solved, but new problems are developing which may be important contributions for the creation of new macromolecules. This seminar contributed significantly to the identification of "Unsolved Problems in Ionic Polymerization," and the discussions shed light for their possible solution.

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