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著者(和文)	KIM HAMIN
Author(English)	Hamin Kim
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論 文 要 旨

THESIS SUMMARY

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学生氏名： Student's Name	HAMIN KIM	指導教員（主）： Academic Supervisor(main)	石曽根 隆
		指導教員（副）： Academic Supervisor(sub)	

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

The title of this thesis is "Anionic Self-Alternating Polymerization of Asymmetric Difunctional Monomer Containing Styrene and 1,1-Diphenylethylene Frameworks" and it is structured into a total of five chapters.

In Chapter 1, "General Introduction", the significance of sequence in polymer is emphasized, providing a comprehensive overview of the synthesis examples and methods about sequence-controlled polymer. Specifically, it is focused on that anionic copolymerization of styrene (St, A) and 1,1-diphenylethylene (DPE, B). This copolymerization is known to provide a copolymer in which St and DPE arranged in alternating fashion, where the non-homopolymerizable DPE serves as important factor to achieve the alternating, $(AB)_n$-type, sequence. Based on this unique copolymerization behavior, a novel perspective to give a sequence-controlled homopolymer is suggested. An asymmetric difunctional monomer containing St and DPE frameworks, 4-vinyl-1,1-diphenylethylene (**VDPE**), is newly designed, and its polymerization is anticipated to yield a homopolymer with $(AB)_n$-type sequenced main chain through the polymerization mechanism of an intermolecular cross-propagation reaction.

In Chapter 2, "Anionic Self-alternating Polymerization of **VDPE**", to investigate the suggested perspective, anionic polymerization of the synthesized **VDPE** was conducted under various conditions. Soluble and linear poly(**VDPE**) with the designed molecular weight and narrow molecular weight distribution is resulted. Structural analysis of poly(**VDPE**) using ^{1}H NMR measurement indicates the presence of remaining carbon-carbon double bonds, assigned to the residues of both frameworks of St and DPE. The evaluation suggests nearly equal amounts of polymerized units from

St and DPE frameworks, indicating the formation of the $(AB)_n$-type sequenced homopolymer, given that the limited homopolymerizable property of the DPE framework. A detailed interpretation of the unique structure of poly(**VDPE**) is achieved through the polymerization of a partially deuterated **VDPE** derivative, hydrogenation reaction of residual double-bonds, and the synthesis of various model polymers. The proposed mechanism for producing this new type of sequence-controlled homopolymer involves an intermolecular cross-propagation reaction. The higher electrophilicity of the double bond of DPE framework, compared to that of the St framework, is considered the driving force for achieving controlled sequence, and the reaction step involving the selective cross-propagation to the double bond of the St framework from the π-stabilized DPE framework carbanion is identified as rate-determining step. This unique polymerization mechanism, capable of affording the sequence-controlled homopolymer, is newly established under the term of "Anionic self-alternating polymerization".

In Chapter 3, "Substituent Effect on Anionic Polymerization of **VDPE** derivatives", the influence of substituents on the anionic polymerization behavior of **VDPE** derivatives is examined. Specifically, derivatives with electron-withdrawing chloro or electron-donating methyl, methoxy, and dimethylamino groups introduced at the *para*-position of the DPE framework are investigated. The polymerization rate of **VDPE** derivatives shows a strong correlation with Hammett parameters, suggesting that the nucleophilicity of the DPE framework carbanion determines the polymerization rate. Structural analysis of the resulting polymers revealed that, when chloro, methyl, and methoxy substituents are present, the same anionic self-alternating polymerization as **VDPE** occurs. Notably, in the case of the chloro substituent, only polymers corresponding to an odd-numbered degree of polymerization are produced, indicating selective initiation to the DPE framework due to the effect of chloro substituent. The combination of two factors, the selective initiation and selective cross-propagation, results in the formation of a perfectly $(AB)_n$-type sequenced homopolymer, represented by the odd-numbered degree of polymerization. In contrast, the polymerization of the **VDPE** derivative containing a strong electron-donating dimethylamino group results in a chemoselective polymerization of the St framework, leading to the formation of $(A)_n$-type sequenced

polymer.

In Chapter 4, “Anionic Polymerization of *meta*- and *ortho*- Isomers of **VDPE**”, the impact of the substituted position of the vinyl group on the anionic polymerization behavior of **VDPE** is investigated. The anionic polymerization of the *meta*-isomer of **VDPE** displays similar polymerization behavior to **VDPE**, resulting in the formation of $(AB)_n$-type sequenced homopolymer. In contrast, anionic polymerization of *ortho*-isomer leads to the formation of a polymer containing an indane-type annular structure. This polymer is characterized by a 70~80% annular structure, distinct from other constitutional isomers, attributed to the involvement of an intramolecular cyclization reaction.

In Chapter 5, “Conclusion”, the results throughout this thesis are summarized and discussed. The primary contribution of this study is the establishment of a novel polymerization pathway and elucidation of a special polymerization mechanism. This pathway allows for the synthesis of sequence-controlled homopolymer through the anionic polymerization of **VDPE** derivatives, which are asymmetric difunctional monomers containing St and DPE frameworks.