Switchable Polymer Materials Controlled by Rotaxane Macromolecular Switches

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ABSTRACT: The synthesis and dynamic nature of macromolecular systems controlled by rotaxane macromolecular switches are introduced to discuss the significance of rotaxane linking of polymer chains and its topological switching. Macromolecular switches have been synthesized from macromolecular [2]-rotaxanes (M2Rs) using sec-ammonium salt/crown ether couples. The successful synthesis of M2Rs possessing a single polymer axle and one crown ether wheel, constituting a key component of the macromolecular switch, has allowed us to develop various unique applications such as the development of topology-transformable polymers. Polymer topological transformations (e.g., linear−star and linear−cyclic) are achieved using rotaxane-linked polymers and rotaxane macromolecular switches. The pronounced dynamic nature of these polymer systems is sufficiently interesting to design sophisticated stimuli-responsive molecules, polymers, and materials.

1. INTRODUCTION

Stimuli-responsive events at the molecular level are universal and observed in nature in biosystems. Various stimuli-responsive molecules and materials, which are also developed in artificial systems, produce a change in self-organization or assembly state and eventually produce a change in function and properties. In organic molecules and materials, particularly soft materials such as polymers, this process is driven by chemical and/or physical changes as a response to a stimulus. For instance, considerable changes in properties frequently occur as a result of the formation of assembled domains of carboxylic acid groups located at the polymer terminals when a polymer with a tert-butyl ester group at its terminals changes its terminal structure to a carboxylic acid group through thermal decomposition. This technique is frequently used. Meanwhile, if the stimulus-responsive function is reversible, the function is called a “switch” and can produce a reversible function or property change. For example, in liquid crystals with azobenzene units, the liquid-crystalline phase can be changed by its photoreversible cis–trans isomerization to achieve reversible control of the properties. This class of artificial polymeric materials that produce a reversible bulk property change are very important because they can provide basic materials for manufacturing various dynamic materials and devices. Polymer systems that are characterized by a reversible change in the secondary polymer structure and accompanied by a chirality change (e.g., helical inversion) can be categorized as molecular switches. A good example of the actual function/property change is provided by the chiral column developed by Maeda, Yashima, and co-workers. They determined that the stationary phase of the column considerably changes its affinity toward the enantiomers when its helical handedness in the column is changed by the addition of a chiral compound (stimulus) before the separation. Meanwhile, poly(N-isopropylacrylamide) showing a lower critical solution temperature (LCST) is a typical stimuli-responsive polymer that undergoes a thermal phase transition by a change in the assembly state depending on the temperature. This type of polymer can be categorized as a polymer that displays its response by changing the secondary or assembly structure.

Among the polymer systems exhibiting reversible structure changes, the mutual structure transformation of polymers with different topologies is typically impossible because most polymers maintain their structures with covalent bonds. Although so-called supramolecular polymers are sufficiently structurally soft to change their structure due to the weak intermolecular interactions between the monomer units, their actual use is limited because of their lower stability under normal conditions. Therefore, the realization of structure transformation and/or reversible transformation between such structure- or topology-different polymers allows us to create infinitely diverse dynamic polymer systems.

The rotaxane molecular switch is exceptional compared with many molecular switches such as azobenzene. A chemical bond is not required between the mechanically linked rotaxane components as switching units. In addition to the structural characteristics, the stability of rotaxanes is remarkably high. Specifically, it is not possible to break the mechanical bond to release the components off the rotaxane molecule unless the applied energy is high enough to break a covalent bond, whereas...
the freedom of mobility of the components is sufficiently high, such as that in supramolecules. The relative position of the components can be reversibly changed if the attractive interaction between the components can be controlled by an appropriate stimulus. To date, various rotaxane molecular switches have been reported. Figure 1 shows that the general simple rotaxane switch consists of a rotaxane axle component with two stations having different levels of attractive interactions with the wheel component; the attractive interaction is sufficiently strong to fix the position of the wheel component at the station but can be controlled by the proper stimulus to make the rotaxane switch. Specifically, the rotaxane molecular switch should have sufficient component mobility for switching, where two stable localized states require two different stimuli.

The fascinating and extraordinary feature of the rotaxane molecular switch is that there is no limit to the length of the axle component because of the gentle “mechanical” binding of the wheel and axle components. This feature clearly indicates that the long-range switches, or macromolecular switches, can be similarly fabricated (Figure 2). In general, it is difficult to prepare such long-range switching systems. Therefore, it is essential to clarify the significance of the macromolecular switch or the usefulness of the rotaxane-structured switch. In this Outlook, we describe the interesting reversible stimuli-responsive dynamic polymer systems produced by rotaxane macromolecular switches (RMSs) (Figure 2) to emphasize their potential applicability.

