

FOCUS REVIEW

Synthesis of topologically crosslinked polymers with rotaxane-crosslinking points

Yasuhito Koyama

This review discusses seven synthetic approaches for fabricating topologically crosslinked polymers with rotaxane structures at the crosslinking points (rotaxane-crosslinked polymers, RCPs). RCPs exhibit unique properties such as high swelling capability, high elasticity and stimuli-responsiveness attributed to the rotaxane-crosslinking points. This article primarily focuses on the four most recently developed strategic approaches for synthesizing RCPs in which various rotaxane components, such as crown ethers/ammonium salts, cyclodextrins/hydrophobic guests and metal-coordinated macrocycles/ligands, are employed. Two of these RCP synthetic methods efficiently introduce special structures and functions into the RCP crosslinking points. Using these methods, we inserted well-studied rotaxane systems that exhibit deslipping behavior into the crosslinking points of network polymers. Notably, each of the resulting RCPs exhibited chemostimuli-responsive or photoresponsive degradability due to the deslipping behavior of the rotaxane system incorporated into the RCP. The other two methods are based on the use of rotaxane crosslinkers to fabricate versatile RCPs containing vinyl trunk polymers. The efficiencies and applications of these recently developed methods are compared with those of conventional methods.

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INTRODUCTION

Topologically crosslinked polymers with rotaxane structures at the crosslinking points (rotaxane-crosslinked polymers, RCPs) have attracted great interest experimentally and theoretically^{1–7} because RCPs exhibit unique properties and functions that are attributed to the movable crosslinking points. RCPs are also known as polyrotaxane networks or slide-ring gels. RCP synthesis methods include seven different approaches (Figure 1). Methods 1 and 2 are statistical methods based on the accidental penetration of polymer termini into a macrocycle. Gibson *et al.* first reported that the polycondensation of a diamine with a 32-membered macrocyclic dicarboxylic acid formed an RCP gelled product (method 1).^{8–13} Zilkha *et al.*,^{14–17} Tezuka *et al.*,¹⁸ and Kubo *et al.*^{19–21} also reported the statistical synthesis of RCPs via the radical copolymerization of vinyl monomers with large macrocycles (method 2). In 1999, de Gennes²² theoretically predicted that RCPs possess unique properties because of easy polymer chain sliding. Ito *et al.*^{23–27} and Yui *et al.*^{28–31} synthesized RCPs by directly linking Harada's cyclodextrin-based polyrotaxanes at the wheels (method 3).^{32,33} The physical properties of RCPs were experimentally elucidated by Ito *et al.*^{23–27} They observed that RCPs undergo significant swelling in several solvents, have high elasticity and can relieve stress effectively. These observations directly supported the validity of de Gennes's predictions. In addition, Yui *et al.*^{28–31} demonstrated that RCP polymer frameworks act as unique biodegradable systems. To take advantage of these very important

features of RCPs, we developed four other synthesis approaches: crosslinking macrocycle-containing polymers using strategic rotaxanation as the crosslinking reaction (method 4) and crosslinking vinyl polymers using a [3]rotaxane (method 5), pseudorotaxane-crosslinked polymer (method 6) or bismacrocycle (method 7) as the crosslinker. Methods 4 and 5 are useful for not only creating new types of RCPs but also inserting special structures and functions into the crosslinking points. We successfully prepared unique RCPs with stimuli-responsiveness and photodegradability. Methods 6 and 7 were developed as practical RCP synthetic methods that allow RCPs containing vinyl trunk polymers to be easily prepared. The resulting vinylic RCPs exhibit unique properties that are attributed to polymer chain sliding. These seven RCP synthetic methods can be distinguished by the (i) need for pre-synthesizing the (poly)rotaxane precursor, (ii) controllability of the crosslinking degree and (iii) polymer versatility. Table 1 classifies these RCP synthetic strategies and indicates that the features of these methods are orthogonal. This review describes recent progress on the synthesis of RCPs via methods 4–7, which were developed by Takata *et al.*,^{34–37} and their applications. Related research topics and future perspectives on RCPs are also described.

STIMULI-DEGRADABLE ROTAXANE-CROSSLINKED POLYMERS

Stimuli-responsive smart materials have attracted considerable attention because they not only represent progress in fundamental

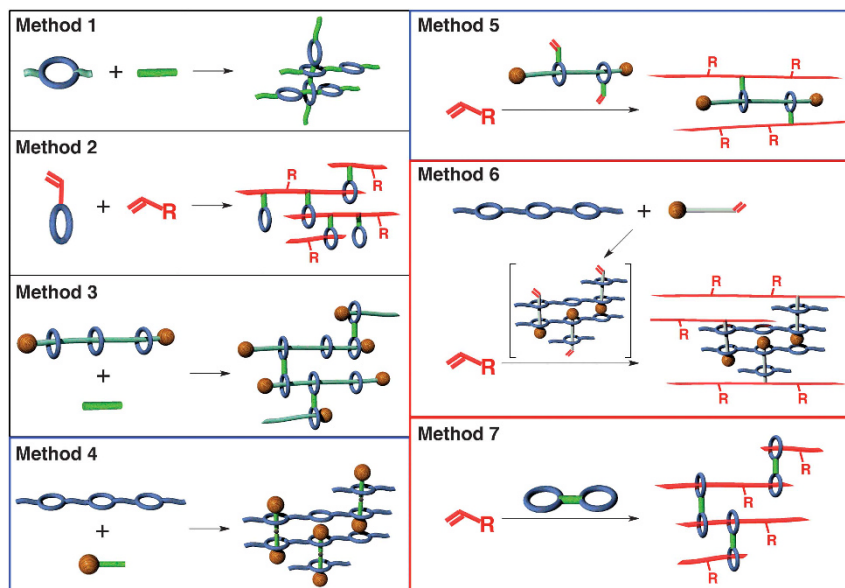


Figure 1 Synthetic strategies for preparing rotaxane-crosslinked polymers (RCPs).

