

FOCUS REVIEW

Synthesis of cyclic polymers and *topology effects* on their diffusion and thermal properties

Takuya Yamamoto

In comparison with their linear counterparts, cyclic polymers exhibit distinctive properties due to their topology. The synthesis of cyclic polymers and the functionalities arising from their unique shapes, namely *topology effects*, are reviewed. The electrostatic self-assembly and covalent fixation (ESA-CF) process was used in conjunction with click chemistry and with olefin metathesis to construct selectively a variety of unprecedented polymer architectures, such as manacle-shaped and tandem multicycles, as well as doubly *fused* tricyclic and triply *fused* tetracyclic topologies. Moreover, the self-assembly of a cyclic amphiphilic block copolymer, which was prepared by intramolecular metathesis, produced micelles that exhibited an increase in thermal stability of approximately 50 °C compared with the micelles formed from the linear prepolymer. Single-molecule spectroscopic studies also revealed different diffusion modes for cyclic and linear polymers.

Polymer Journal (2013) 45, 711–717; doi:10.1038/pj.2012.213; published online 12 December 2012

Keywords: cyclic polymer; electrostatic self-assembly and covalent fixation process; self-assembly; topology effect

INTRODUCTION

Remarkable progress in the synthesis of polymers with a tailored architecture has extended polymer design from conventional linear structures to nonlinear and complex topologies composed of branched and cyclic segments. Unprecedented opportunities exist for the design of functional polymeric materials through the manipulation of their topologies. Among the various types of topologies, cyclic constructions attract particular attention because of their unique properties, which arise from the lack of chain ends. Cyclic polymers exhibit distinctive static and dynamic properties, including smaller hydrodynamic volumes, lower viscosities and higher glass transition temperatures. Cyclic polymers exhibit diffusion modes that are distinct from their linear and branched counterparts.^{1–4}

Recently, new synthetic protocols have been developed to produce diverse cyclic polymers with a high purity, providing a new platform for the design of polymeric materials with novel topologies.^{1–3,5–11} Monocyclic structures, multicyclic structures and linear–cyclic topological block copolymers have been obtained through the use of these novel synthetic protocols. Based on studies of these ring-containing polymers, unusual properties and functions of the polymeric materials, that is, *topology effects*, have been revealed that are unattainable by either their traditional linear or branched^{12–14} counterparts.^{8,15,16} The properties of a self-assembled cyclic amphiphilic block copolymer have attracted a great deal of attention because the topology effect was reported to be amplified.¹⁷ This review focuses on recent studies of the synthesis of cyclic polymers and on the unique properties arising from their self-assembly.

SYNTHESIS OF CYCLIC POLYMERS

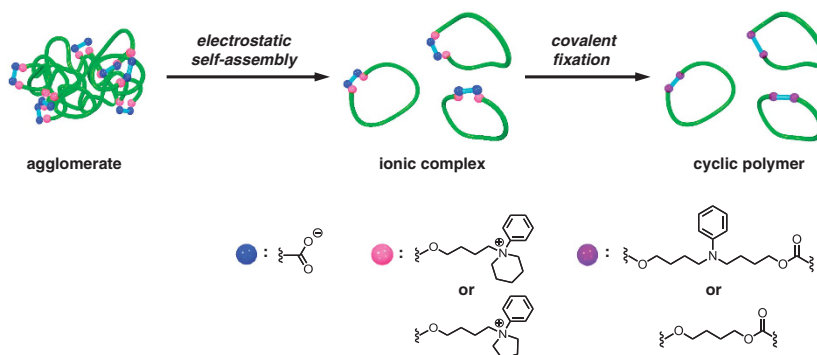
The most straightforward synthetic approach for preparing cyclic polymers is a reaction between the reactive end groups of a linear prepolymer, namely a telechelic polymer, and a bifunctional coupling reagent.⁷ The disadvantage of this *bimolecular* cyclization protocol is that the process must be performed with strictly equimolar amounts of a telechelics and a coupling reagent.^{18–20} Therefore, this process is considered impractical. *Unimolecular* processes, which involve the end-to-end reaction of a telechelics and do not require equimolar amounts of two components, were later developed.^{21,22} Recently, Grayson and co-workers²³ prepared a telechelic polystyrene with ethynyl and azido end groups, and they cyclized the polymer via click chemistry. However, this approach involves synthetic difficulties in the preparation of asymmetric telechelics. Ring-expansion polymerization, which proceeds via the successive insertion of monomers into a cyclic initiator to expand the ring, has also been explored.^{24,25} In contrast with the aforementioned end-to-end cyclization of a linear prepolymer, ring-expansion polymerization does not require dilute conditions. Grubbs and co-workers^{24,26,27} invented cyclic catalysts with a ruthenium–alkylidene bond that can polymerize cyclic olefins, such as 1,5-cyclooctadiene and cyclooctene, using the ring-expansion technique. In the end, back-biting eliminates the initial catalyst complex and forms cyclic polybutadiene and poly(cyclooctene). The obtained cyclic poly(cyclooctene) was hydrogenated to give cyclic polyethylene, which exhibits topology effects distinctive from the commercial linear polyethylene.²⁶ Recently, Waymouth and co-workers^{25,28} used an N-heterocyclic carbene

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, Japan.

Correspondence: Dr T Yamamoto, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1, S8-41 O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

E-mail: yamamoto.t.ay@m.titech.ac.jp.

Received 21 May 2012; revised 12 August 2012; accepted 11 October 2012; published online 12 December 2012



Scheme 1 Schematic illustration for the electrostatic self-assembly and covalent fixation (ESA-CF) process.

compound as an initiator for ring-expansion polymerization of lactides to form cyclic polylactides with a narrow polydispersity index. In these studies, control of the molecular weight of cyclic polymers was achieved for the first time.

