

博士論文 (要約)

Development of chain-growth supramolecular polymerization and related studies

(連鎖成長リビング超分子重合の開発と関連研究)

姜志亨

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Introduction

Since Staudinger experimentally proved the existence of covalent macromolecular chains in the late 1920s, after a long debate on the controversial concept of colloidal aggregates, numerous essential achievements in the field of polymer science have precipitated major innovations in everyday life. In the late 1980s, alongside significant progress in the field of non-covalent chemistry, research groups led by Lehn and Meijer breathed life into the controversial concept of colloidal aggregates. These authors demonstrated that linear aggregates, *i.e.*, supramolecular polymers, of small molecules that are tailored by complementary hydrogen bonding (H-bonding) interactions, are sufficiently stable even in dilute solution and behave like covalent linear polymers under appropriate conditions. With a view to reduce the dynamic nature of supramolecular polymerization, Manners and coworkers reported in 2007 a strategy utilizing crystallizable monomers upon self-assembly and successfully obtained well-defined block copolymers. This achievement, together with some related works reported later, indicated several new possibilities of supramolecular polymerization in the context of precision macromolecular engineering. However, because of the preconceived notion that supramolecular polymerization mechanistically follows step-growth polymerization (Fig. 1A, upper), a challenge to realize noncovalent ‘chain-growth’ polymerization has received little attention until recently. Encouraging reports to this end utilized thermally chopped supramolecular polymers as seeds for non-covalently polymerizing their monomers, where time-dependent elongation of polymer chains were observed by atomic force microscopy (AFM) and/or transmission electron microscopy (TEM). Nevertheless, even at this stage, no strategic rationale has been proposed for achieving chain-growth supramolecular polymerization (Fig. 1A, lower). In contrast with step-growth polymerization, chain-growth polymerization utilizes monomers that do not polymerize spontaneously without initiators. However, to the best of our knowledge, such monomers have yet to be reported for supramolecular polymerization.

Over the last decade, significant progress in supramolecular polymerization has had a substantial impact on the design of functional soft materials. In contrast with soft materials designed by only covalent crosslinking, supramolecular soft materials can exhibit new functions derived from their dynamic nature for example, self-healing, exceptional toughness, recyclability and responsiveness to external stimuli. Therefore, if chain-growth supramolecular polymerization were realized, a paradigm shift in precision macromolecular engineering for development of soft materials would be expected.

A rational strategy for the realization of chain-growth supramolecular polymerization

As described in Introduction, the author aimed at designing a metastable monomer that is temporarily disabled for spontaneous polymerization in the absence of initiators. It was found that a particular C_5 -symmetric corannulene derivative (**M**) with five amide-appended thioalkyl side chains (Figs 1B and 1C) can be molecularly dispersed in methylcyclohexane solution without any spontaneous polymerization through the formation of intra-molecular h-bonding network. Importantly, monomer **M** can one-dimensionally polymerize upon heating since polymeric state (inter-molecular h-bonding network)

is thermodynamically more stable than monomeric state (intra-molecular h-bonding network). Inspired by the unique behavior of monomer **M**, the author also designed initiator **I** by simple methylation of amide groups of monomer **M**, which is ineligible for intramolecular H-bonding and does not self-assemble, but serves as a proton-acceptor for H-bonding interactions (Figs 1B and 1C).

To confirm chain-growth supramolecular polymerization with monomer **M** and initiator **I**, the author performed experiments as below. As a typical example of the polymerization, a solution of **I** (1.0 mM) in MCHex (10 μ L) was added to a solution of **M** (1.0 mM) in MCHex (5 mL), and the mixture was allowed to stand at 25 $^{\circ}$ C for 6 hours, during which **M** gradually transformed into a supramolecular polymer with a small polydispersity index (PDI). Noteworthy, using MCHex/ CHCl_3 (1/1 v/v) as eluent at 4 $^{\circ}$ C, size-exclusion chromatography (SEC) with a polystyrene gel column could be used for tracing the chain growth process in this multi-stage polymerization. As shown in Fig. 2A, the elution peak of the produced polymer, though exhibiting slight broadening, shifted stepwise toward a higher molecular weight region. The average degrees of polymerization (D_p) of the polymers formed at individual stages, as estimated using polystyrene standards for calibration, were in a linear relationship over a wide range with the total monomer-to-initiator mole ratios ($[\mathbf{M}]_{\text{total}}/[\mathbf{I}]_0$) employed (Fig. 2B, filled circles). Equally important, the PDI values of the

