

論文の内容の要旨

論文題目 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)

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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 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 \mathbf{M}_R and \mathbf{M}_S polymerize in a precise stereoselective manner using \mathbf{I}_R and \mathbf{I}_S , respectively, as chiral initiators (Fig. 3A). For example, when \mathbf{I}_R was added at 25 °C to a MCHex solution of \mathbf{M}_R at $[\mathbf{M}_R]_0/[\mathbf{I}_R]_0 = 500$, \mathbf{M}_R polymerized in the same way as \mathbf{M} , thereby yielding a polymer with a small PDI in 6 hours. In stark contrast, the opposite enantiomer \mathbf{M}_S did not polymerize with \mathbf{I}_R even with a prolonged reaction time, whereas it polymerized readily upon mixing with initiator \mathbf{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 \mathbf{M}_{rac} , a racemic mixture of \mathbf{M}_R and \mathbf{M}_S , can be optically resolved by polymerization using \mathbf{I}_R or \mathbf{I}_S as the initiator (Figs 3B and 3C).

The author presumes that the chain growth proceeds through an H-bond-assisted transition state, where \mathbf{M} is preorganized with the growing end of the polymer as well as initiator \mathbf{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.

Tough self-healing elastomer from supramolecular polymerization

The author succeeded in developing an extremely tough and autonomously self-healable elastomer formed by supramolecular polymerization. Supramolecular elastomer has been expected to exhibit unique mechanical properties such as self-healability, which cannot be accessed by conventional elastomer based on covalently cross-linked polymer chains. However, since most previously reported stretchable self-healing materials are based on weak dynamic bonds, they easily break around damaged locations and are susceptible to fatigue under large deformation due to weak mechanical strength and low fracture toughness. Their weak mechanical properties have limited their applications. Up to date, design strategy for tough self-healing elastomer using supramolecular chemistry has not been proposed and remained challenging.

Recently, significantly toughened elastomers with improved stretchability have been realized by incorporating sacrificial bonds within a triple network. However, rupturing of the sacrificial network results in 'irreversible' damage to the elastomer after the initial stretch. To enable recoverable mechanical properties, a reversible energy dissipation mechanism is needed. Indeed, such a concept has been used for tough hydrogel designs and is only recently applied to other elastomers. For example, Guan *et al.* introduced non-covalent sacrificial bonds into a covalent polymer network and observed significantly enhanced ductility and toughness. Holten-Andersen *et al.* reported a design concept of combining two types of metal-ligand crosslinks to control polymer network mechanical properties. Such a reversible energy dissipation system is also needed for autonomous self-healing. The author developed a markedly enhanced self-healing elastomer by strategically tuning the ratio of strong and weak

cross-linking hydrogen bonds in supramolecular structure that exhibits superior mechanical properties in stretchability, toughness and self-healability.

From results described in Chapter 1, the author learned the lessons that multiple h-bonding bonds can serve as a strong non-covalent bond comparable to covalent bond and supramolecular polymerization can be selectively formed by elaborate molecular designs. The author designed a series of polydimethylsiloxane (PDMS) polymers with various ratios of 4,4'-methylenebis(phenyl urea) (MPU) and isophorone bisurea units (IU) (Fig. 5). All the **PDMS-MPU_x-IU_{1-x}** polymers form colorless and transparent film by supramolecular polymerization. Resultant film can be stretched to 16 times its original length at a loading rate of 20 mm/min (200%/min) without rupturing. Most remarkably, the polymer film was able to achieve notch-insensitive stretching up to 1200% strain, demonstrating its exceptional toughness (Fig. 6).

The author hypothesizes that the origin of the remarkable mechanical properties of the **PDMS-MPU_x-IU_{1-x}** may be due to the different crosslink strength of MPU and IU. The MPU units are able to form quadruple hydrogen bonding in a cooperative manner with counter MPU units whereas the IU units can only form maximum dual hydrogen bonding with another IU unit due to the steric hindrance from the isophorone moieties (Fig. 5C). The multivalent effect hence results in MPU-MPU interaction being much stronger than IU-IU interaction, such that the MPU-MPU cross-linking can better hold the elastomer together to impart elasticity. In particular, **PDMS-MPU_{0.4}-IU_{0.6}** film could dissipate strain energy efficiently (Fig. 5B). If the polymer film was first allowed to rest for 30 minutes and stretched again, the stress-strain curves recovered completely. Remarkably, **PDMS-MPU_{0.4}-IU_{0.6}** film exhibits notch-insensitive stretching and a record-high fracture energy (~12,000 J/m²) among reported intrinsically tough materials as well as self-healing polymers. In addition, since all crosslinking bonds are based on dynamic h-bondings and T_g of polymer film is below 0 °C, **PDMS-MPU_{0.4}-IU_{0.6}** film exhibits autonomous self-healing property (Fig. 6D).

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.