From another point of view, this Outlook can be regarded as a review of supramolecular polymers characterized by structural flexibility. This article primarily focuses on the construction and function of such dynamic macromolecular systems that can undergo dynamic structure or topological changes to induce changes in properties and/or functions. To construct these dynamic systems, RMSs are essential and depend on the development of macromolecular [2]rotaxanes. The change of M2Rs to RMSs and their application to topology-transformable polymers as stimuli-responsive materials are the main topics of this Outlook, which also discusses how the polymer chain mobility affects the polymer properties. An illustrative description of the contents of this Outlook is summarized in Figure 3.

2. ROTAXANE MACROMOLECULAR SWITCH

2.1. Non-macromolecular Rotaxane Molecular Switch. Structure- and/or property-changeable systems driven by various stimuli are attractive for the design of stimuli-responsive materials, which usually require dynamic or structure-changeable molecular units. Dynamic units that use mechanical linkages have attracted considerable attention because of their scientific interest and actual applications, such as in smart devices and materials. Specifically, rotaxane linkages are most promising because in rotaxanes there are no interactions between the components, which are also characterized by high mobility. Therefore, molecules containing rotaxane-linked units frequently exhibit unique properties that have not been previously reported.

Various rotaxane molecular switches that work in response to stimuli, such as light (UV and visible), temperature, acids/bases, and so on, have been reported in which the rotaxane components reversibly change their relative position. Among them, the most clear and understandable rotaxane molecular switch may be the “molecular elevator,” which was developed by Stoddart et al. Although the sec-ammonium group in the axle of a crown ether-type rotaxane cannot be converted into the neutral amine group unless the second station in the axle component is able to sufficiently interact with the wheel moiety, neutralization of the sec-ammonium group to afford the amine group can occur in the presence of a stable cationic group (e.g., a pyridinium group), forming an attractive molecular switch, as shown in Figure 4. By the combination of three rotaxane units that consist of crown ether wheels and sec-ammonium axes with additional bipyridinium stations, acid/base treatment produces elevator-like motion through the effective switching of the three rotaxane units.

2.2. Synthesis of the Rotaxane Molecular Switch. Among several typical wheel components, crown ethers are widely used because of their commercial availability and diverse possibilities for modification. The interaction between the sec-ammonium/crown ether or metal/ligand complexes is applied to the synthesis of rotaxanes because it is sufficiently strong to maintain the structure of the complex, i.e., the pseudorotaxane is the key intermediate during the synthesis process. Scheme 1 shows a typical synthesis of an ammonium/crown ether rotaxane. An effective way to use the rotaxane in sophisticated dynamic polymer systems is as a tool to control the properties and function. Thus, the “macromolecular switch” is based on a rotaxane because a molecular switch with a long-distance movement is required for big or essential polymer structural changes. No RMS had been reported before 2010. To prepare it, Takata et al. designed and synthesized a two-station-type rotaxane molecular switch that consisted of an axle component

Figure 1. Rotaxane molecular switch driven by two different stimuli.

Figure 2. Schematic illustration of a rotaxane macromolecular switch with two stations on the axle ends for the wheel of the macromolecular [2]rotaxane.

Figure 3. Stimuli-responsive dynamic macromolecular systems: (a) linear–star and (b) linear–cyclic topological transformations controlled by a rotaxane macromolecular switch.

Figure 4. Schematic illustration of the synthesis of a typical rotaxane molecular switch.
with two sec-ammonium moieties and a 24-membered crown ether as the wheel component, as shown in Scheme 2.51 The position of the wheel was fixed at the sec-ammonium moiety, whereas the other amine moiety was deactivated with an appropriate protecting group. The successive protection/deprotection protocol readily produces an effective rotaxane molecular switch through the active transport of the crown ether wheel from right to left, and the transport is reversible.

A simpler switch for easier synthesis and operation was also prepared by the introduction of an axle functional group with a weaker attractive interaction with the wheel component in addition to the ammonium group with a stronger interaction. The first group uses the interaction between a crown ether and a benzyl methylene unit of an ester group as a weak interaction that functions as an acid–base stimulus toward a tert-amine station (Scheme 3).49,50 The tert-ammonium group has a moderately attractive interaction with the crown ether wheel, and treatment with a typical stronger amine base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is sufficient to obtain the tert-amine group, which is considerably different from the sec-ammonium group.

