Title	ストップフロー重合法を用いた新規オレフィンブロックコポリマーの合成それらを応用したMgCl2担持型チーグラー触媒における立体特異的活性種の解析
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Stopped-Flow Polymerization Method for Synthesis of Novel Olefin Block Copolymer and Its Application for Investigation of Stereospecific Active Sites on MgCl2-Supported Ziegler Catalyst

Mikio Yamahiro

School of Materials Science,
Japan Advanced Institute of Science and Technology

(Supervised by Prof. Dr. Minoru Terano)

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Abstract

This dissertation describes the modified stopped-flow polymerization method for the synthesis of polypropene-block-poly(ethene-co-propene) (PP-b-(PE-co-PP)), and its application for the investigation of stereospecific active sites on MgCl2-supported Ziegler catalyst. The commercial polypropene (PP) can be usually divided into three grades, that is homopolymer, random copolymer, and block-type copolymer. Among them, block-type copolymer increases its importance because of the high performance. It should be noted that poly(ethylene-co-propylene) (PE-co-PP) is not chemically linked with PP in the block-type copolymer which can be regarded as a complicated composite of PP, PE-co-PP, and polyethene because of rapid chain transfer reaction. Therefore, synthesis of the exact block copolymer is impossible by the industrial polymerization process. The stopped-flow polymerization method, by which a reaction can be carried out within an extremely short period, has been extensively applied to various kinds of investigations of olefin polymerization using MgCl2-supported Ziegler catalysts. This method is exceedingly useful for estimating the accurate kinetic parameters for the olefin polymerization because the states of the active sites are stable without time-dependent change within this extremely short period. First approach for the application of a stopped-flow polymerization method for the synthesis of PP-b-(PE-co-PP) was investigated in terms of the design and synthesis of novel polyolefins having a well-defined structure. The synthesis of PP-b-(PE-co-PP) was carried out using the stopped-flow polymerization method without unfavorable side reaction. The results from gel permeation chromatography, cross fractionation chromatography, 13C NMR, differential scanning calorimetry, and phase-contrast microscopy consistently indicate not only the formation of the exact block copolymer with a chemical linkage between the PP block and the PE-co-PP block, but also the regulation of the crystalline morphology in the block copolymer by changing the composition of each block part. Further the synthesis of block copolymer having higher isotacticity of PP segment as well as its having controlled molecular weight were achieved by choosing suitable

polymerization conditions. Thermal behavior and mechanical properties of the resulting PP-b-(PE-co-PP) also supported the formation of exact block copolymer. Further PP/PE-co-PP blend containing PP-b-(PE-co-PP) was much different from that of the corresponding blends. Kinetic investigation of ethene-propene copolymerization on each stereospecific active sites based on the characterization of fractionated PP-b-(PE-co-PP) was conducted by using temperature rising elution fractionation (TREF). The kinetic results exhibit the stereospecificity of the active sites does not affect the reactivity of ethene during the initial copolymerization stage. The stopped-flow polymerization method combined with TREF technique is believed to be useful for an understanding the nature of active sites and the correlation to the olefin copolymerization. PP-b-(PE-co-PP) obtained in this study is considered to be one of the most promising materials for a toughening agent as well as a low-temperature brittleness-resistant thermoplastic elastomer, which can open new areas of application for the polyolefins.

Publication list

[1] M. Yamahiro,H. Mori, K. Nitta, M. Terano : "Synthesis and basic characteristics of polypropene-block-poly(ethene-co-propene) by modified stopped-flow polymerization with MgCl2-supported Ziegler catalyst" *Macromol. Chem. Phys.* **200**,134 (1999).

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