Table 1 Classification of RCP synthetic strategies

Method	Synthetic approach	Need for pre-synthesis of (poly)rotaxane	Controllability of crosslinking degree	Polymer versatility
Method 1	Statistical	×	L	M
Method 2	Statistical	×	L	H
Method 3	Strategic	○	M	L
Method 4	Strategic	×	H	L
Method 5	Strategic	○	H	H
Method 6	Strategic	×	M	H
Method 7	Semi-strategic	×	M	H

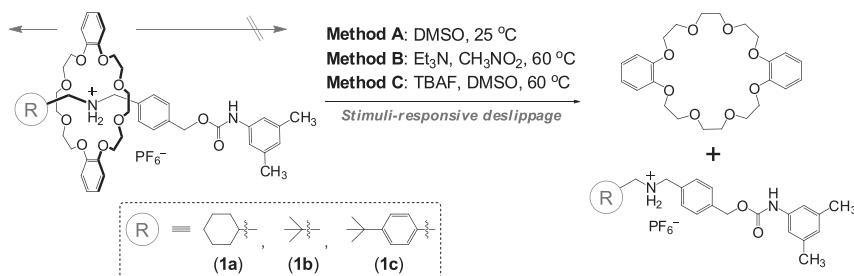
Abbreviations: H, high; M, middle; L, low.

chemistry but are also advanced, sophisticated materials. Stimuli-degradable gels comprise one family of smart materials that are mainly employed in intelligent devices based on sol–gel transitions, drug delivery systems, dynamic pattern formation, and so on. Most stimuli-degradable systems are based on cleaving weak noncovalent bonds, such as hydrogen bonds, π – π interactions and hydrophobic interactions. The properties of gels are attributed to the presence of these noncovalent bonds, and thus, they are typically chemically and thermally unstable. In addition, soaking a gel in an excess of an appropriate solvent past the gel point leads to the decomposition of the gel. Therefore, more robust, stimuli-responsive materials are needed. To develop stable, stimuli-degradable covalently crosslinked polymers, we hypothesized that rotaxanes with stimuli-responsive deslipping behavior could serve as crucial crosslinking structures. Thus, two stimuli-degradable systems of covalently crosslinked polymers were developed via methods 4 and 5.

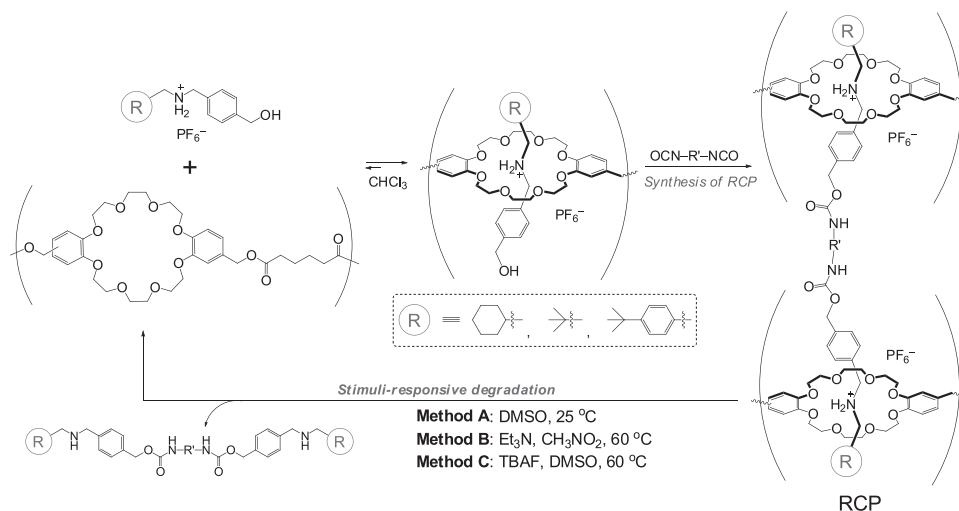
In method 4,³⁴ the axle component serves as the crosslinker and has an end group size that is complementary to that of the macrocyclic cavity on the trunk polymer.^{38–41} The end groups provide an energy barrier to slow dissociation, thereby kinetically stabilizing the rotaxane skeleton. The RCP normally stabilizes the

network structure, but it can be de-crosslinked under certain conditions, such as exposure to chemostimuli that accelerate the dissociation of the rotaxane skeleton. Furthermore, the stability and de-crosslinking capability of RCPs can be adjusted by changing the size of the axle end groups. We first investigated the size-complementary effect using crown ether/ammonium salt [2] rotaxanes (Scheme 1). Rotaxanes with suitable end groups (R = cyclohexyl (**1a**), *tert*-butyl (**1b**), and 4-*tert*-butylphenyl (**1c**)) were sufficiently stable and maintained their rotaxane structures because of the bulky end groups and hydrogen bonds between the dibenzo-24-crown-8-ether (DB24C8) and ammonium groups. However, these rotaxanes dissociated into two components when the hydrogen bonds were disrupted by an appropriate stimulus. When dissolved in dimethylsulfoxide (DMSO), for example, only **1a** underwent deslipping, and the half-life ($\tau_{1/2}$) was estimated to be 5.8 h. On the other hand, neutralizing the rotaxanes by adding Et_3N caused the prompt deslipping of **1a** ($\tau_{1/2} = 2.6$ h) and slow deslipping of **1b** ($\tau_{1/2} = 18$ d), while **1c** barely underwent deslipping. We also examined exchanging the counter anion of the ammonium salt with TBAF.⁴² Based on the HSAB principle, fluoride should strongly interact with the ammonium moiety and replace the crown ether. In fact, the addition of TBAF led to the rapid deslipping of all three rotaxanes. The half-life of **1a** was too rapid to measure, whereas those of **1b** and **1c** were 0.70 and 88 h, respectively. Thus, this model clearly indicated that the deslipping rates of size-complementary rotaxanes depend on both the end group size and type of external stimulus.

We next examined the de-crosslinking of RCPs with size-complementary end groups at the crosslinking points. Poly(crown ether) (M_n 4000, PDI 1.35) was treated with *sec*-ammonium salts bearing suitable end groups (R = cyclohexyl, *tert*-butyl, and 4-*tert*-butylphenyl) in CHCl_3 , to afford the corresponding pseudopolyrotaxanes, which were then crosslinked with a diisocyanate (MDI) to obtain a quantitative RCP yield (Scheme 2). The degradabilities of these RCPs were examined using three methods: solvation in DMF, neutralization with Et_3N and counter anion exchange with TBAF. The cyclohexyl-terminated RCP was gradually de-crosslinked in DMF at room temperature, giving a homogeneous solution after 90 min.



Scheme 1 Deslippage of model [2]rotaxanes. A full color version of this scheme is available at *Polymer Journal* online.



Scheme 2 Synthesis of RCPs with chemo-responsive degradability via method 4 and their de-crosslinking reactions. A full color version of this scheme is available at *Polymer Journal* online.