Another switch has a urethane station besides the ammonium station on the axle. With regard to the urethane group–crown ether interaction, Gibson et al. reported that the formation of hydrogen bonding between the urethane NH group and the crown ether wheel resulted in the generation of a significant thermodynamic driving force for the threading complexation to form a polyrotaxane from polyurethane and crown ether.52–55 Thus, the urethane moiety on the axle acts as a second station when the tert-ammonium group is neutralized with the base (Scheme 3).56

Trichloroacetic acid is known to decompose to carbon dioxide and chloroform with catalysis by amines. When an ammonium-type rotaxane has trichloroacetate as a counter-anion, the decomposition by heating produces a neutralized amine-type rotaxane in addition to carbon dioxide and chloroform as gaseous products (Scheme 4).58,59 Therefore, it is a good rotaxane molecular switch that can work in the solid state because there is no accumulation of any byproducts. In fact, helical polyacetylene with a rotaxane switch function in the side chain underwent the helical structure change by switching even in the solid state.60

2.3. Synthesis of M2Rs. For the synthesis of RMSs, a synthetic strategy for M2Rs, the simplest polyrotaxanes, is required in addition to the molecular design of the RMSs. The synthesis and application of various polyrotaxanes, primarily main-chain-type polyrotaxanes, have been reported and directed toward the development of innovative polymeric materials using the dynamic nature of the components in addition to the novel polymer synthesis. Several comprehensive reviews and books have been published to describe these polyrotaxanes.16–23 Although many polyrotaxanes have been reported in the past three decades, few structure-definite polyrotaxanes have been described, presumably because of synthetic difficulties. In particular, the synthesis of M2Rs with one polymer axle and one threaded wheel remains a big challenge because the
introduction of a single wheel component into the polymer chain requires a high level of synthetic strategy and experimental skill. However, it has been a difficult synthetic target because of the difficulty of combining the rotaxane and polymer moieties while keeping the pseudorotaxane structure as a key intermediate. M2Rs have considerable potential as key compounds in the development of dynamic polymer materials driven by macromolecular switches (Figure 2) on the basis of the controllable location and mobility of the components.

Figure 5 shows the synthetic strategies for M2Rs: (a) the rotaxane end-cap method and (b) the rotaxane-from method.61 The rotaxane end-cap method (Figure 5a) has a key step that connects a terminal-bulky polymer as an axle polymer and a pseudo[2]rotaxane carrying the wheel component. Because the key step involves the end-cap reaction of the axle terminal of the pseudo[2]rotaxane with the polymer containing a reactive terminal, a highly efficient reaction (e.g., a click reaction) is required. Even with click reactions, excess pseudo[2]rotaxane is usually needed to complete the successful binding of the two termini. Despite such a restriction, the method has some merits in the structural diversity of polymers used for the end-cap reaction.

However, the rotaxane-from method (Figure 5b) requires a pseudo[2]rotaxane as an initiator for the living polymerization of monomers to prepare the axle polymer chain, which is followed by the reaction of the propagation end with a bulky end cap to prevent the dethreading of the wheel component. It is advantageous that excess pseudo[2]rotaxane is not required in this method, where one pseudo[2]rotaxane initiator produces one M2R when the initiator efficiency is 100%. Compared with the difficult purification of M2Rs during the removal of the polymer agent used in the end-cap reaction in the rotaxane end-
To synthesize an RMS, the M2R components should have a relative-position-controllable function similar to that of the above-mentioned rotaxane molecular switches. The interaction between the sec-ammonium/crown ether complex or metal/ligand complex within the M2R component is sufficiently strong to maintain the complex structure but can be removed by some stimuli, allowing the wheel to change its relative position. Meanwhile, the design of M2Rs consisting of cyclodextrin as a wheel and a polymer as an axle is difficult because the number of wheels and relative positions of the components are usually uncontrollable. Fustin et al. reported the successful synthesis of a macromolecular [2]rotaxanate and rotaxane-linked block copolymer (RLBC) by the rotaxane end-cap method. Aoki and Takata developed an effective synthetic protocol for M2Rs via the rotaxane-from-method, which provides high yields of M2Rs with high purity (Scheme 5). An M2R can be regarded as an ideal structure-definite polyrotaxane in which the mobility and relative positions of the components are stimuli-responsive as in an RMS. Fustin et al. also reported the successful synthesis of a macromolecular [2]rotaxane end-cap method. They used a macrocyclic Pd complex with a pseudorotaxanate structure as the end-cap agent.

