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Polymers with Special Properties Through Ordered Structures

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10. Stirring optional, may be useful in large (> 100 L) reactors; boiling liquid N_2 provides agitation and a reduction of the average density of the charge.

In view of these characteristics, the Leidenfrost reactor was adopted for low-temperature polymerization of isobutylene and copolymerization of isobutylene-isoprene (butyl rubber) charges.

POLYMERS WITH SPECIAL PROPERTIES THROUGH ORDERED STRUCTURES

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The material properties of polymers depend on both the structure and morphology of the bulk polymer and on the primary structure of the macromolecules. It is a challenge to specifically control the supermolecular structure of polymeric systems by the architecture of the individual macromolecule as it is realized, for example, in biopolymers.

Macromolecules in which two different monomer units are always linked in the same way and alternate in a regular fashion along the chain are one example of polymers with tailored structures and thus materials with special properties. Access to such alternating copolymers has been considerably expanded by the concept of modifying the reactivity ratio of a comonomer pair through complexation of one of the comonomers by a third nonpolymerizable component. Aspects of polymer synthesis and tailoring of macromolecules by terpolymerization are touched on; the special properties of these ordered polymer molecules are illustrated with several examples for copolymers based on acrylics and olefins.

Segmented block copolymers with an alternating sequence of two different blocks along the chain, where either one or both blocks are characterized by distinct length, are another class of polymer materials

with interesting properties. The chain architecture can be controlled first by a stepwise building of the individual segments (telechelics of regular constitution and uniform length), which are linked in a subsequent polyreaction to yield the multiblock copolymer. The differences in the chemical structure of the segments result in multiphase polymer systems, and the supermolecular structure can be influenced by both the segment length distribution and the variation of specific constitutive units in the segments. The effects of the variation on the chain architecture on the superstructure and thus the material properties are discussed with the example of segmented polyurethane elastomers with tailored primarily structure.

POLYMERIZATION OF LACTAMS

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The interesting results of the study of lactam polymerization (2-pyrrolidone, ϵ-caprolactam, η-capryloctam) at the Department of Polymers of the Prague Institute of Chemical Technology are presented.

With regard to the anionic polymerization of 2-pyrolidone, the scheme of fundamental steps is summarized and unexpected results are discussed: (a) thermal degradation of poly(2-pyrrolidone), (b) influence of transient cooling of polymerization mixture on the course of polymerization, and (c) polymerization accelerated with *N*-iminolactam.

In the case of anionic polymerization of ϵ-capralactam, the industrial application of continuous anionic polymerization is mentioned. The aim of the synthesis of block copolymers of polyamides is to improve the toughness of material. The results of preparation of poly(ϵ-caprolactam)-polybutadiene block copolymers and their mechanical properties illustrate the possibilities of the described method.

Autopolymerization of η-caprylolactam is an example of noncatalyzed polymerization of lactams; the mechanism is discussed.