

Synthesis of Ultra-High-Molecular-Weight Polyacrylonitrile by Anionic Polymerization

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Abstract—The anionic polymerization of acrylonitrile in DMF initiated by lithium 1,2-bis(diethylamino)-2-oxoethanolate in the range -60 to 0°C has been studied. The initiator efficiency at low temperatures (-60 to -40°C) is 2–6%; it remains nearly invariable with conversion owing to the associated state of the initiator. The low concentration of growing active centers is constant throughout the process; as a result, polymers with $M > 3 \times 10^5$ are produced. The polymers are characterized by a narrow molecular-mass distribution, $M_w/M_n = 1.3$ – 1.6 , and contain insignificant amounts of low-molecular-mass fractions. It has been shown that controlled polymerization processes can be carried out at moderately low temperatures (-30 to 0°C), and experimental conditions for freezing of polymerization and its recommencement have been ascertained. Optimum conditions for the synthesis of a high-molecular-mass polyacrylonitrile with $M > 3 \times 10^5$ have been established, and the method for preparing polymers with $M = (6.50$ – $8.5) \times 10^5$ on an enlarged scale using high concentrations of the monomer has been developed.

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