Meanwhile, Aoki and Takata developed an effective synthetic protocol for M2Rs via the rotaxane-from-method, which provides high yields of M2Rs with high purity (Scheme 5). An M2R can be regarded as an ideal structure-definite polyrotaxane in which the mobility and relative positions of the components are stimuli-responsive as in an RMS. The most important point for the synthesis of M2Rs via the rotaxane-from method is that a pseudo[2]rotaxane used as the initiator maintains its threaded structure during the initiation, propagation, and end-capping processes, even using the sec-ammonium salt/dibenzo-24-crown-8 (DB24C8) couple. Aoki and Takata eventually chose diphenyl phosphate (DPP)-catalyzed living ring-opening polymerization (ROP) of a cyclic monomer (e.g., a lactone) as a suitable polymer chain synthesis, according to the method reported by Kakuchi et al.

To apply a pseudo[2]rotaxane comprising DB24C8 and a sec-ammonium salt to the DPP-catalyzed polymerization, pseudo[2]rotaxane 1-OH possessing a sec-ammonium salt axle with a terminal primary hydroxyl group was designed (Scheme 5). Because the polymerization proceeded under weakly acidic conditions, 1-OH efficiently initiated the ROP of 6-valerolactone (VL) and ε-caprolactone (CL) without decomposition. Treatment of the propagation OH terminal with bulky isocyanate to form the end cap afforded the sec-ammonium salt/crown ether-based M2R with a PVL axle. The M2Rs were produced via a one-pot reaction in high isolated yields (76–91%) with a degree of polymerization (DP) of 10–97.

Because the most intriguing property of M2Rs is their dynamic nature, mobility control of the components of M2R_F was carried out by removing the attractive interaction between the two components by N-acetylation to convert the ionic structure into the nonionic structure (Scheme 6). The wheel component of M2R_M remains at the urethane terminal of the axle by hydrogen bonding. If a methyl group is introduced on the nitrogen atom of M2R_F, acid–base treatment should produce a simple RMS that is similar to the simple switches shown in Schemes 3 and 4.

The component-mobility-dependent property of these polymers is of considerable interest. To evaluate the effect of the component mobility in M2Rs, the crystallinity of the axle polymer (PVL), which is a suitable probe that is strongly affected by the component mobility, was measured by differential scanning calorimetry (DSC). Single endothermic peaks originating from the phase transition of the PVL moiety from crystalline to amorphous were observed at 38–60 °C in the DSC results for M2R_F with DP = 15 and those for M2R_M with DP = 20. The difference in crystallinity between M2R17_F (crystalline) and M2R17_M (amorphous) was attributed to the change in the mobility of the components (Figure 6). Thus, polymer crystallinity is suitable for evaluating the switching behavior.

2.4. Synthesis of RMSs. RMSs with two sec-ammonium-type stations were first constructed by Takata et al., as shown in Scheme 7. Similar to the low-molecular-weight switch (Scheme 2), the polymer terminals have unprotected and protected sec-amine moieties for the unidirectional movement of the wheel component on the axle component by the successive protection/deprotection protocol. The reverse reaction or movement of the wheel smoothly proceeds by a similar protocol. Other RMSs besides the one shown in Scheme 7, which are based on rotaxane molecular switches illustrated in Schemes 3 and 4.
and 4, will be directly introduced and discussed in the following sections.

3. APPLICATION OF RMS TO TOPOLOGY-TRANSFORMABLE POLYMERS

3.1. Linear–Branched Polymer Topological Transformation. Various sophisticated dynamic polymer systems are conceivable using RLBCs, i.e., RMSs possessing a polymer chain on the wheel component, the polymer topology of which can be changed between linear and branched by the movement of the wheel component, as shown in Figure 7.

![Scheme 6. Synthesis of a Macromolecular [2]Rotaxane with Movable Components (M2R_M) by Removal of the Attractive Interaction between the Two Components of M2R_F](image)

For the M2R with two polymer chains, poly(methyl acrylate) (PMA) and poly(ethylene oxide) (PEO) (PMA-rot-PEO), prepared by Fustin et al., the component mobility is limited owing to the strong Pd(II) rotaxanate.\(^{39}\) Takata et al. used the rotaxane-from method to synthesize various RLBCs by introducing polymer chains into the components of the M2R.\(^{64}\) Scheme 8 shows the two synthetic methods, i.e., the grafting-from and grafting-onto pathways, to yield the RLBCs PVL-rot-PEO, PVL-rot-PMA, and PVL-rot-polystyrene (PS). An M2R with a functional-group-tethering wheel was prepared, and then the PEO chain was added to the wheel component via a click process to give PVL-rot-PEO_F in relatively high isolated yields with high purity.