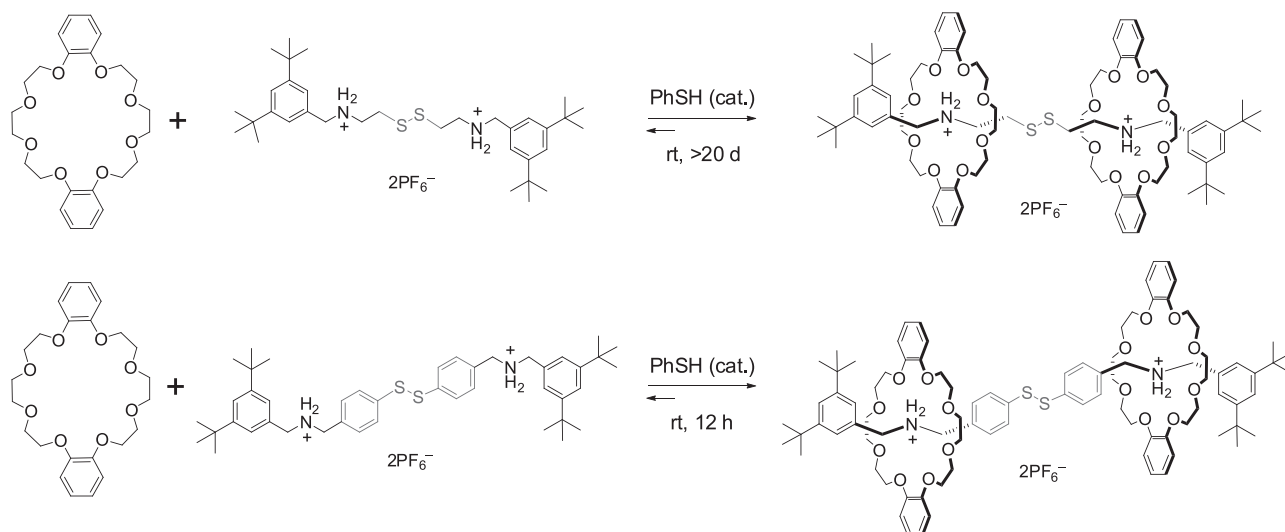
The *tert*-butyl- and *tert*-butylphenyl-terminated RCPs were insoluble in all solvents and only swelled, indicating that these gels had high chemical stability due to the kinetic stability of the rotaxane-crosslinking points. On the other hand, treatment of the cyclohexyl- and *tert*-butyl-terminated RCPs with Et₃N resulted in slow de-crosslinking, and homogeneous solutions were formed after 60 and 360 min, respectively. In contrast, the *tert*-butylphenyl-terminated RCP retained its shape under these conditions without any degradation. Furthermore, all the RCPs were smoothly de-crosslinked by TBAF, giving homogeneous solutions after 20 min (cyclohexyl), 75 min (*tert*-butyl) and 96 h (*tert*-butylphenyl). Notably, the degradation behavior of these RCPs was consistent with the dissociation behavior of the model [2]rotaxanes. The recyclability of the RCPs was also evaluated by recovering the poly(crown ether) in 98% yield from a homogeneous solution of the cyclohexyl-terminated RCP in DMF. The ¹H NMR spectrum and size-exclusion chromatography profile of the recovered poly(crown ether) matched those of the starting polymer, clearly indicating that the rotaxane skeleton was selectively degraded, while the polymer backbone remained intact.

We also developed an alternative approach for preparing RCPs with excellent photodegradability (method 5).³⁵ In this method, a vinylic [3]rotaxane with a photoreactive aromatic disulfide on the axle and polymerizable vinyl moieties on the wheels was utilized to crosslink a vinyl polymer. In fact, [3]rotaxanes can be efficiently synthesized via the reversible cleavage of a disulfide linkage in the presence of a catalytic thiol (Scheme 3),^{43–49} and aromatic disulfide linkages react

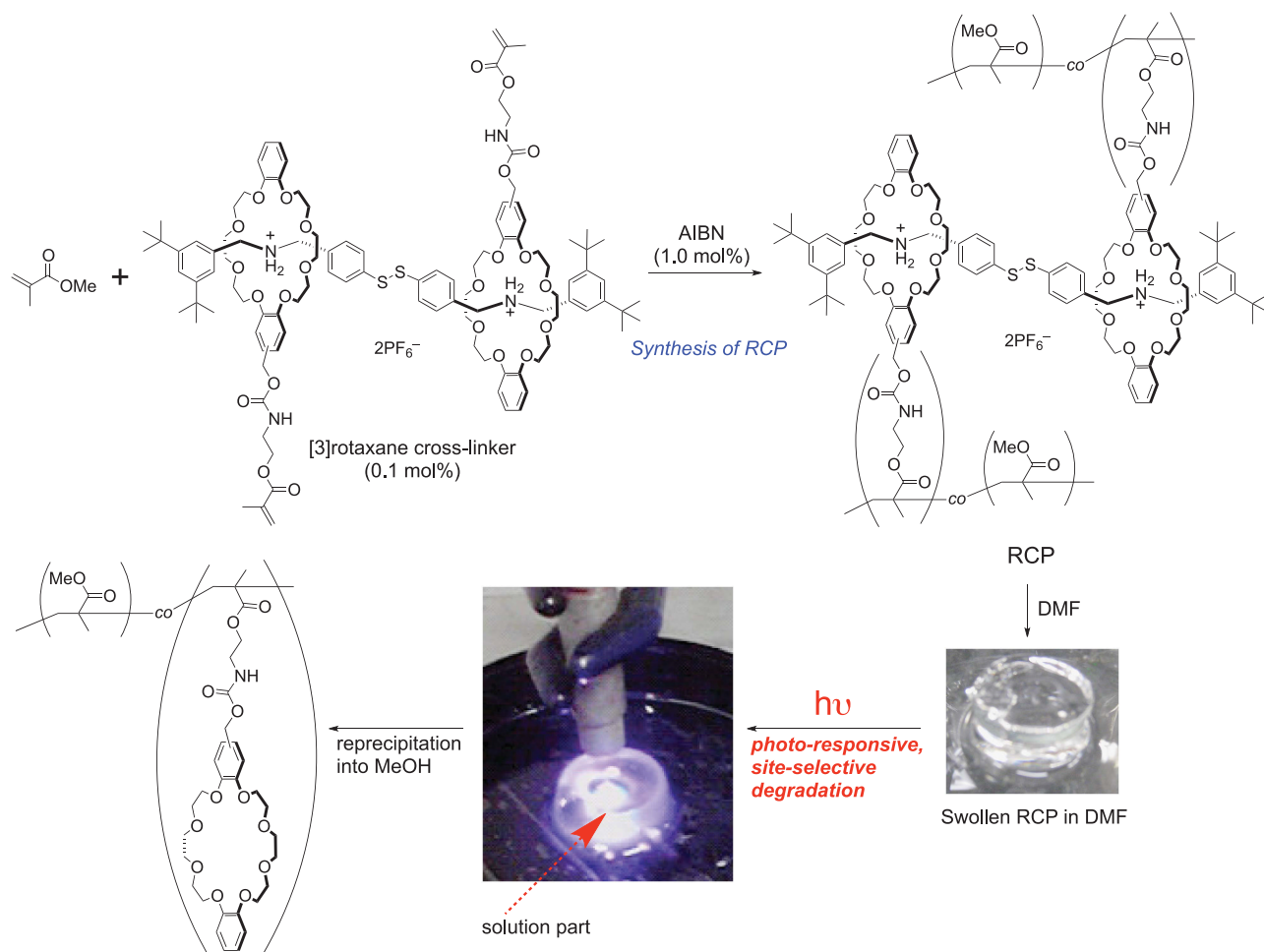
more rapidly than their aliphatic disulfide counterparts. UV irradiation of aromatic disulfide-containing [3]rotaxanes in DMF results in the cleavage of the aromatic S–S bond and subsequent deslippage to afford the original components.