Electrostatic self-assembly and covalent fixation process

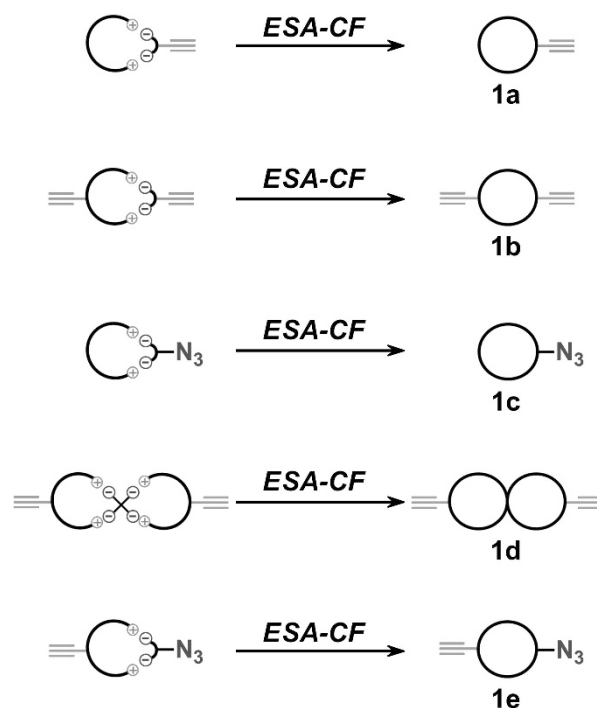
We have developed a process called electrostatic self-assembly and covalent fixation (ESA-CF), which utilizes a linear or star telechelic prepolymer with cyclic ammonium end groups and a multicarboxylate counterion.^{29–32} The prescribed combination of a telechelics and a counteranion forms a predesigned architecture via *electrostatic self-assembly*. In this process, a kinetic agglomerate at a high concentration restructures to yield a thermodynamically favored ionic complex with the smallest possible number of components in a dilute solution by keeping the charge balance (Scheme 1). Subsequently, the ionic complex solution is refluxed, leading to the selective ring opening of the cyclic ammonium end groups, which covalently link the predesigned construction (covalent fixation).

This method has been used for the construction of cyclic polymers using a wide variety of telechelics, including poly(THF) (poly(tetrahydrofuran)),³⁰ poly(ethylene oxide),³³ polystyrene³⁴ and poly(dimethylsiloxane),³⁵ which were prepared by living polymerization and by subsequent end-capping with cyclic amines. Through the use of a functionalized telechelics and/or a counterion, a variety of monocyclic polymers with prescribed functional groups at designated positions have been prepared.³⁶ These functionalized macrocyclic prepolymers (*kyklo*-telechelics) have been utilized to construct multicyclic polymeric topologies with higher complexities.³⁷

Bridged tricyclic and tetracyclic topologies

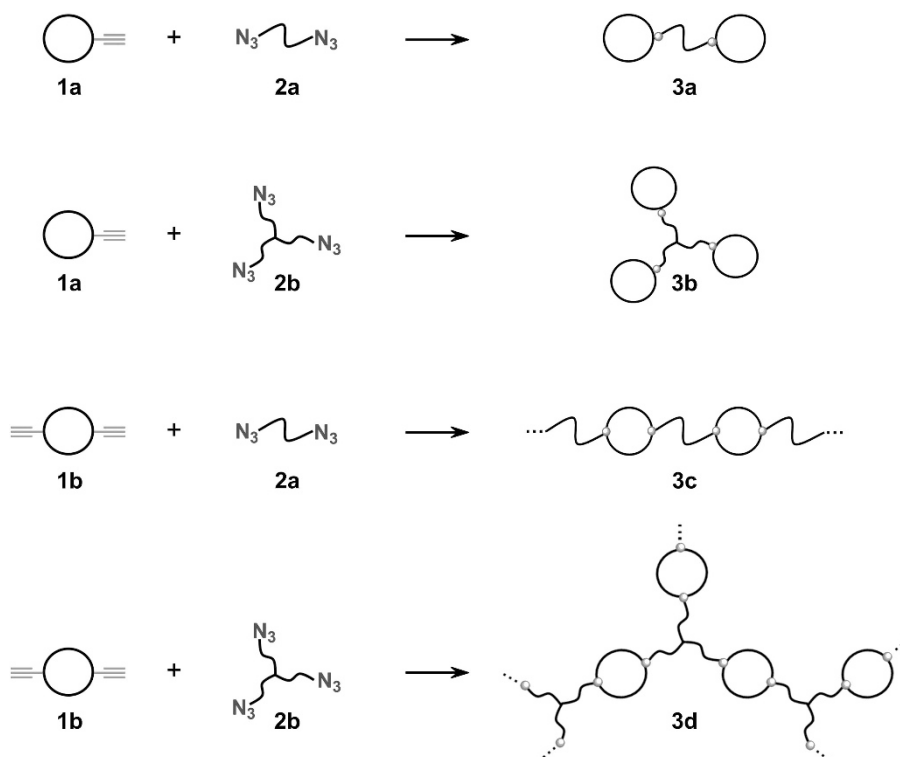
A series of monocyclic poly(THF) *kyklo*-telechelics with an ethynyl group (**1a**), with two ethynyl groups at opposite positions (**1b**), with an azido group (**1c**), and with ethynyl and azido groups at opposite positions (**1e**) were prepared using the ESA-CF process (Scheme 2). Unfunctionalized and ethynyl-functionalized *N*-phenylpyrrolidinium-terminated poly(THF) prepolymers complexed with ethynyl- and azido-functionalized dicarboxylate counteranions were used.³⁸ Furthermore, a bicyclic 8-shaped prepolymer with two ethynyl groups at opposite positions (**1d**) was also synthesized (Scheme 2). These prepolymers were fully characterized by ¹H-nuclear magnetic resonance (NMR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and size exclusion chromatography (SEC).