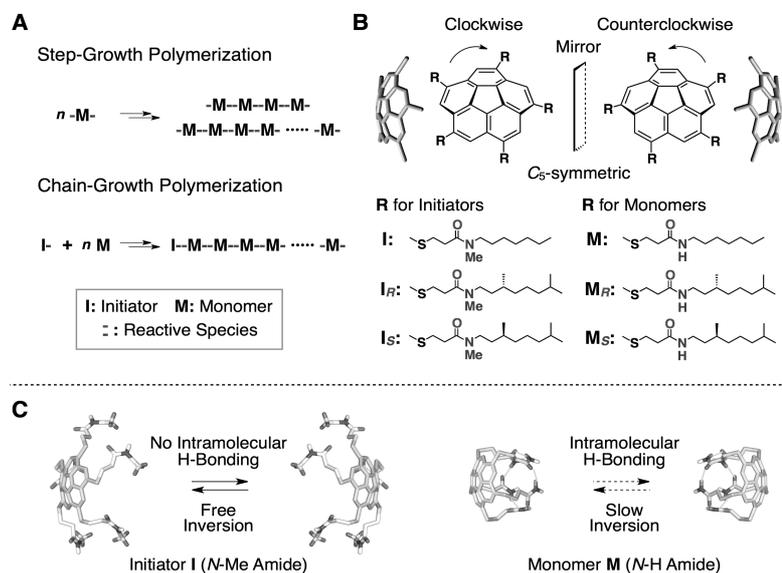


Figure 1. (A) Schematic representations of step-growth and chain-growth polymerizations. (B) Chemical structures of C_5 -symmetric corannulene-based chiral initiators and monomers carrying amide-appended side chains. (C) Schematic representations of the conformational and configurational aspects of the initiator and monomer families.

polymers were all determined to lie in the range of 1.2–1.3 (Fig. 2b, filled squares), which is much smaller than that for a polymer formed upon heating without initiator **I**.

Stereoselective polymerization using chiral initiators has been a primary issue in the field of covalent chain-growth polymerization. The author was motivated to investigate this possibility in noncovalent manner, because our polymerization system is the first example that consists of the defined initiation step. Unlike **M**, compounds **M_R** and **M_S**, together with their respective *N*-methylated derivatives **I_R** and **I_S** (Fig. 1B), carry chiral side chains, each chain having a stereogenic center in proximity to the H-bonding amide unit. It was found that **M_R** and **M_S** polymerize in a precise stereoselective manner using **I_R** and **I_S**, respectively, as chiral initiators (Fig. 3A). For example, when **I_R** was added at 25 °C to a MCHex solution of **M_R** at $[M_R]_0/[I_R]_0 = 500$, **M_R** polymerized in the same way as **M**, thereby yielding a polymer with a small PDI in 6 hours. In stark contrast, the opposite enantiomer **M_S** did not polymerize with **I_R** even with a prolonged reaction time, whereas it polymerized readily upon mixing with initiator **I_S** (Fig. 3A). Namely, the polymerization occurs only when the stereogenic centers of the monomer and initiator in their chiral side chains are identical in configuration to one another. The precise stereoselection indicates a large energetic penalty for stereochemical mismatching in the sequence. Interestingly, the author found that **M_{rac}**, a racemic mixture of **M_R** and **M_S**, can be optically resolved by polymerization using **I_R** or **I_S** as the initiator (Figs 3B and 3C).

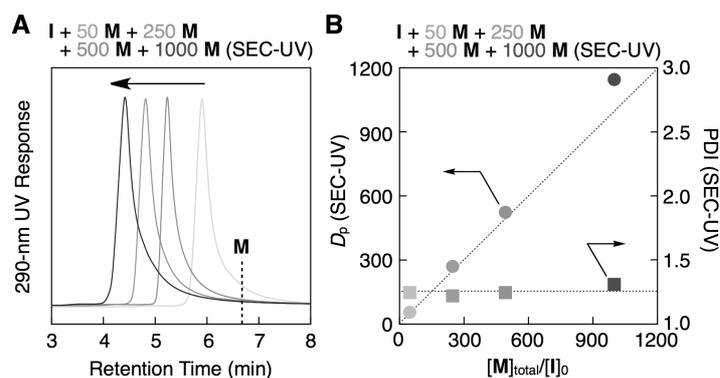


Figure 3. (A) SEC traces of polymers formed at $[M]_{total}/[I]_0 = 50, 250, 500$, and 1000, monitored using an UV detector at 290 nm. A broken line represents the peak-top position of **M**. (B) Plots of the D_p and polydispersity indexes (PDI) versus $[M]_{total}/[I]_0$, estimated from the SEC-UV traces using polystyrene standards for calibration.