Building on these model studies, a vinylic [3]rotaxane was designed, prepared and employed as the crosslinker in the radical polymerization of MMA in the presence of AIBN (Scheme 4). The radical polymerization was performed at 60 °C for 19 h to afford a gelled product. To evaluate its chemical stability, the gel was soaked in excess DMF for 1 d to produce a swollen organogel. In contrast to unstable non-covalently crosslinked polymers soaked in an appropriate solvent, the swollen gel maintained its shape in DMF for an additional day without any degradation.

The photodegradation behavior of the swollen gel in DMF was then investigated. UV irradiation of the gel at room temperature caused the rapid and selective degradation of the irradiated RCP section within 30 min, implying photoresponsive de-crosslinking occurred. This behavior is attributed to the homolysis of the aromatic disulfide S–S linkage of the rotaxane moiety and subsequent deslippage of the axle component from the wheel, which led to the decomposition of the RCP network structure. The de-threading of the axle component, which was stabilized by intramolecular hydrogen bonding in highly polar DMF, is consistent with a previous report on the solvent polarity-dependent complex formation of *sec*-ammonium/crown ether-type rotaxanes.^{43–49} The systems were not susceptible to thermal degradation because of their stability.



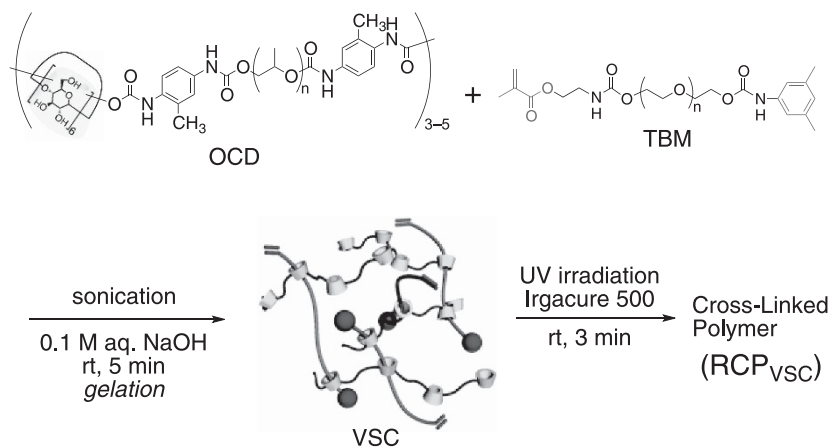
Scheme 3 Formation and dissociation of [3]rotaxanes utilizing reversible disulfide linkages. A full color version of this scheme is available at *Polymer Journal* online.



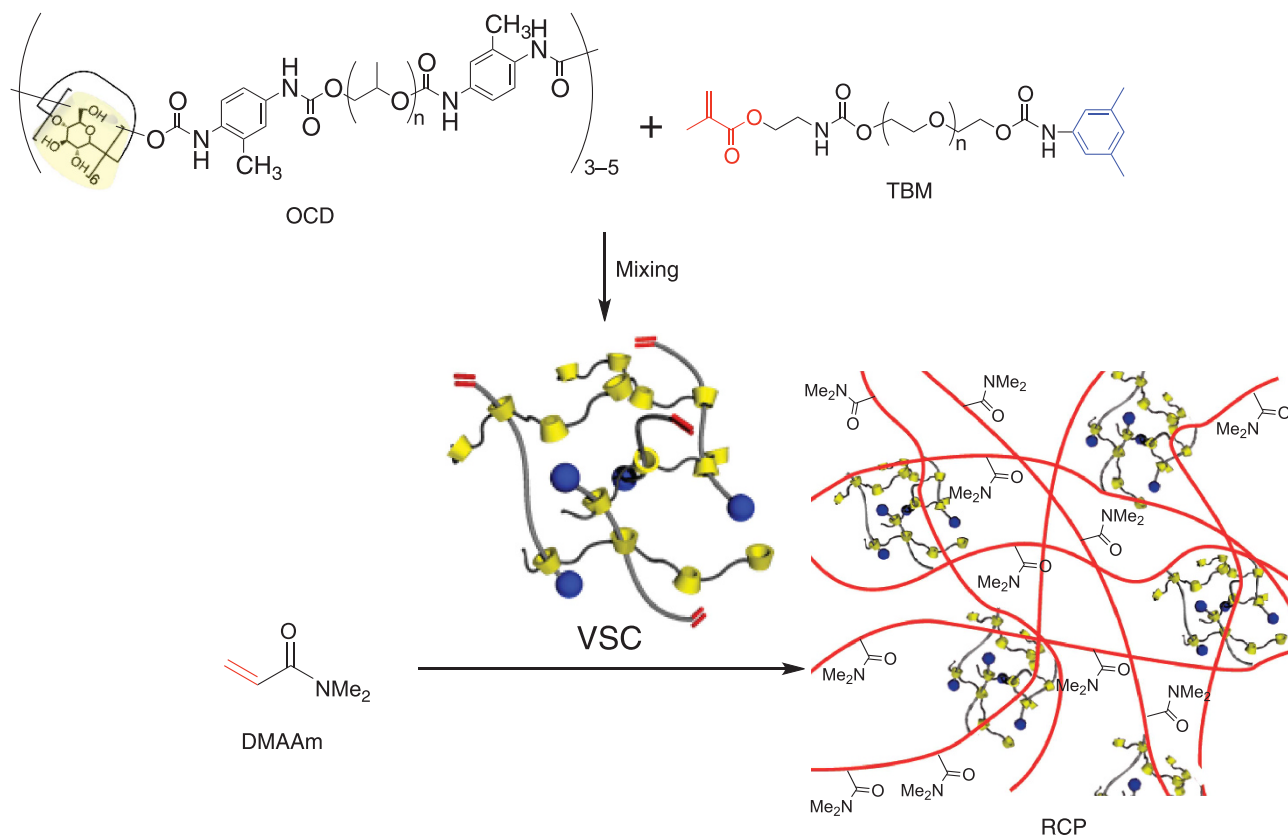
Scheme 4 Synthesis of a photodegradable RCP via method 5 using a [3]rotaxane crosslinker and its site-selective photoresponsive de-crosslinking reaction.