The monocyclic prepolymer with an ethynyl group (**1a**, 2.4–2.5 kDa) was subjected to click chemistry using an azido-



Scheme 2 Preparation of functionalized cyclic prepolymers (*kyklo*-telechelics) using the electrostatic self-assembly and covalent fixation (ESA-CF) process. A full color version of this figure is available at *Polymer Journal* online.

functionalized linear telechelic precursor (**2a**, 2.1 kDa) and using a three-armed star (**2b**, 4.6 kDa) telechelic precursor to produce selectively *bridged* bicyclic (**3a**, 6.7 kDa) and tricyclic (**3b**, 11.1 kDa) paddle-shaped polymers, respectively (Scheme 3).³⁸ The formation of these products was evaluated with SEC, which showed a noticeable peak shift to a higher molecular weight. The yields of **3a** and **3b** were determined to be 48% and 57%, respectively, based on their weights and on the SEC peak area ratios of the crude products. Subsequent isolation was achieved by preparative SEC fractionation. Furthermore, the degrees of volume shrinkage in **3a** and **3b** were calculated based on the ratios of the SEC peak molecular weights to the number-average molecular weights determined using ¹H-NMR ($M_p(\text{SEC})/M_n(\text{NMR})$). The ratio was 0.68 for both **3a** and **3b**, which was comparable to the ratios previously reported for various multicyclic topologies, such as for the 8-shaped (0.69–0.80),^{30,39}



Scheme 3 Synthesis of *bridged* multicyclic polymers by click chemistry. A full color version of this figure is available at *Polymer Journal* online.

trefoil-shaped (0.65),³⁰ θ -shaped (0.63)^{30,40} and δ -graph (0.61)³⁹ polymers. The selective reaction between the ethynyl and the azido groups was confirmed by comparing the ¹H-NMR spectra of the prepolymers with those of the products. The infrared absorbance from the azido group in the prepolymers disappeared, which indicated the completion of the reaction. The MALDI-TOF MS spectra of the products exhibited a uniform series of peaks with an interval of 72 mass units, which correspond to the repeating THF units. Each peak matched the total molar mass of the prepolymers exactly. Furthermore, the sum of twice the molar mass of **1a** and the molar mass of **2a** equaled the molar mass of **3a**. Consistent results were also observed for **3b**. These results confirmed the formation of *bridged* multicyclic **3a** and **3b**.

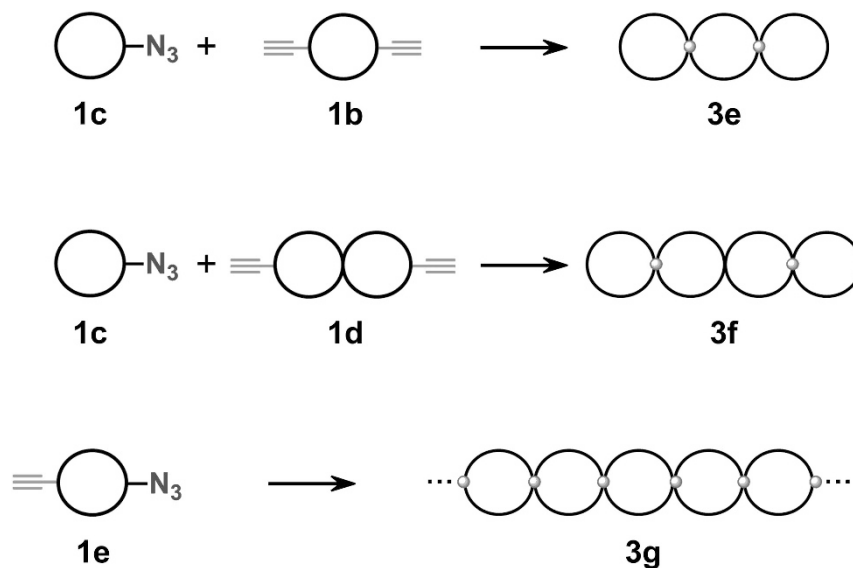
Spiro tricyclic and tetracyclic topologies

Likewise, a monocyclic prepolymer with two ethynyl groups at opposite positions (**1b**) and a bicyclic 8-shaped analog (**1d**) were cross-coupled to a monocyclic precursor with an azido group (**1c**) to produce selectively *spiro* tricyclic (**3e**) and tetracyclic (**3f**) polymers, respectively (Scheme 4).³⁸ The $M_p(\text{SEC})$ value for **3e** (7.4 kDa) was almost equal to the sum of the $M_p(\text{SEC})$ values of the precursors: the sum of two units of **1c** and one unit of **1b** ($2 \times 2.1 + 3.1 = 7.3$ kDa). In contrast, the $M_p(\text{SEC})$ value of tetracyclic **3f** (9.2 kDa) was slightly smaller than the total $M_p(\text{SEC})$ values of the prepolymers: the sum of two units of **1c** and one unit of **1d** ($2 \times 2.4 + 5.9 = 10.7$ kDa). The yields of **3e** and **3f** were calculated to be 76% and 71%, respectively, based on their weights and on the SEC peak area ratios of the crude products. Subsequently, the isolation of **3e** and **3f** was achieved via SEC fractionation. The $M_p(\text{SEC})/M_n(\text{NMR})$ values of the isolated **3e** and **3f** products were determined to be 0.67 and 0.66, respectively, which were consistent with the values of **3a** (0.68) and **3b** (0.68). These data suggest that an increase in the number of ring units in

