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Introduction

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Introduction

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Ring-opening chain growth polymerization of heterocyclics is an important method for the preparation of polymers with heteroatoms in the polymer chain. These polymers usually have higher molecular weight than condensation polymers obtained by step growth polymerization. Polymers from ethylene oxide, propylene oxide, epichlorohydrin, bis[chloromethyl] oxetane, and trioxane, as well as polyamides and polyesters prepared by ring-opening polymerization have achieved industrial importance. Fundamental studies are necessary to understand the mechanisms by which these polymers are formed, to provide new approaches for the polymerization of new monomers.

POLYMERIZATION MECHANISM

Ring-opening polymerization of heterocyclics is carried out with ionic initiators. Cyclic ethers polymerize with Lewis acid with oxonium cations as an intermediate. Saegusa measured quantitatively the growing oxonium ions in THF polymerization by his phenoxyl end-capping method, derived absolute rate constants and related monomer reactivity with their structure.

Initiators behave differently in initiation and termination and consequently influence initiator activity and degree of polymerization. Further understanding of initiation and termination mechanisms should provide means to control these polymerizations. The coordination of monomers plays an important role in the polymerization of epoxides: this had been demonstrated by studying the polymerization

of asymmetric epoxides. Trioxane can be polymerized cationically by several types of initiation; the mechanism will be discussed by Dr. Enikolopyan.

NEW POLYMERS

Episulfides formally resemble epoxides in their structure although different initiators are used for some episulfide polymerizations. Dr. Lautenschlarger's review will discuss this phenomenon.

Fluoroepoxides are a novel class of epoxides which were prepared from fluoro-olefins. Fluoroepoxides polymerize anionically with fluoride ions as the initiator. The properties of such polymers are of interest because perfluoro polymers show great stability towards radical and ionic degradation as we will hear from Dr. Eleuterio.

Lactams and lactones are not new monomers, but they are industrially very important. High molecular weight polyamides and polyesters can be made from them under moderate polymerization conditions. The polymerization of lactams was known to be initiated by anionic and cationic initiators, but the detailed polymerization mechanisms have not been well understood. Dr. Sebenda will illuminate this problem on the basis of his newest research.

Lactones have been investigated intensively by Dr. Brode and others for the industrial preparation of polyesters, especially the polymers of ϵ-caprolactone. Although polycaprolactone is an aliphatic polyester, a group of polymers not widely used industrially as high molecular polymers, it has now achieved industrial importance.

Dr. Cherdron will give a lecture on new trioxane copolymers which are very important engineering plastics. Several polymer properties, especially thermal and oxidative stability, processability and dyeing properties can be modified by copolymerization of trioxane with appropriate comonomers.

FUTURE PROBLEMS

Ring-opening polymerization has become a useful technique for the preparation of new polymers. It is starting to rival radical and ionic polymerizations of vinyl monomers as well as the polymerization of hydrocarbon monomers by coordination initiators in importance.

There are, however, many unsolved problems in the ring-opening polymerization of heterocyclics, e.g., the alternate ring-opening copolymerization and the copolymerizations of cyclic monomers with other types of monomers such as olefins, diolefins, and vinyl

monomers. The preparation of cyclic oligomer may be important in relation to enzyme-like substances, because some macrocyclic compounds have attracted the attention of biochemists.