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著者(和文)	KIM HAMIN
Author(English)	Hamin Kim
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論文要約

Anionic Self-Alternating Polymerization of Asymmetric Difunctional Monomer Containing Styrene and 1,1-Diphenylethylene Frameworks

HAMIN KIM

Anionic copolymerization of styrene (St) and 1,1-diphenylethylene (DPE) is known to provide a copolymer in which St and DPE arranged in alternating fashion, where the non-homopolymerizable property of DPE serves as important factor to achieve the alternating copolymerization. This unique copolymerization behavior has inspired a novel perspective to give a sequence-controlled homopolymer. If the St (A) and DPE (B) frameworks consist of a single molecular structure as a polymerizable functional groups, its anionic polymerization may also yield a polymer with a controlled sequence of the main chain. This main chain would comprise two polymerized units of St and DPE frameworks, while the unreacted St and DPE frameworks would remain in every monomeric unit as residues along the main chain.

To investigate this suggested perspective, 4-vinyl-1,1-diphenylethylene (**VPDE**) was synthesized, and anionic polymerization of **VDPE** was conducted under various polymerization conditions. Soluble and well-defined poly(**VDPE**) could be obtained without any concerned side reactions, such as intermolecular chain branching, which is often observed in the polymerization of divinyl monomers. The ^{1}H NMR spectrum of the poly(**VDPE**) showed remaining proton peaks associated with carbon-carbon double bonds, which were assigned to the residues of each polymerized St and DPE frameworks. By estimating the proton signal of each residue, it could be evaluated that almost equal amounts of polymerized units of the A and B were derived, indicating the formation of an $(AB)_n$-type sequence homopolymer. This result is attributed to the strictly limited non-homopolymerizable property of the DPE framework. Various evidences supporting the participation of the DPE framework in the polymerization were presented using prepared model polymers, and these findings once again demonstrated the formation of the $(AB)_n$-type sequence homopolymer. To describe the synthesis of this new type of sequence-controlled homopolymer, an intermolecular cross-propagation polymerization mechanism was proposed. The higher electrophilicity of the DPE framework compared to that of the St framework is considered the driving force for achieving the controlled sequence, and the reaction step involving the selective cross-propagation to the St framework from the very stable DPE framework carbanion determines the polymerization rate in this proposed mechanism. This unique polymerization mechanism, capable of affording the sequence-controlled homopolymer, has been newly established

under the term of “Anionic self-alternating polymerization”.

Substituent effect was also investigated. Due to the entirely extended π-conjugation system of **VDPE** molecules, it was anticipated that the electronic effect of substituents on the DPE skeleton would influence both the reactivities of the monomer and its generated carbanion. To explore this aspect, several **VDPE** derivatives with substituents, including electron withdrawing group of chloro (**Cl**) or donating groups of methyl, methoxy and dimethylamino (**NMe2**) on the DPE skeleton, were newly synthesized and then subjected to the anionic polymerization. Although these polymerizations yielded soluble and well-defined polymers, notable differences in the polymerization rate were observed depending on the introduced substituent. The relationship of the estimated electron density, measured by the beta carbon chemical shift of carbon-carbon double bonds on the St and DPE frameworks of **VDEP** derivatives, and the polymerization rate according to the reported Hammett parameters showed a confined and effective substituent effect on the DPE framework. This indicates that the polymerization behavior of **VDPE** derivatives may be governed by the reactivity of the DPE framework. The evaluation of the sequences of the synthesized polymers could support this assumption well. Especially, the polymerization of **Cl** synthesized a polymer carrying only an odd-numbered degree of polymerization, which can be interpreted as the formation of a perfect alternating $(AB)_n$-type sequence by achieving both selective initiation to the DPE framework and an exclusive DPE-type terminal. In contrast, the polymerization of **NMe2** largely deviated from the proposed polymerization anionic self-alternating polymerization of **Cl**. Due to the relatively strong electron-donating nature of the dimethylamino substituent, the decreased electrophilicity of the DPE framework resulted in St framework chemoselective polymerization, affording an $(A)_n$-type sequence. Thus, it has been revealed that the substituents on the DPE framework significantly affect the polymerization modes by tuning the electron density of the π-conjugation system.

To investigate the effect of the substituted position of the vinyl group on the anionic polymerization behavior of **VDPE**, 3-vinyl (***m*-H**) and 2-vinyl-1,1-diphenylethylene (***o*-H**) were also subjected to the anionic polymerization system. While ***m*-H** was evaluated to construct the $(AB)_n$-type sequence through the anionic self-alternating polymerization mechanism similar to the polymerization of **H**, the anionic polymerization of ***o*-H** exhibited distinct polymerization behavior compared to that of other **VDPE** derivatives. Although the predictable molecular weight of poly(***o*-H**) was synthesized without the intermolecular side-branching reactions, the ^{1}H NMR spectrum showed a negligible proton signal of the carbon-carbon double bonds. It is believed that ***o*-H** undergoes an anionic polymerization process that differs significantly from that of **H** and ***m*-H**. The possible mechanism involves successive intramolecular and intermolecular addition reactions that form an annular main chain.