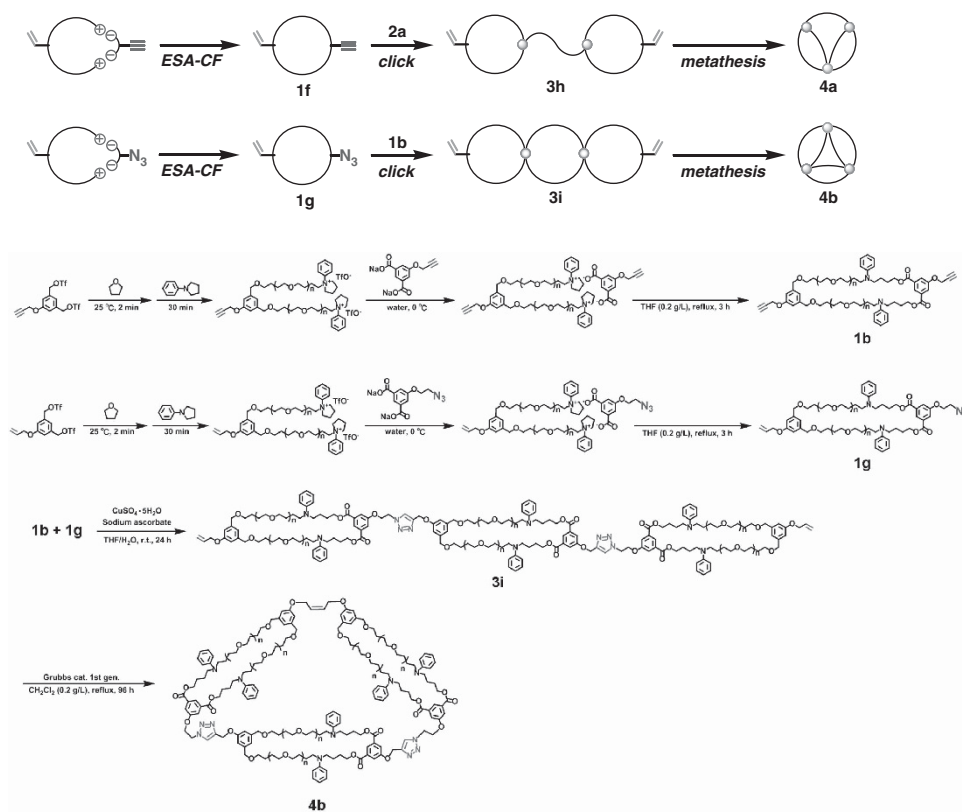
bridged and *spiro* multicyclic polymers causes a comparative shrinkage in their volumes. By comparing the ¹H-NMR spectra of the products with those of the prepolymers, the selective reaction between the ethynyl and the azido groups was confirmed, as observed in the characterization of the *bridged* polymers. The MALDI-TOF MS spectra of **3e** and **3f** also showed a uniform series of peaks with an interval of 72 mass units, which correspond to the repeating THF units, and each peak matched the total molar mass of the complementary precursors exactly. These results confirmed the successful construction of *spiro* **3e** and **3f**.

Repeating cyclic, alternating cyclic/linear and alternating cyclic/star topologies

Click chemistry was applied to the polyaddition of a monocyclic prepolymer with ethynyl and azido groups at opposite positions (**1e**) to produce a tandem *spiro*-type multicyclic polymer (**3g**) (Scheme 4).³⁸ Moreover, co-polyaddition of a monocyclic precursor possessing two ethynyl groups (**1b**) with linear (**2a**) and with three-armed star-shaped (**2b**) azido precursors produced multicyclic polymers with alternating cyclic/linear (**3c**) and with alternating cyclic/star (**3d**) structures, respectively (Scheme 3). Initially, the reaction conditions used to produce **3a**, **3b**, **3e** and **3f** (THF/water, CuSO₄ and sodium ascorbate) were applied, but these conditions resulted in gelation. The modified reaction conditions (THF, CuBr and 2,2'-bipyridine) prevented the gelation of **3c** and **3g**, but the reaction used to produce **3d** still yielded an insoluble fraction under these conditions. The indiscrete multicyclic polymeric products of **3g**, **3c** and **3d** were obtained with 82%, 67% and 72% yields, respectively. The progress of the reactions was monitored using the emergence of a triazole signal, which replaced the ethynyl and azido signals in the ¹H-NMR spectra. The infrared absorbance from the azido groups observed in the prepolymers decreased but was still visible in the



Scheme 4 Synthesis of *spiro* multicyclic polymers by click chemistry. A full color version of this figure is available at *Polymer Journal* online.



Scheme 5 Synthesis of doubly *fused* tricyclic and triply *fused* tetracyclic polymers using the electrostatic self-assembly and covalent fixation (ESA-CF) process, click chemistry and olefin metathesis (top). Complete synthetic scheme for **4b** (bottom). A full color version of this figure is available at *Polymer Journal* online.

spectra of the products, suggesting that a small portion remained unreacted. The unreacted portion was expected to be the end groups of the polymers. SEC analysis showed notable peak shifts to a higher molecular weight with multimodal distributions. The $M_p(\text{SEC})$ value of **3g** went as high as 10.5 kDa, indicating the formation of a hexacyclic structure on average. Similarly, the highest $M_p(\text{SEC})$ value

observed for **3c** was 12.8 kDa, which was apparently due to multicyclic polymers that were composed of four rings connected with three chains. The $M_p(\text{SEC})$ value of the soluble fraction of **3d** was determined to be 20.1 kDa, which corresponds to the combination of four units of **1b** and three units of **2b**. In addition, the SEC traces indicated that concurrent intramolecular reactions occurred. Thus, an

8-shaped product was produced from the *unimolecular* reaction of **1e**, and a θ -shaped polymer was produced from the *bimolecular* reaction of **1b** and **2a**.

Doubly fused tricyclic and triply fused tetracyclic topologies

Doubly *fused* tricyclic and triply *fused* tetracyclic polymers were synthesized using a combination of the ESA-CF process, click chemistry and olefin metathesis (Scheme 5).⁴¹ Monocyclic prepolymers with ethynyl and ethenyl functionalities (**1f**) and with azido and ethenyl functionalities (**1g**) at opposite positions in the cyclic unit were prepared using the ESA-CF process. Subsequently, click chemistry was carried out to combine cyclic **1f** with linear **2a** and cyclic **1g** with cyclic **1b** to produce *bridged* dicyclic **3h** and tandem *spiro* tricyclic **3i**, respectively, which have two ethenyl groups at opposite positions in the cyclic units. These products were isolated by preparative SEC with 63% and 64% yields, respectively. The $M_p(\text{SEC})/M_n(\text{NMR})$ ratios were 0.82 and 0.63, in agreement with the reported values for the aforementioned polymers.³⁸ The $^1\text{H-NMR}$ spectra showed that the signals for the ethynyl and azidomethylene protons were replaced by the triazole proton signal, indicating the completion of the click reaction, and the $M_n(\text{NMR})$ values were determined to be 10 and 11 kDa for **3h** and **3i**, respectively. In the MALDI-TOF mass spectra, a uniform series of peaks with an interval of 72 mass units, which correspond to the repeating THF units, was observed, and each peak matched the molar mass that was calculated from the chemical structure of the investigated product.