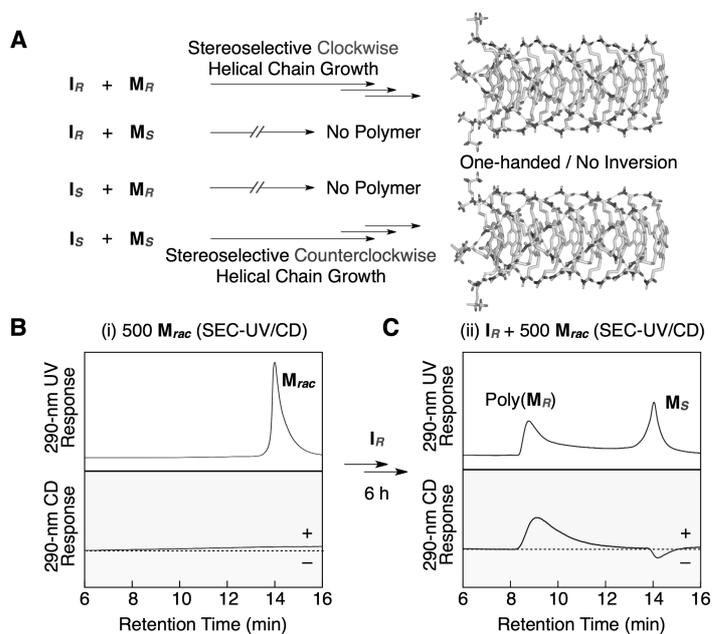


Figure 2. (A) Schematic representation of the stereoselective chain-growth supramolecular polymerization of monomers **M_R** and **M_S** with initiators **I_R** and **I_S**, respectively, where the monomers and initiators both carry chiral side chains. The polymerization proceeds only when the absolute configurations of their side-chain stereogenic centers are identical to one another. (B) SEC-UV and (C) SEC-CD traces at 290 nm of **M_{rac}** and its polymerized mixture initiated with **I_R** at $[M_{rac}]_0/[I_R]_0 = 500$ in MCHex at 25 °C for 6 hours.

The author presumes that the chain growth proceeds through an H-bond-assisted transition state, where **M** is preorganized with the growing end of the polymer as well as initiator **I**, both having free amide C=O groups and transforms its H-bonding mode from intra-molecular to inter-molecular (Fig. 4). The transition state is energetically less demanding than self-cleavage of the H-bonded amide network in the monomer for opening its conformation.

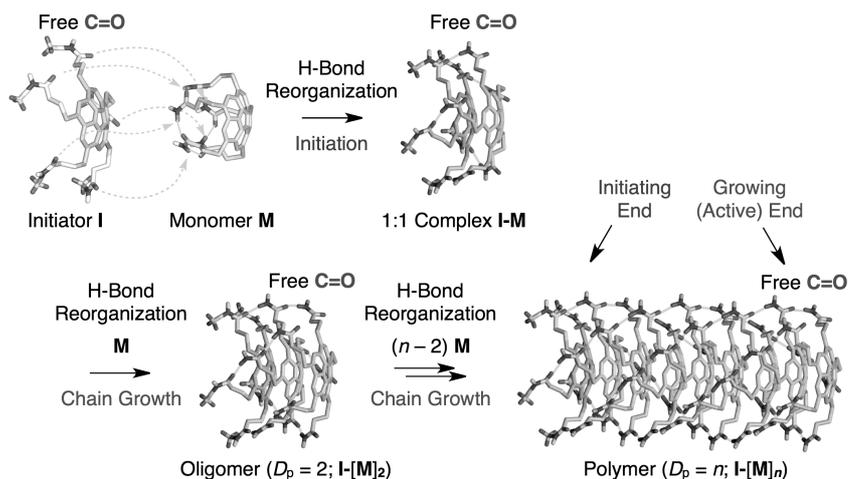


Figure 4. A schematic representation of the chain-growth supramolecular polymerization of monomer **M** initiated with **I**, where the chain-growth is accompanied by the H-bond reorganization of **M**.

Summary

The author succeeded in developing a rational strategy for the realization of chain-growth supramolecular polymerization^{1,2}. The key of the success is the design of metastable monomer and initiator. The supramolecular system developed by the author enabled perfect control of molecular weight of one-dimensional supramolecular polymer with small polydispersity. In addition, it was found that polymerization took place in perfect stereo-selective manner. With lessons from development of chain-growth supramolecular polymerization, the author developed extremely tough self-healing elastomer through supramolecular polymerization³.

[1] J. Kang, D. Miyajima, Y. Itoh, T. Mori, H. Tanaka, M. Yamauchi, Y. Inoue, S. Harada, T. Aida, *J. Am. Chem. Soc.* **2014**, 136, 10640

[2] J. Kang, D. Miyajima, T. Mori, Y. Inoue, Y. Itoh, T. Aida, *Science*. **2015**, 347, 646

[3] J. Kang, *et al.* Under review.