The remaining DMF-soluble product was then precipitated in MeOH, and the white precipitate was collected by filtration. The ^1H NMR spectrum of the filtrate indicated that the polymer was mainly

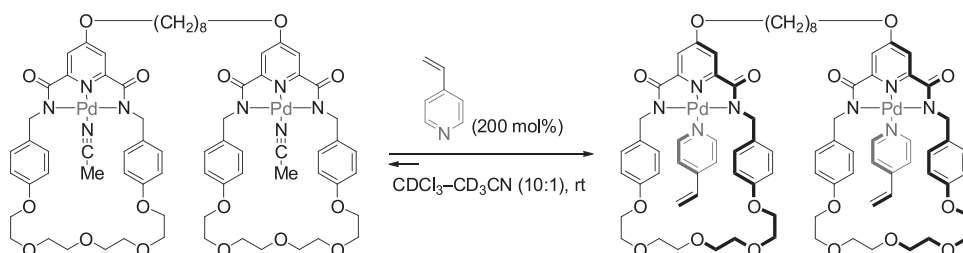
composed of PMMA, suggesting that the RCP was selectively photochemically degraded due to the photodissociation of the aromatic disulfide linkage and structural properties of the interlocked linkage.



Scheme 5 Synthesis of RCP_{VSC} (VSC, vinylic supramolecular crosslinker). A full color version of this scheme is available at *Polymer Journal* online.



Scheme 6 Synthesis of RCP_{DMAAm} via the radical polymerization of DMAAm in the presence of VSC (method 6).

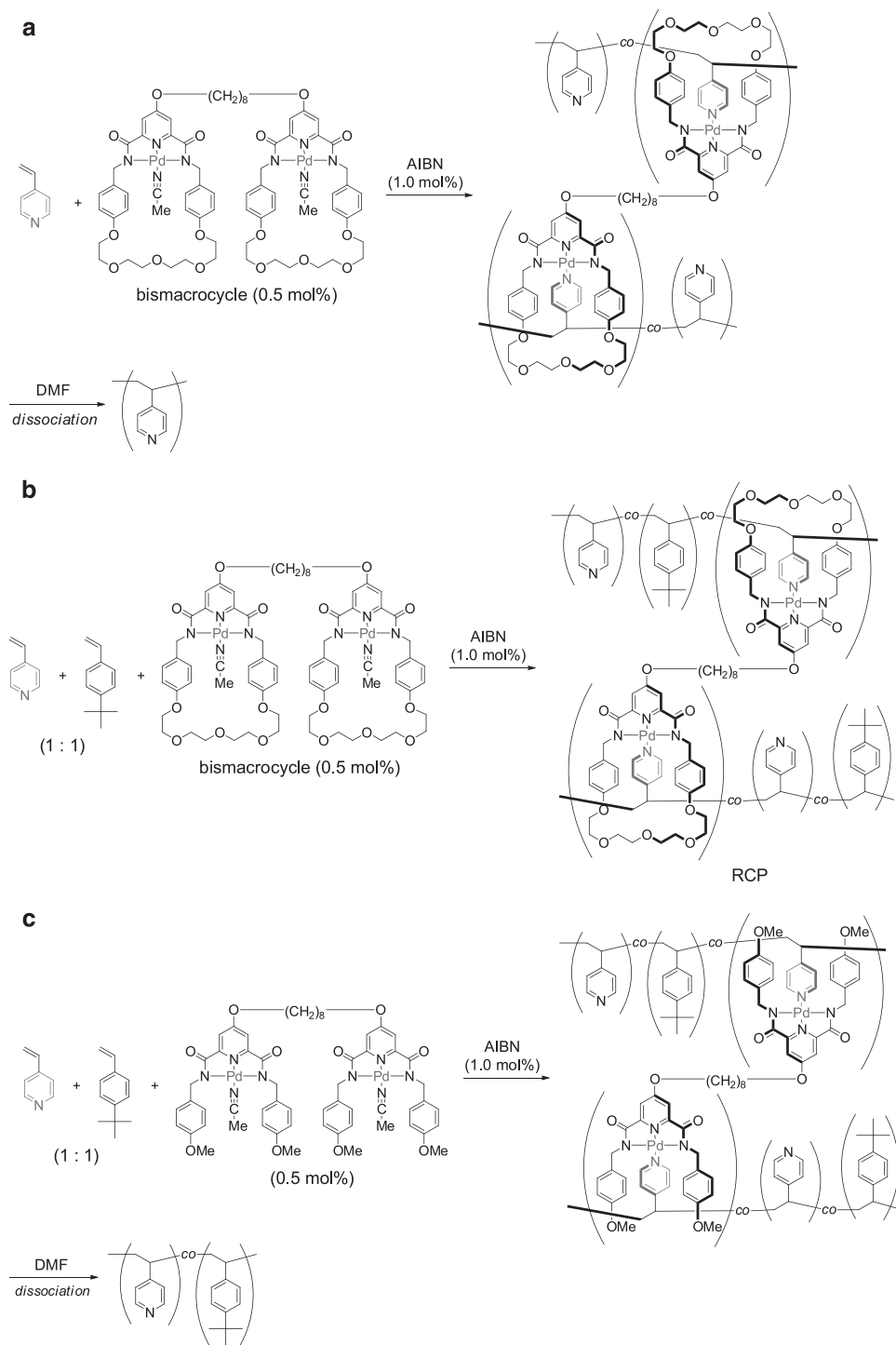


Scheme 7 Coordination of 4-vinylpyridine to a Pd-templated bismacrocycle. A full color version of this scheme is available at *Polymer Journal* online.

MOVABLE ROTAXANE CROSSLINKS IN VINYL POLYMERS

To facilitate the synthesis of RCPs, we recently developed a very simple, effective protocol for directly introducing rotaxane crosslinks into vinyl polymers via the radical polymerization of the corresponding vinyl monomers with a crosslinker (method 6).³⁶ This protocol is the first approach for preparing RCPs that does not require the pre-synthesis or crosslinking of the polyrotaxane before transforming the

crosslinker structure. The crosslinker was a CD-based vinylic supramolecular crosslinker (VSC) consisting of an oligocyclodextrin (OCD) and terminal, bulky end-tethering, polyethylene glycol-type methacrylate (TBM). An OCD and TBM mixture in 0.1 M aq. NaOH was sonicated for 5 min at room temperature to produce a white viscous gel (Scheme 5). As the OCD feed ratio increased, the viscosity increased remarkably and reached a maximum of $\sim 40 \text{ Pa s}^{-1}$ at OCD



Scheme 8 Radical polymerization of 4-vinylpyridine in the presence of a Pd complex: (a) formation and dissociation of a pseudo-RCP, (b) synthesis of chemically stable RCP_{VP} using a bismacrocycle crosslinker via method 7 and (c) formation and dissociation of a Pd complex gel using a bispincer-type Pd complex. A full color version of this scheme is available at *Polymer Journal* online.

concentrations $> 100 \text{ g l}^{-1}$. The change in the VSC viscosity indicated that OCD formed a network structure with TBM, which penetrated into the OCD cavities. Direct UV irradiation of the resultant VSC in the presence of a photoinitiator (Irgacure 500) for 3 min produced a self-standing gelled film (RCP_{VSC}), clearly demonstrating the VSC threaded structure and polymerizability of the VSC vinyl groups.