The subsequent intramolecular olefin metathesis of **3h** and **3i** was performed with the repeated addition of the first-generation Grubbs catalyst in dilution (0.2 g l^{-1}). The final products, **4a** and **4b**, were isolated by column chromatography on silica gel and/or by preparative SEC fractionation with 28% and 55% yields, respectively. The comparison of the $^1\text{H-NMR}$ spectra of isolated **4a** and **4b** with the spectra of their respective precursors showed that the signals for the terminal olefin units were replaced by those for the inner olefinic units. This change in the spectra indicates that the metathesis went to completion. MALDI-TOF MS also confirmed the construction of the intended structures. Because **4a** and **4b** were produced from **3h** and

3i, respectively, with the elimination of an ethylene molecule, the molecular weights differed by 28 mass units. The degrees of volume shrinkage of *fused* tricyclic **4a** relative to *bridged* dicyclic **3h** and of *fused* tetracyclic **4b** relative to *spiro* tricyclic **3i** were determined from the $M_p(\text{SEC})/M_n(\text{NMR})$ ratios. These calculations revealed a noticeable reduction from 0.82 to 0.60 for **4a** and from 0.63 to 0.52 for **4b**. Therefore, the polymer folding resulted in unusually compact conformations.

TOPOLOGY EFFECTS

Topology effects, which are the differences in physical and chemical properties arising from the shape of a polymer, have been extensively studied in monocyclic homopolymers that are in solution and in the solid state.^{1–3,8,16} Functionalized cyclic polymers with high purity offer new opportunities in synthetic polymer chemistry and in the design of polymeric materials based on topology. Our recent collaborative studies on topology effects focused on the diffusion of a cyclic polymer, which was investigated using single-molecule fluorescence spectroscopy,⁴² and focused on the self-assembly of a cyclic block copolymer to form a thermally stable micelle.¹⁷

Single-molecule fluorescence spectroscopic study of the diffusion of a cyclic polymer

The reptation mechanism accounts for the diffusion dynamics of linear and branched polymers, where the chain ends of the polymer molecules play a critical role.^{43–45} In contrast, cyclic polymers are characterized by the absence of chain ends, and, therefore, non-reptation dynamics can be expected.

Using single-molecule fluorescence spectroscopy to monitor cyclic and linear polymers with a perylene chromophore unit, we successfully determined that the cyclic polymer undergoes a multiple-mode diffusion process that differs from the single-mode process of its linear counterpart (Figure 1).⁴² Linear telechelic poly(THF) with *N*-phenylpiperidinium (six-membered ring)⁴⁶ end groups and a perylene-dicarboxylate counteranion were prepared, and a cyclic polymer with a perylene unit was subsequently formed from the elimination of *N*-phenylpiperidine during the ESA-CF process ($M_n = 3800$, $M_w/M_n = 1.19$). A linear counterpart was also synthesized analogously ($M_n = 4200$, $M_w/M_n = 1.12$). A related cyclic polymer was obtained using an alternative telechelics with *N*-phenylpyrrolidinium (five-membered ring) end groups. However, this product could not be analyzed using single-molecule fluorescence spectroscopy because the fluorescence was quenched by the *N*-phenylamine group formed from the ring-opening reaction of *N*-phenylpyrrolidinium.

Single-molecule imaging experiments, where the perylene-labeled cyclic and the perylene-labeled linear poly(THF) was mixed in a matrix of non-labeled linear poly(THF) (10^3 g l^{-1} , $M_n = 3000$), were carried out to reveal the motions of the single polymer molecules over time.

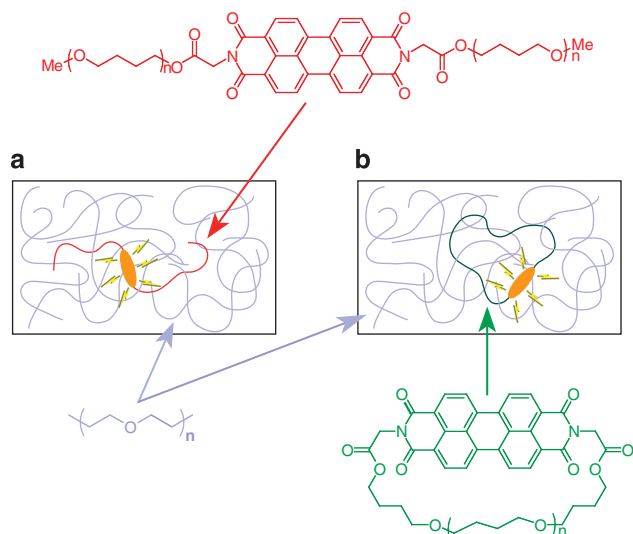
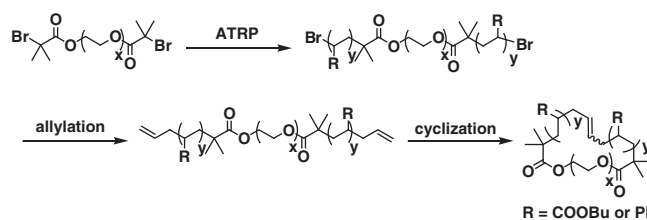


Figure 1 Schematic representation of perylene-labeled (a) linear and (b) cyclic poly(THF) mixed in an unlabeled linear poly(THF) matrix. THF, tetrahydrofuran.



Scheme 6 Synthesis of cyclic amphiphilic block copolymers by atom transfer radical polymerization (ATRP), allylation and intramolecular olefin metathesis.