By means of the grafting-from method, the PMA- or PS-chain-tethering M2Rs PVL-rot-PMA_M and PVL-rot-PS_F were obtained. The sec-ammonium moiety was acetylated to produce a polymer chain on the wheel component that is movable on the axle polymer chain (Scheme 8b), which is also accompanied by the polymer topology change (Figure 7).

To evaluate the effect of the polymer topology change, the rotaxane-linked polymer 2-PVL_F was synthesized, which included identical chains on the axle and wheel components (Scheme 8b). The neutralization of 2-PVL_F by N-acetylation afforded 2-PVL_M, whose wheel component was located around the urethane terminal as previously mentioned.\(^{65}\)

The solution properties of 2-PVL_F and 2-PVL_M were examined by gel-permeation chromatography (GPC) and compared with that of the corresponding model linear polymer with a similar DP of PVL equal to the sum of the DPs of the two polymer units of 2-PVL_F (Figure 8).\(^{65}\) Interestingly, 2-PVL_F and 2-PVL_M showed very similar GPC profiles, which clearly suggested that these polymers had similar hydrodynamic volumes. Therefore, these 2-PVLs have a similar linear structure.

Therefore, 2-PVL_M should have a linear topology but not a branched one even after the removal of the attractive interaction, which strongly indicates that the axle terminal urethane moiety has a certain attractive interaction with the crown ether wheel that is sufficient to produce a linear topology.\(^{64,65}\) Namely, the wheel component tethering the polymer chain is moved from the \(\alpha\) end to the \(\omega\) end of the axle polymer upon removal of the sec-ammonium−DB24C8 interaction.

As discussed above, the polymer topological transformation results in macroscopic property changes in the bulk and in solution. Until the year 2000, topology-changeable molecules had been limited mainly to small molecules; however, recent progress in synthetic organic and polymer chemistry has made...
the topology change of polymer molecules possible.\textsuperscript{66−69}

Compared with linear polymers, the corresponding topology-
different polymers (e.g., star polymers,\textsuperscript{70−72} cyclic polymers,\textsuperscript{73−75} dendrimers,\textsuperscript{76−78} and hyperbranched polymers\textsuperscript{79})
typically show smaller hydrodynamic volumes, lower solution
viscosities, and less polymer entanglement in the bulk. Therefore, the
development of polymers whose topology is transformable in response to a specific stimulus is particularly
attractive to control polymer properties and construct novel
stimuli-responsive materials. However, most of the topological
polymers reported to date are not transformable because they
are constructed from covalent bonds; there have been a few
reports on polymer topology reconstruction using weak
interactions.\textsuperscript{80−82}

Takata et al. reported the topology-transformable star
polymer derived from a crown ether-based M2R with
sec-ammonium and urethane moieties on the polymer axle, which
can be regarded as two-station-type RMS.\textsuperscript{83} Scheme 10 shows
the structure of the star polymer (3-PVL\_A) and its topology
conversion to the linear polymer (3-PVL\_U) when the
intercomponent interaction is changed from sec-ammonium
moiety−crown ether to urethane moiety−crown ether through
simple N-acetylation.

Figure 9 shows the GPC profiles of (a) the product mixture
without end capping with bulky isocyanate during the synthesis
of 3-PVL\_A, (b) 3-PVL\_A, and (c) 3-PVL\_U. The broad GPC
peak of the product mixture (Figure 9a) compared with those of
3-PVL\_A and 3-PVL\_U clearly suggests the occurrence of
decomposition to the two polymers connected to the axle and
wheel components due to the absence of the bulky end cap. This
result clearly shows that the wheel component carrying a
polymer chain readily moves along the axle polymer chain to the
polymer end to eventually unthread from the polymer end when
released from the strong intercomponent sec-ammonium—
crown ether interaction upon N-acetylation.\textsuperscript{83} Meanwhile, the
unimodal GPC peak of 3-PVL\_U appeared at an earlier elution
time (higher-molecular-weight region) compared with that of
3-PVL\_A without a change in \( M_w/M_n \). It is concluded that this
peak shift was caused by an increase in hydrodynamic volume,
which clearly supports the occurrence of the topological
transformation from star to linear.\textsuperscript{83}