Next, the usefulness of VSCs as crosslinkers was examined using a vinyl monomer. A mixture of *N,N*-dimethylacrylamide (DMAAm), a VSC, and a photoinitiator was UV-irradiated in water at room temperature for 3 min to afford the corresponding transparent RCP_{DMAAm} film in 84% yield (Scheme 6). In addition to photopolymerization (method A), thermal polymerization using a redox-type radical initiator ($\text{K}_2\text{S}_2\text{O}_8$ and tetramethylethylenediamine, method B) was also effective (97%). The mechanical properties of the resulting RCP_{DMAAm} samples were compared with those of covalently crosslinked polymers. The RCP_{DMAAm} films exhibited larger elongation and Young's modulus values than the covalently crosslinked DMAAm films prepared using a polyethylene glycol-based diacrylate as the crosslinker instead of OCD in the radical polymerization of DMAAm. As the elongation and Young's modulus values are typically inversely proportional, our results suggested that the rotaxane crosslink has a unique effect on the mechanical properties.

We also employed a Pd-templated bismacrocycle as a topological crosslinker to enable the efficient penetration of the propagating end into the macrocyclic cavity during radical polymerization (method 7)³⁷ for the following reasons: (1) the coordination bond between the Pd complex and ligand-containing polymer axle should be highly stable compared with other intermolecular interactions, such as hydrophobic interactions, hydrogen bonding and electrostatic interactions, and thus should maintain the interlocked structure even under polymerization conditions; (2) the Pd complex method should be applicable to macrocycles with cavities larger than the vinyl polymers, leading to novel RCPs; and (3) the distance of the macrocycle along the polymer axle should be easily controlled by introducing bulky groups into the axle in varying concentrations to act as stopper groups. The inherent sliding of RCPs can also be studied by controlling the distance of the macrocycle along the polymer axle.

Thus, a Pd-templated bismacrocycle was prepared in good yield using a slightly modified procedure based on our previously established protocol. As we previously found that rotaxanes were formed efficiently from a Pd-templated macrocycle and pyridine-containing axle,^{50–52} 4-vinylpyridine was selected as the vinyl monomer. Before the RCP synthesis, the coordination behavior of 4-vinylpyridine with the Pd-templated bismacrocycle was evaluated (Scheme 7), and it was determined via ¹H NMR analysis that a coordination complex was formed, strongly indicating that the bismacrocycle is a suitable topological crosslinker for poly(4-vinylpyridine).

Next, RCPs were synthesized via ligand exchange on the Pd bismacrocycle with 4-vinylpyridine during radical polymerization. The radical polymerization of 4-vinylpyridine in the presence of the Pd-templated bismacrocycle (0.5 mol%) and AIBN (1.0 mol%) was performed in DMF at 60 °C to afford a gelled product in quantitative yield (Scheme 8a). However, diluting the gel with a large amount of DMF led to its prompt dissociation to poly(4-vinylpyridine) and the bismacrocycle. This behavior is typical of conventional crosslinked polymers formed via metal–ligand interactions, indicating that the gel included only topological crosslinking points without any covalent interactions. To prepare a stable RCP, 4-*tert*-butylstyrene was added to the reaction mixture as a vinyl comonomer. It was assumed that the bulky monomer would sufficiently prevent the dissociation of the RCP components. The radical polymerization of a 1:1 mixture of

4-vinylpyridine and 4-*tert*-butylstyrene afforded an RCP that was stable even when highly diluted in DMF (Scheme 8b). This result indicated that the 4-*tert*-butylbenzene moieties in the gel trunk polymer acted as stopper moieties and prevented the polymer axle from deslipping from the macrocyclic components. To elucidate the role of the rotaxane crosslinks and the significance of the topological crosslinker, the polymerization was performed in the presence of a bis pincer-type Pd complex (Scheme 8c). A gel was obtained in quantitative yield, and after treatment with a large amount of DMF, it immediately transformed into a sol containing the trunk polymer. These results confirmed that the macrocyclic structure of the crosslinker is important for the formation of stable gelled products.

CONCLUSIONS AND OUTLOOK

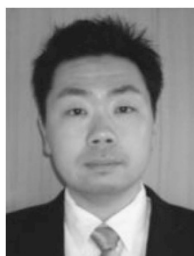
This paper summarizes four strategic approaches for synthesizing RCPs that have been recently developed by Takata *et al.*^{34–37} and are described in Figure 1. The fabrication of novel RCPs is expected to be achieved using suitable rotaxane components, including crown ethers/ammonium salts, cyclodextrins/hydrophobic guests and metal-coordinated macrocycles/ligands, in these synthetic approaches. These approaches could provide rational and efficient pathways for inserting rotaxane-crosslinking points into polymers. They are also promising methods for programming network polymers with macroscopic transformation systems that are linked to the dynamic behavior of rotaxane architectures with unique switching capabilities. The development of this type of system could, in turn, result in the creation of new stimuli-responsive materials based on versatile rotaxane chemistry (for a recent report concerning the synthesis of stimuli-responsive RCPs via method 4, see Iijima *et al.*⁵³). We are currently developing stimuli-responsive fluorescent switching materials that exploit a fluorescence rotaxane switching system.