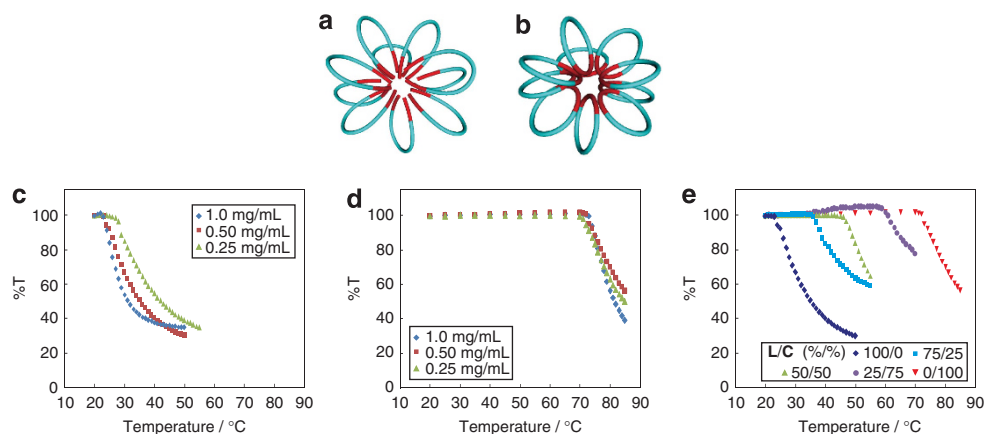


Figure 2 Schematic illustrations of micelles formed from (a) linear and (b) cyclic amphiphilic block copolymers. Temperature dependence of the turbidity of the micellar solutions formed from (c) linear and (d) cyclic copolymers. (e) From a mixture of micelles formed with the linear and cyclic copolymers.

Multimode diffusion was observed for a synthetic cyclic polymer for the first time; this diffusion pattern corresponded to the presence and the absence of a linear matrix polymer threading into the cyclic structure.

Self-assembly of a cyclic block copolymer to form a thermally stable micelle

In 2010, we demonstrated a significant topology effect upon self-assembly of a cyclic amphiphilic block copolymer (poly(*n*-butyl acrylate)-*b*-poly(ethylene oxide), $M_n = 1600\text{--}2600$ or $1400\text{--}2800$) to exhibit the enhanced thermal stability of the micelle in comparison with the stability of one from a linear counterpart (poly(*n*-butyl acrylate)-*b*-poly(ethylene oxide)-*b*-poly(*n*-butyl acrylate), $M_n = 800\text{--}2600\text{--}800$ or $700\text{--}2800\text{--}700$).¹⁷ This study was influenced by the cyclic structure of the cell membrane lipids of thermophilic archaea, which are single-cell microorganisms that inhabit high-temperature environments.^{47–50} The cyclic amphiphilic block copolymers were synthesized by the intramolecular olefin metathesis of the respective linear ABA-type prepolymers, which were prepared by atom transfer radical polymerization using a poly(ethylene oxide) macroinitiator (Scheme 6).⁵¹ The obtained cyclic amphiphilic block copolymer and the linear ethenyl-telechelic prepolymer were self-assembled to produce micelles (Figures 2a and b). The critical micelle concentrations (linear: 0.13 mg mL^{-1} ; cyclic: 0.14 mg mL^{-1}) and the number-average hydrodynamic volumes (linear: $D_h = 20\text{ nm}$; cyclic: $D_h = 20\text{ nm}$) were essentially indistinguishable. AFM and transmission electron microscopy revealed that the size and the spherical morphology of the micelles were consistent with the diameters determined by dynamic light scattering.

Interestingly, the thermostability of the micelle was drastically increased by the linear-to-cyclic topological conversion of the amphiphilic copolymer. The micellar solution produced using the linear block copolymer became turbid at approximately $25\text{ }^\circ\text{C}$ when heated from $20\text{ }^\circ\text{C}$ (Figure 2c), whereas the cyclic counterpart was transparent until the temperature reached over $70\text{ }^\circ\text{C}$ (Figure 2d).¹⁷ Furthermore, tuning of the cloud point was achieved by coassembly of the linear and cyclic copolymers and by changing the mixing ratio (Figure 2e). This ability to tune the cloud point of the mixtures was the result of the large difference in the thermal stabilities of the two micelles. It is expected that this remarkable topology effect will be applicable to the design of heat-responsive molecular devices to enclathrate and release guest molecules. Such topology-based polymeric materials could be suitable for biological applications, such as drug delivery; in

this context, changes in the chemical structure and in the molecular weight often have considerable effects on toxicity and biocompatibility.

Amphiphilic block copolymers composed of hydrophobic polystyrene segments are versatile and are widely used in academics and in industry. The self-assembly of linear polystyrene-*b*-poly(ethylene oxide) has been extensively studied to explore the formation of micelles, vesicles and more complex entities.^{52,53} Thus, the study of cyclic amphiphilic copolymers that contain a polystyrene segment could reveal general topology effects on self-assembly. We prepared cyclic polystyrene-*b*-poly(ethylene oxide) using a similar procedure.⁵⁴ Polystyrene segments were grown from a poly(ethylene oxide) macroinitiator by atom transfer radical polymerization, and the subsequent allylation of the Br termini was carried out using allyltrimethylsilane and TiCl_4 (Scheme 6). Finally, intramolecular olefin metathesis was carried out in the presence of the second-generation Grubbs catalyst to produce cyclic amphiphilic polystyrene-*b*-poly(ethylene oxide).

CONCLUSIONS

Through intensive research efforts, a variety of cyclic polymers with unique topologies have been constructed and fully characterized. The present achievements in the syntheses could contribute to advances in polymer science as well as in supramolecular chemistry. Future studies on self-assembled topological polymers will likely be pursued in the context of functional molecular systems. For example, the synthesis of complex multicyclic polymers could lead to the discovery of enhanced topology effects on diffusion and on the thermal properties. Furthermore, polymeric material designs, which are currently limited to linear and branched topologies, could be renovated by the controlled synthesis of cyclic and multicyclic polymers.

ACKNOWLEDGEMENTS

I thank Professor Yasuyuki Tezuka and the students of the research group. This work was partially supported by the Challenging Research President's Honorary Award, Tokyo Institute of Technology, Mizuho Foundation for the Promotion of Sciences, The Kurata Memorial Hitachi Science and Technology Foundation and KAKENHI (nos. 23106709 and 23685022).

- 1 Semlyen, J. A. *Cyclic Polymers* (Kluwer Academic Publishers, Dordrecht, 2000).
- 2 Deffieux, A. & Borsali, R. in *Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*. (eds Matyjaszewski, K., Gnanou, Y. & Leibler, L.) 875–908 (Wiley, Weinheim, 2007).