The topological transformation was also supported by the
viscosity change. To compare the viscosities, the covalently
connected model star and linear polymers shown in Figure 10
were prepared. The intrinsic viscosity \( [\eta] \) of 3-PVL\_U was
higher than that of 3-PVL\_A, which demonstrated the
topological transformation from the star polymer to the linear
polymer; the value of \( g' \) (the ratio of the intrinsic viscosities of
the covalently connected star and linear polymers with the same
molecular weights as 3-PVL) was similar to that of 3-PVL\_A and
3-PVL\_U. The report presented the first topology-transformable polymer,\textsuperscript{83} which can reversibly change its topology
between linear and star topologies by the action of a pH-
responsive RMS with the N-methyl group, as shown for the
rotaxane switches in Scheme 3.

Three same-structure polymer-chain-tethering rotaxane-
linked polymers were studied. Meanwhile, different-structure
polymer-chain-containing rotaxane-linked polymers (e.g., star
block copolymers) have attracted considerable interest from
both scientific and practical perspectives. In particular, star
polymers comprising three types of different polymer chains
show unique characteristics such as microphase-separated
structures in response to their topology, as reported by

Scheme 8. Syntheses of RLBCs via the (a) Grafting-Onto and
(b) Grafting-From Pathways\textsuperscript{64}

Scheme 9. Synthesis of 2-PVL\_M by N-Acetylation of 2-
PVL\_F\textsuperscript{85}
Matsushita et al.84,85 The reported linear and star ABC triblock copolymers cannot be interchanged with each other because these polymers are covalently connected. To extend the capability and applicability of the topology-transformable systems based on M2Rs, Takata and Aoki synthesized a topologically transformable ABC terpolymer containing the RMS system.86 The pseudo[2]rotaxane initiator 3F with three functional groups capable of linking three polymer chains through the rotaxane linkage was designed as the key trifunctional rotaxane for the star polymer synthesis (Scheme 11).86 The living ring-opening polymerization of VL initiated by 3F and successive propagation and end capping was followed by the reversible addition−fragmentation chain transfer polymerization of styrene to give the corresponding [2]rotaxane PVL33-rot-PS49 tethering two polymer chains. The final polymer connection via a click reaction with azide-terminated PEO afforded the rotaxane-linked ABC star terpolymer PEO45-b-PVL33-rot-PS49_A.86 The strong sec-ammonium−DB24C8 interaction fixed the wheel component at the center of the axle polymer chain to connect the arm polymer chains to the axle chain (star polymer). The N-acetylation of the sec-ammonium moiety of PEO45-b-PVL33-rot-PS49_A resulted in the transformation of the initial polymer topology from star to linear (PEO45-b-PVL33-rot-PS49_U) by the emergence of the urethane−crown ether interaction at the end of the axle PVL chain. The GPC peak shift to higher molecular weight strongly supported not only the structure but also the dynamic nature of the topology-transformable ABC terpolymer (Figure 11).86

3.2. Application of RMSs to Reversible Linear−Cyclic Topological Transformation. Although cyclic polymers73−75,87,88 have attracted considerable interest from both fundamental and applied viewpoints, the syntheses of cyclic polymers require tedious preparation and difficult purification. In general, the syntheses of cyclic polymers are accomplished by two major methods: intramolecular cyclization of linear-shaped polymer with homo- or heteroditopic ends and ring-expansion polymerization using a cyclic initiator. Although cyclization of linear polymers is the most commonly used method, it requires high reactivity of both polymer ends and high cyclization efficiency under high dilution to prevent the intermolecular reaction. Moreover, isolation of the pure cyclic polymer from the mixture of the resulting cyclic polymer and unreacted and formed linear polymers is also difficult. However, most ring-
expansion polymerizations are not well-controlled with respect to molecular weight and polydispersity. Thus, these problems in the two methods prevent the effective synthesis, isolation in pure form, and precise characterization of cyclic polymers. Takata, Aoki, and co-workers proposed a novel strategy for the effective synthesis of these cyclic polymers to solve problems, which involves the topological transformation of a linear polymer with a macromolecular [1]rotaxane (M1R) structure, which can be obtained by linking the wheel and axle components of an M2R (Figure 12).51,56,57