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- 1 Takata, T., Kihara, N. & Furusho, Y. Polyrotaxanes and polycatenanes: recent advances in syntheses and applications of polymers comprising of interlocked structures. *Adv. Polym. Sci.* **171**, 1–75 (2005).
- 2 Huang, F. & Gibson, H. W. Polypseudorotaxanes and polyrotaxanes. *Prog. Polym. Sci.* **30**, 982–1018 (2005).
- 3 Harada, A. Supramolecular polymers based on cyclodextrins. *J. Polym. Sci. Part A: Polym. Chem.* **44**, 5113–5119 (2006).
- 4 Wenz, G., Han, B.-H. & Mueller, A. Cyclodextrin rotaxanes and polyrotaxanes. *Chem. Rev.* **106**, 782–817 (2006).
- 5 Takata, T. Polyrotaxane and polyrotaxane network: supramolecular architectures based on the concept of dynamic covalent bond chemistry. *Polym. J.* **38**, 1–20 (2006).
- 6 Mayumi, K. & Ito, K. Structure and dynamics of polyrotaxane and slide-ring materials. *Polymer* **51**, 959–967 (2010).
- 7 Takata, T., Arai, T., Kohsaka, Y., Shioya, M. & Koyama, Y. Polyrotaxane network as a topologically cross-linked polymer: synthesis and properties. in *Supramolecular Polymer Chemistry* (ed. Harada, A.) Ch. 15, 331–346 (Wiley-VCH, Weinheim, Germany, 2012).
- 8 Delaviz, Y. & Gibson, H. W. Macrocyclic polymers 2. Synthesis of poly(amide crown ethers) based on bis(5-carboxy-1,3-phenylene)-32-crown-10. Network formation through threading. *Macromolecules* **25**, 4859–4862 (1992).
- 9 Gong, C. & Gibson, H. W. Supramolecular chemistry with macromolecules. Macromolecular knitting, reversible formation of branched polyrotaxanes by self-assembly. *Macromol. Chem. Phys.* **199**, 1801–1806 (1998).