- 3 Kricheldorf, H. R. Cyclic polymers: synthetic strategies and physical properties. *J. Polym. Sci. Part A* **48**, 251–284 (2010).
- 4 Robertson, R. M. & Smith, D. E. Strong effects of molecular topology on diffusion of entangled DNA molecules. *Proc. Natl. Acad. Sci. USA* **104**, 4824–4827 (2007).
- 5 Endo, K. Synthesis and properties of cyclic polymers. *Adv. Polym. Sci.* **217**, 121–183 (2008).
- 6 Grayson, S. M. Polymers kept in the loop. *Nat. Chem.* **1**, 178–179 (2009).
- 7 Laurent, B. A. & Grayson, S. M. Synthetic approaches for the preparation of cyclic polymers. *Chem. Soc. Rev.* **38**, 2202–2213 (2009).
- 8 Yamamoto, T. & Tezuka, Y. in *Complex Macromolecular Architectures: Synthesis, Characterization, and Self-Assembly*. (eds Hadjichristidis, N., Hirao, A., Tezuka, Y. & Du Prez, F.) 3–19 (Wiley, Singapore, 2011).
- 9 Yamamoto, T. & Tezuka, Y. Topological polymer chemistry by programmed self-assembly and effective linking chemistry. *Eur. Polym. J.* **47**, 535–541 (2011).
- 10 Yamamoto, T. & Tezuka, Y. in *Synthesis of Polymers* (eds Schlüter, D., Hawker, C. & Sakamoto, J.) 531–545 (Wiley, Weinheim, 2012).
- 11 Jia, Z. & Monteiro, M. J. Cyclic polymers: methods and strategies. *J. Polym. Sci. Part A* **49**, 2085–2097 (2012).
- 12 Hadjichristidis, N., Iatrou, H., Pitsikalis, M. & Mays, J. Macromolecular architectures by living and controlled/living polymerizations. *Prog. Polym. Sci.* **31**, 1068–1132 (2006).
- 13 Tsarevsky, N. V. & Matyjaszewski, K. 'Green' atom transfer radical polymerization: from process design to preparation of well-defined environmentally friendly polymeric materials. *Chem. Rev.* **107**, 2270–2299 (2007).
- 14 Hirao, A., Watanabe, T., Ishizu, K., Ree, M., Jin, S., Jin, K. S., Deffieux, A., Schappacher, M. & Carloti, S. Precise synthesis and characterization of fourth-generation dendrimer-like star-branched poly(methyl methacrylate)s and block copolymers by iterative methodology based on living anionic polymerization. *Macromolecules* **42**, 682–693 (2009).
- 15 Fox, M. E., Szoka, F. C. & Fréchet, J. M. J. Soluble polymer carriers for the treatment of cancer: the importance of molecular architecture. *Acc. Chem. Res.* **42**, 1141–1151 (2009).
- 16 Yamamoto, T. & Tezuka, Y. Topological polymer chemistry: a cyclic approach toward novel polymer properties and functions. *Polym. Chem.* **2**, 1930–1941 (2011).
- 17 Honda, S., Yamamoto, T. & Tezuka, Y. Topology-directed control on thermal stability: micelles formed from linear and cyclized amphiphilic block copolymers. *J. Am. Chem. Soc.* **132**, 10251–10253 (2010).
- 18 Vollmert, B. & Huang, J.-x. Coil properties of ring-shaped polymer-chains. theoretical calculation and experimental determination of $[r]$ ring/ $[r]$ open. *Makromol. Chem. Rapid Commun.* **1**, 333–339 (1980).
- 19 Hild, G., Kohler, A. & Remp, P. Synthesis of ring-shaped macromolecules. *Eur. Polym. J.* **16**, 525–527 (1980).
- 20 Geiser, D. & Höcker, H. Synthesis and investigation of macrocyclic polystyrene. *Macromolecules* **13**, 653–656 (1980).
- 21 Schappacher, M. & Deffieux, A. Synthesis of macrocyclic poly(2-chloroethyl vinyl ether)s. *Makromol. Chem. Rapid Commun.* **12**, 447–453 (1991).
- 22 Tezuka, Y. & Komiya, R. Metathesis polymer cyclization with telechelic poly(THF) having allyl groups. *Macromolecules* **35**, 8667–8669 (2002).
- 23 Laurent, B. A. & Grayson, S. M. An efficient route to well-defined macrocyclic polymers via 'click' cyclization. *J. Am. Chem. Soc.* **128**, 4238–4239 (2006).
- 24 Bielawski, C. W., Benitez, D. & Grubbs, R. H. An 'endless' route to cyclic polymers. *Science* **297**, 2041–2044 (2002).
- 25 Culkun, D. A., Jeong, W., Csihony, S., Gomez, E. D., Balsara, N. P., Hedrick, J. L. & Waymouth, R. M. Zwitterionic polymerization of lactide to cyclic poly(lactide) by using N-heterocyclic carbene organocatalysts. *Angew. Chem. Int. Ed.* **46**, 2627–2630 (2007).
- 26 Bielawski, C. W., Benitez, D. & Grubbs, R. H. Synthesis of cyclic polybutadiene via ring-opening metathesis polymerization: the importance of removing trace linear contaminants. *J. Am. Chem. Soc.* **125**, 8424–8425 (2003).
- 27 Xia, Y., Boydston, A. J., Yao, Y., Kornfield, J. A., Gorodetskaya, I. A., Spiess, H. W. & Grubbs, R. H. Ring-expansion metathesis polymerization: catalyst-dependent polymerization profiles. *J. Am. Chem. Soc.* **131**, 2670–2677 (2009).
- 28 Jeong, W., Shin, E. J., Culkun, D. A., Hedrick, J. L. & Waymouth, R. M. Zwitterionic polymerization: a kinetic strategy for the controlled synthesis of cyclic poly(lactide). *J. Am. Chem. Soc.* **131**, 4884–4891 (2009).
- 29 Tezuka, Y. & Oike, H. Designing polymer topology by electrostatic self-assembly and covalent fixation. *Macromol. Symp.* **161**, 159–167 (2000).
- 30 Oike, H., Imaizumi, H., Mouri, T., Yoshioka, Y., Uchibori, A. & Tezuka, Y. Designing unusual polymer topologies by electrostatic self-assembly and covalent fixation. *J. Am. Chem. Soc.* **122**, 9592–9599 (2000).