Because this cyclization is achieved by intramolecular transport of the wheel component along the polymer axle of the linear polymer, the conversion efficiency reaches 100% irrespective of the concentration, which differs from other methods. The initial small cyclic part in the linear polymer end is gradually expanded according to the translation of the wheel to form a large cyclic polymer. The first topological transformation from linear to cyclic topology was reported by Takata et al. using an M2R.51

Scheme 12 shows the actual synthetic scheme of the linear polymer M1R_L and its topological transformation to the cyclic polymer M1R_C.56 The pseudo[2]rotaxane initiator 2P-OH with two pentenyl substituents and one benzyl alcohol terminal is the key to synthesizing the M1R. The DPP-catalyzed living ring-opening polymerization of CL and the successive end-cap reaction to give 2P-M2R were followed by ring-closing metathesis between the two pentenyl groups at the terminal rotaxane moiety of 2P-M2R, which yielded the corresponding linear M1R (M1R_L). The topological transformation from the linear polymer to the cyclic polymer was achieved by N-acetylation of the sec-ammonium moiety of M1R_L. The transport of the wheel component from the α end to the ω end resulted in the successful formation of the cyclic polymer (M1R_C) in 88% isolated yield. The hydrodynamic volume decrease, which was observed from the GPC profile change, clearly indicated the topological transformation to the cyclic form (Figure 12). The molecular weight ratio with respect to the model polymer (M1R_C/M2R_U = 0.89; Figure 13) was consistent with the reported ratio.56 The formation of the cyclic structure was also supported by replacing the urethane ω terminal of M1R_C with a more acidic urethane moiety (M1R_C_CF), which further promoted the transport of the wheel to the ω terminal. In fact, the substitution of the terminal dimethylphenyl moiety for the bis(trifluoromethyl)phenyl moiety increased the ratio of the largest cyclic polymer, which was suggested by the change in the apparent molecular weight ratio (0.84).56

Reversible linear–cyclic polymer topological transformation is a very attractive event, and it is a characteristic of the described rotaxane protocol. It is easy to move the wheel component back to the original α end from the ω end because the protocol consists only of simple transport of the wheel component from the α end to the ω end of the linear polymer. The reversible topological transformation between linear and cyclic polymers was carried out using polymer M1R_L (Scheme 12), in which the macromolecular switch with a tert-amine/ammonium couple was driven by the acid/base stimulus on the axle component, as shown in Scheme 13.56 Specifically, N-methylated cyclic polymer M1R_C_N was treated with NH4PF6 to generate a tert-ammonium group, which interacted with the crown ether wheel more strongly than the urethane moiety, finally resulting in the formation of the linear polymer M1R_L_N. Treatment with base (NaHCO3) converted the structure from linear to cyclic by neutralization of the ammonium group. A similar RMS behavior was confirmed with the noncylized rotaxane system M2R_U (Figure 13), suggesting the role of the urethane moiety as the effective station for the wheel.

The RMS works under solvent-free or solid-state conditions, which is important in polymer systems because polymeric materials are usually used in the solid state. Therefore, the rotaxane switch shown in Scheme 4 is useful; it can work in the solid state without the accumulation of byproducts because chloroform and carbon dioxide as the decomposition products do not remain in the solid material at elevated temperature. In fact, this was confirmed by thermal decomposition studies of two linear polymers with different counteranions, PF6− and CCl3COO−.56 The thermal decomposition of linear polymers with CCl3COO− occurred at approximately 120 °C and produced chloroform and carbon dioxide in addition to the neutral tert-amine product, which readily changed its topology...
from linear to cyclic during the TGA study, via crown ether wheel movement to the urethane end. On the contrary, no decomposition occurred for the polymer with PF$_6^-$ under the same conditions, indicating the importance of CCl$_3$COO$^-$ as the counteranion.$^8$9

A similar reversible topological transformation using an RMS was achieved with a macromolecular rotaxane containing two amine/ammonium-type stations (Scheme 14). An MIR with a protected sec-amine group at the $\omega$ terminal (MIR$\_THF$ A) as a linear polymer was subjected to N protection with trichloroethyl chloroformate at the $\alpha$ terminal and successive N’ deprotection with an arenethiol at the $\omega$ terminal to convert it to cyclic polymer (MIR$\_THF$ U), which was then treated with o-nitrobenzensulfonyl chloride and Zn/AcOH and reverted to the linear polymer. In this case, the use of amine/ammonium stations with strong attractive interaction with the wheel component resulted in a 100% reversible conversion of

![Scheme 11. Synthesis of the Rotaxane-Linked ABC Star Triblock Copolymer PEO$_{45}$$\text{-}$$b$$\text{-}$$PVL$_{33}$$\text{-}$$rot$$\text{-}$$PS$_{49}$ A and Its Topology Conversion to Linear Topology (PEO$_{45}$$\text{-}$$b$$\text{-}$$PVL$_{33}$$\text{-}$$rot$$\text{-}$$PS$_{49}$ U)](image)
the polymer topology. The solution properties of the polymers reasonably depended upon their topology (Figure 14).