- 10 Gibson, H. W., Nagvekar, D. S., Powell, J., Gong, C. & Bryant, W. S. Polyrotaxanes by in situ self threading during polymerization of functional macrocycles. Part 2. Poly(ester crown ether)s. *Tetrahedron* **53**, 15197–15207 (1997).
- 11 Gong, C. & Gibson, H. W. Self-Threading-based approach for branched and/or cross-linked poly(methacrylate rotaxane)s. *J. Am. Chem. Soc.* **119**, 5862–5866 (1997).
- 12 Gong, C. & Gibson, H. W. Controlling polymeric topology by polymerization conditions: mechanically linked network and branched poly(urethane rotaxane)s with controllable polydispersity. *J. Am. Chem. Soc.* **119**, 8585–8591 (1997).
- 13 Gibson, H. W., Nagvekar, D. S., Yamaguchi, N., Bhattacharjee, S., Wang, H., Vergene, M. & Hercules, D. M. Polyamide pseudorotaxanes, rotaxanes, and catenanes based on bis(5-carboxy-1,3-phenylene)-(3x+2)-crown-x ethers. *Macromolecules* **37**, 7514–7529 (2004).
- 14 Zada, A., Avny, Y. & Zilkha, A. Monomers for non-bond crosslinking of vinyl polymers. *Eur. Polym. J.* **35**, 1159–1164 (1999).
- 15 Zada, A., Avny, Y. & Zilkha, A. Monomers for non-bond crosslinking of vinyl polymers. II. Cyclic octaethylene glycol 5-methacrylamido-isophthalate. *Eur. Polym. J.* **36**, 351–357 (2000).
- 16 Zada, A., Avny, Y. & Zilkha, A. Monomers for non-bond crosslinking of vinyl polymers. III. Some characteristics of the system. *Eur. Polym. J.* **36**, 359–364 (2000).
- 17 Zilkha, A. Non-bond crosslinked polymer hydrogels. *Eur. Polym. J.* **37**, 2145–2146 (2001).
- 18 Oike, H., Mouri, T. & Tezuka, Y. A cyclic macromonomer designed for a novel polymer network architecture having both covalent and physical linkages. *Macromolecules* **34**, 6229–6234 (2001).
- 19 Kubo, M., Hibino, T., Tamaura, M., Uno, T. & Itoh, T. Synthesis and copolymerization of cyclic macromonomer based on cyclic polystyrene: gel formation via chain threading. *Macromolecules* **35**, 5816–5820 (2002).
- 20 Kubo, M., Kato, N., Uno, T. & Itoh, T. Preparation of mechanically cross-linked polystyrenes. *Macromolecules* **37**, 2762–2765 (2004).
- 21 Kubo, M., Matsuura, T., Morimoto, H., Uno, T. & Itoh, T. Preparation and polymerization of a water-soluble, nonbonding crosslinking agent for a mechanically crosslinked hydrogel. *J. Polym. Sci. Part A Polym. Chem.* **43**, 5032–5040 (2005).
- 22 de Gennes, P. G. Sliding gels. *Physica A* **271**, 231–237 (1999).
- 23 Okumura, Y. & Ito, K. The polyrotaxane gel: a topological gel by figure-of-eight cross-links. *Adv. Mater.* **13**, 485–487 (2001).
- 24 Ito, K. Slide-ring materials using topological supramolecular architecture. *Curr. Opin. Solid State Mater. Sci.* **14**, 28–34 (2010).
- 25 Kato, K. & Ito, K. Dynamic transition between rubber and sliding states attributed to slidable cross-links. *Soft Matter* **7**, 8737–8740 (2011).
- 26 Mayumi, K., Tezuka, M., Bando, A. & Ito, K. Mechanics of slide-ring gels: novel entropic elasticity of a topological network formed by ring and string. *Soft Matter* **8**, 8179–8183 (2012).
- 27 Kato, K. & Ito, K. Polymer networks characterized by slidable crosslinks and the asynchronous dynamics of interlocked components. *React. Funct. Polym.* **73**, 405–412 (2013).
- 28 Watanabe, J., Ooya, T., Park, K. D., Kim, Y. H. & Yui, N. Preparation and characterization of poly(ethylene glycol) hydrogels cross-linked by hydrolyzable polyrotaxane. *J. Biomater. Sci., Polym. Ed.* **11**, 1333–1346 (2000).
- 29 Watanabe, J., Ooya, T., Nitta, K.-H., Park, K. D., Kim, Y. H. & Yui, N. Fibroblast adhesion and proliferation on poly(ethylene glycol) hydrogels crosslinked by hydrolyzable polyrotaxane. *Biomaterials* **23**, 4041–4048 (2002).
- 30 Ichi, T., Nitta, K., Lee, W. K., Ooya, T. & Yui, N. Preparation of porous hydrolyzable polyrotaxane hydrogels and their erosion behavior. *J. Biomater. Sci. Polym. Ed.* **14**, 567–579 (2003).
- 31 Ooya, T., Ichi, T., Furubayashi, T., Katoh, M. & Yui, N. Cationic hydrogels of PEG crosslinked by a hydrolyzable polyrotaxane for cartilage regeneration. *React. Funct. Polym.* **67**, 1408–1417 (2007).
- 32 Harada, A., Li, J. & Kamachi, M. The molecular necklace: a rotaxane containing many threaded α -cyclodextrins. *Nature* **356**, 325–327 (1992).
- 33 Harada, A., Li, J. & Kamachi, M. Double-stranded inclusion complexes of cyclodextrin threaded on poly(ethylene glycol). *Nature* **370**, 126–128 (1994).
- 34 Kohsaka, Y., Nakazono, K., Koyama, Y. & Takata, T. Size-complementary rotaxane cross-link: effect on stabilization and degradation of supramolecular network. *Angew. Chem., Int. Ed.* **50**, 4872–4875 (2011).
- 35 Koyama, Y., Yoshii, T., Kohsaka, Y. & Takata, T. Photo-degradable cross-linked polymer derived from a vinylic rotaxane cross-linker possessing aromatic disulfide axle. *Pure Appl. Chem.* **85**, 835–842 (2013).
- 36 Arai, T., Jang, K., Koyama, Y., Asai, S. & Takata, T. Versatile supramolecular cross-linker: a rotaxane cross-linker that directly endows vinyl polymers with movable cross-links. *Chem. Eur. J.* **19**, 5917–5923 (2013).
- 37 Ogawa, M., Kawasaki, A., Koyama, Y. & Takata, T. Synthesis and properties of polyrotaxane network prepared from Pd-templated bis-macrocycle as a topological cross-linker. *Polym. J.* **43**, 909–915 (2011).
- 38 Ashton, P. R., Baxter, I., Fyfe, M. C. T., Raymo, F. M., Spencer, N., Stoddart, J. F., White, A. J. P. & Williams, D. J. Rotaxane or pseudorotaxane? That is the question! *J. Am. Chem. Soc.* **120**, 2297–2307 (1998).
- 39 Tachibana, Y., Kihara, N., Furusho, Y. & Takata, T. Is the tert-butyl group bulky enough to end-cap a pseudorotaxane with a 24-crown-8-ether wheel? *Org. Lett.* **6**, 4507–4509 (2004).
- 40 Makita, Y., Kihara, N. & Takata, T. Quantitative active transport in [2]rotaxane using a one-shot acylation reaction toward the linear molecular motor. *J. Org. Chem.* **73**, 9245–9250 (2008).
- 41 Akae, Y., Okamura, H., Koyama, Y., Arai, T. & Takata, T. Selective synthesis of a [3]rotaxane consisting of size-complementary components and its stepwise deslippage. *Org. Lett.* **14**, 2226–2229 (2012).
- 42 Nakanozo, K. & Takata, T. Neutralization of a sec-ammonium group unusually stabilized by the “rotaxane effect”: synthesis, structure, and dynamic nature of a ‘free’ sec-amine/crown ether-type rotaxane. *Chem. Eur. J.* **16**, 13783–13794 (2010).
- 43 Furusho, Y., Hasegawa, T., Tsuboi, A., Kihara, N. & Takata, T. ‘Unlock-lock’ approach to [2] and [3]rotaxanes: entering of a ring through disulfide linkage that is unlocked by thiol ‘key’. *Chem. Lett.* **29**, 18–19 (2000).
- 44 Furusho, Y., Oku, T., Hasegawa, T., Tsuboi, A., Kihara, N. & Takata, T. Dynamic covalent approach to [2]- and [3]rotaxanes by utilizing a reversible thiol-disulfide interchange reaction. *Chem. Eur. J.* **9**, 2895–2903 (2003).
- 45 Oku, T., Furusho, Y. & Takata, T. First poly[3]rotaxane synthesized through the noncovalent step-growth polymerization of a homoditopic dumbbell compound and a macrocycle with a reversible thiol-disulfide interchange reaction. *J. Polym. Sci. Part A Polym. Chem.* **41**, 119–123 (2003).
- 46 Oku, T., Furusho, Y. & Takata, T. Rotaxane-stabilized thiophosphonium salt from disulfide and phosphine. *Org. Lett.* **5**, 4923–4925 (2003).
- 47 Oku, T., Furusho, Y. & Takata, T. A concept for recyclable cross-linked polymers: topologically networked polyrotaxane capable of undergoing reversible assembly and disassembly. *Angew. Chem. Int. Ed.* **43**, 966–968 (2004).
- 48 Bilig, T., Oku, T., Furusho, Y., Koyama, Y., Asai, S. & Takata, T. Polyrotaxane networks formed via rotaxanation utilizing dynamic covalent chemistry of disulfide. *Macromolecules* **41**, 8496–8503 (2008).
- 49 Yoshii, T., Kohsaka, Y., Moriyama, T., Suzuki, T., Koyama, Y. & Takata, T. An efficient synthetic entry to rotaxanes utilizing reversible cleavage of aromatic disulfide bonds. *Supramol. Chem.* **22**, 1029–0478 (2010).
- 50 Furusho, Y., Matsuyama, T., Takata, T., Moriuchi, T. & Hirao, T. Synthesis of novel interlocked systems utilizing a palladium complex with 2,6-pyridinedicarboxamide-based tridentate macrocyclic ligand. *Tetrahedron Lett.* **45**, 9593–9597 (2004).
- 51 Miyagawa, N., Watanabe, M., Matsuyama, T., Koyama, Y., Moriuchi, T., Hirao, T., Furusho, Y. & Takata, T. Successive catalytic reactions specific to Pd-based rotaxane complexes as a result of wheel translation along the axle. *Chem. Commun.* **46**, 1920–1922 (2010).
- 52 Miyagawa, N., Kawasaki, A., Watanabe, M., Ogawa, M., Koyama, Y. & Takata, T. Synthesis and properties of metal-templated polyrotaxane. *Kobunshi Ronbunshu* **68**, 702–709 (2011).
- 53 Iijima, K., Kohsaka, Y., Koyama, Y., Nakazono, K., Uchida, S., Asai, S. & Takata, T. Stimuli-degradable cross-linked polymers synthesized by radical polymerization using a size-complementary [3]rotaxane cross-linker. *Polym. J.* **46**, 67–72 (2013).



Dr Yasuhito Koyama is currently an associate professor in Catalytic Research Center (CRC), Hokkaido University, Japan. He was born in Hokkaido, Japan, in 1978. He received his Bachelor Degree (2000), Master Degree (2002) from Hokkaido University under the supervision of Prof. Akio Murai, and Doctorate Degree (2005) from Tohoku University under the supervision of Prof. Masahiro Hirao. He was a postdoctoral researcher of Japan Society for the Promotion of Science (JSPS) in Tokyo Institute of Technology under the supervision of Prof. Keisuke Suzuki (2005–2007). In 2007, he became an assistant professor of Tokyo Institute of Technology under Prof. Toshikazu Takata. In 2013, he moved to the laboratory of Prof. Tamaki Nakano, CRC, Hokkaido University. His current research interests include organic chemistry, supramolecular chemistry, and synthesis of biopolymers. He received the Award for Encouragement of Research in Polymer Science from the Society of Polymer Science, Japan (2012).