- 31 Tezuka, Y. Topological polymer chemistry by electrostatic self-assembly. *J. Polym. Sci. A* **41**, 2905–2917 (2003).
- 32 Tezuka, Y. Topological polymer chemistry by dynamic selection from electrostatic polymer self-assembly. *Chem. Rec.* **5**, 17–26 (2005).
- 33 Tezuka, Y., Mori, K. & Oike, H. Efficient synthesis of cyclic poly(oxyethylene) by electrostatic self-assembly and covalent fixation with telechelic precursor having cyclic ammonium salt groups. *Macromolecules* **35**, 5707–5711 (2002).
- 34 Oike, H., Hamada, M., Eguchi, S., Danda, Y. & Tezuka, Y. Novel synthesis of single- and double-cyclic polystyrenes by electrostatic self-assembly and covalent fixation with telechelics having cyclic ammonium salt groups. *Macromolecules* **34**, 2776–2782 (2001).
- 35 Tezuka, Y., Iwase, T. & Shiomi, T. Tailored synthesis of star and network poly(dimethylsiloxane)s through electrostatic self-assembly and subsequent covalent fixation of telechelics having cyclic onium salt groups. *Macromolecules* **30**, 5220–5226 (1997).
- 36 Oike, H., Kobayashi, S., Mouri, T. & Tezuka, Y. *Kyko*-telechelics: tailored synthesis of cyclic poly(tetrahydrofuran)s having two functional groups at opposite positions. *Macromolecules* **34**, 2742–2744 (2001).
- 37 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).
- 38 Sugai, N., Heguri, H., Ohta, K., Meng, Q., Yamamoto, T. & Tezuka, Y. Effective click construction of *bridged*- and *spiro*-multicyclic polymer topologies with tailored cyclic prepolymers (*kyko*-telechelics). *J. Am. Chem. Soc.* **132**, 14790–14802 (2010).
- 39 Tezuka, Y. & Fujiyama, K. Construction of polymeric δ -graph: a doubly fused tricyclic topology. *J. Am. Chem. Soc.* **127**, 6266–6270 (2005).
- 40 Tezuka, Y., Tsuchitani, A., Yoshioka, Y. & Oike, H. Synthesis of θ -shaped poly(THF) by electrostatic self-assembly and covalent fixation with three-armed star telechelics having cyclic ammonium salt groups. *Macromolecules* **36**, 65–70 (2003).
- 41 Sugai, N., Heguri, H., Yamamoto, T. & Tezuka, Y. A programmed polymer folding: *click* and *clip* construction of doubly fused tricyclic and triply fused tetracyclic polymer topologies. *J. Am. Chem. Soc.* **133**, 19694–19697 (2011).
- 42 Habuchi, S., Satoh, N., Yamamoto, T., Tezuka, Y. & Vacha, M. Multimode diffusion of ring polymer molecules revealed by a single-molecule study. *Angew. Chem. Int. Ed.* **49**, 1418–1421 (2010).
- 43 De Gennes, P.-G. *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- 44 McLeish, T. C. B. Tube theory of entangled polymer dynamics. *Adv. Phys.* **51**, 1379–1527 (2002).
- 45 Strobl, G. *The Physics of Polymers: Concepts for Understanding their Structures and Behavior* (Springer, Berlin, 2007).
- 46 Adachi, K., Takasugi, H. & Tezuka, Y. Telechelics having unstrained cyclic ammonium salt groups for electrostatic polymer self-assembly and ring-emitting covalent fixation. *Macromolecules* **39**, 5585–5588 (2006).
- 47 De Rosa, M. & Gambacorta, A. The lipids of archaeobacteria. *Prog. Lipid Res.* **27**, 153–175 (1988).
- 48 Kates, M. in: *The Biochemistry of Archaea (Archaeobacteria)*. (eds Kates, M., Kushner, D. J. & Matheson, A. T.) Ch. 9, 261–295 (Elsevier, Amsterdam, 1993).
- 49 Yamagishi, A. Thermophiles and life science in space. *Biol. Sci. Space* **14**, 332–340 (2000).
- 50 Arakawa, K., Eguchi, T. & Kakinuma, K. 36-Membered macrocyclic diether lipid is advantageous for archaea to thrive under the extreme thermal environments. *Bull. Chem. Soc. Jpn.* **74**, 347–356 (2001).
- 51 Adachi, K., Honda, S., Hayashi, S. & Tezuka, Y. ATRP-RCM synthesis of cyclic diblock copolymers. *Macromolecules* **41**, 7898–7903 (2008).
- 52 Yu, K., Zhang, L. & Eisenberg, A. Novel morphologies of 'crew-cut' aggregates of amphiphilic diblock copolymers in dilute solution. *Langmuir* **12**, 5980–5984 (1996).
- 53 Cameron, N. S., Corbierre, M. K. & Eisenberg, A. Asymmetric amphiphilic block copolymers in solution: a morphological wonderland. *Can. J. Chem.* **77**, 1311–1326 (1999).
- 54 Baba, E., Honda, S., Yamamoto, T. & Tezuka, Y. ATRP-RCM polymer cyclization: synthesis of amphiphilic cyclic polystyrene-*b*-poly(ethylene oxide) copolymers. *Polym. Chem.* **3**, 1903–1909 (2012).



Dr Takuya Yamamoto was born in Kyoto, Japan in 1977. He received his BS degree in 1999 from the University of Utah and his PhD degree in 2004 from the University of Utah under the supervision of Professor Peter J Stang. He joined JST ERATO Aida Nanospace Project as a researcher in 2005. Since 2008, he has been an assistant professor of the Department of Organic and Polymeric Materials, Tokyo Institute of Technology. His current research interests include the synthesis and self-assembly of cyclic polymers for the development of functional materials. He was a recipient of the Tokyo Tech Young Investigator Engineering Award from Tokyo Institute of Technology in 2010, Award for Encouragement of Research in Polymer Science from the Society of Polymer Science, Japan in 2011 and Challenging Research President's Honorary Award from Tokyo Institute of Technology in 2011.