The linear to cyclic polymer topological transformation technique was also applied to the synthesis of a cyclic block copolymer using CL and hexanolactone (HL) as the monomers (Scheme 15).

A similar GPC profile change corresponding to Figure 12.

Scheme 12. Synthesis of Cyclic Polymer M1R_C via the Topological Transformation of Linear Polymer M1R_L56

Scheme 13. Reversible Topological Transformation between Cyclic and Linear Polymers Using an Acid/Base-Responsive RMS89

Scheme 14. Reversible Linear—Cyclic Polymer Topological Transformation Using an M1R with Two Amine/Ammonium Stations51

Figure 13. GPC profiles of the model linear polymer (M2R_U) and the cyclic polymer (M1R_C)56

Figure 12. Synthetic strategy for producing a cyclic polymer by the “RMS protocol” via the topological transformation of a macromolecular \([1]rotaxane\) as a linear polymer.51
the topological change suggested the successful synthesis of the cyclic block copolymer. The topology-dependent crystallinity change of the axle polymer was also a good method for evaluating the topology difference: the cyclic polymer had a higher melting point than the linear polymer.57

The recent progress of this rotaxane protocol for the effective synthesis of cyclic polymers allowed us to achieve a selective high-yielding, large-quantity synthesis of cyclic polymers. Takata, Aoki, and co-workers recently discovered a convenient method for synthesizing a cyclic polymer (Figure 15).90 The selective dimerization of station-tethering cyclic molecules involves spontaneous cyclization, which produced a [c2]daisy chain-type homoditopic initiator with two reactive terminals that can be used for the introduction of a polymer chain. The described spontaneous dimerization overcame the difficulty of introducing a cyclic unit into the polymer or initiator, which is essential for the synthesis of the cyclic polymer.90

As shown in Scheme 16, the cyclization of two self-complementary sec-ammonium-containing crown ether molecules quantitatively gave rotaxane dimer D-OH_A. Axle terminal OH groups initiated the living ring-opening polymerization of CL, which was followed by end capping of the propagation-end OH with a bulky isocyanate group. The cyclic dimer structure was markedly stable and retained its form during the polymerization.90 The subsequent N-acylative neutralization of D-PCL_A afforded ca. 10 g of the corresponding cyclic polyester D-PCL_U in one batch in a typical laboratory experiment using a 50 mL flask.

A decrease in hydrodynamic volume and viscosity by the N-acetylation of D-PCL_A to D-PCL_U was also confirmed, unambiguously revealing the occurrence of the topological transformation of the linear polymer to the cyclic polymer. Although Scheme 14 indicates a unidirectional transformation from linear to cyclic polymer topology, the reversible topological transformation between the linear and cyclic forms can be readily achieved by N-methylation instead of N-acetylation for acid/base switching, as in Schemes 3 and 15.

4. CONCLUSIONS AND OUTLOOK

The synthesis and application of RMSs, which are obtained on the basis of the fact that the length of the axle component of the
rotaxane switch is unlimited, have been described, and the significance of the RMSs has been emphasized. Specifically, the use of RMSs to control the polymer topology, which is accompanied by big structure changes that cannot be attained in covalent systems, is remarkably effective for constructing sophisticated dynamic polymeric materials such as switchable materials or stimuli-responsive materials. To convey the importance of RMSs to the readers, this review has described only a few examples of the application of RMSs in the linear—star and linear—cyclic topological transformation systems. For the synthesis of RMSs, M2Rs are essential, and the successful synthesis actually expanded the diversity of RMSs. However, the crown ether/ammonium couple is the only currently widely available system. In addition, the ability of RMSs to work under solvent-free conditions should attract considerable attention because of the usefulness of condensed material systems. In the near future, by the use of RMSs it will be possible to produce various topology-switchable polymers as very smart polymers because the polymer function and properties strongly depend on the polymer topology.

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Notes
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