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Effective Approach to Cyclic Polymer from Linear Polymer: Synthesis and Transformation of Macromolecular [1]Rotaxane

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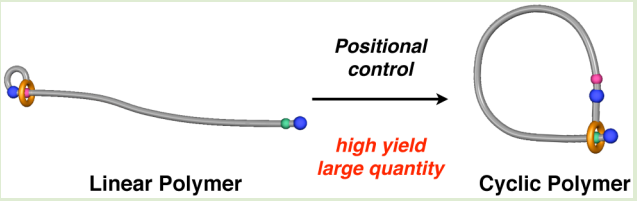
Supporting Information

ABSTRACT: We report a convenient and scalable synthesis of cyclic poly(ε-caprolactone) (PCL) from its linear counterpart based on the rotaxane protocol. Cyclic PCL was prepared by ring-opening polymerization of ε-caprolactone (ε-CL) initiated by a pseudo[2]rotaxane initiator in the presence of diphenylphosphate (DPP) as a catalyst, followed by capping of the propagation end by using a bulky isocyanate to afford macromolecular [2]rotaxane. The successive intramolecular cyclization to macromolecular [1]rotaxane at the polymer terminus proceeded with good yield. The attractive interaction of the terminal ammonium/crown ether moiety was removed via N-acetylation. This enabled movement of the crown ether wheel along the axle PCL chain to the urethane region of the other terminus in solution state. Size-exclusion chromatography and 2D diffusion-ordered spectroscopy (DOSY) results demonstrated the formation of cyclic PCL from linear PCL, which is further supported by thermal property or crystallinity change before and after transformation.



Recent interest in cyclic polymers as a new class of polymer material enables exploration of the property differences between linear and cyclic polymers on the basis of the difference in structure and chain end.[1−7] However, synthesis of cyclic polymers has been a formidable challenge, requiring more general and scalable methods. A few synthetic strategies have been developed to generate cyclic polymers and address the entropic and enthalpic barriers for cyclization. Ring-expansion polymerization of cyclic monomers using cyclic metal complexes as initiators is very useful but limited in structural diversity.[8−10] In contrast, most approaches involving cyclization of linear polymer precursors under high-dilution conditions tend to result in poor yields and the occurrence of competing reactions that require tedious purification steps.[11−18]

We recently reported a novel strategy for cyclic polymer synthesis based on the structural transformation of macromolecular [1]rotaxane based on the rotaxane protocol (Figure 1a).[19] As this cyclization strategy involves the movement of the wheel component along the polymer axle of macromolecular [1]rotaxane, the efficiency is 100% irrespective of concentration, which differs from cyclization between two polymer ends. The initial small cyclic part of the linear polymer macromolecular [1]rotaxane is gradually expanded according to the movement of the wheel to form a large cyclic polymer (Figure 1a). However, this method has room for improvement as introducing the [1]rotaxane moiety to the polymer terminus requires an excess of stabilized [1]rotaxane in a less polar solvent. Thus, we have studied the synthesis of cyclic polymer by the rotaxane protocol and recently developed a convenient synthetic method using the "rotaxane-from method", which exploits a living polymerization initiated by a stable pseudorotaxane initiator to generate the polymer axle.[20]

In this study, we describe a new synthetic method to form a cyclic polymer from a linear polymer, which is characterized by three important processes: (i) simple and versatile synthesis of macromolecular [2]rotaxane by using a pseudorotaxane initiator for the polymerization, based on the "rotaxane-from method",[20−22] (ii) efficient cyclization of [2]rotaxane to [1]rotaxane by using two adjacent reactive groups fixed by the ammonium/crown ether interaction, and (iii) reliable cyclic polymer formation from a linear polymer (macromolecular [1]rotaxane) through the transposition of the rotaxane component, based on the rotaxane protocol, as shown in Figure 1b.

Macromolecular [2] and [1]rotaxanes were prepared according to Schemes 1 and 2. Pseudo[2]rotaxane initiator **3** was generated in situ from *sec*-ammonium salt with both pentenyl and benzyl alcohol termini **1** and dibenzo-24-crown-8-ether possessing pentenyl substituent **2** and then used for the polymerization of ε-CL at a feed ratio of $[\varepsilon\text{-CL}]_0/[\mathbf{3}]_0 = 30/1$ in the presence of acid catalyst DPP (100 mol %)[20−23] (Scheme 1). The OH propagation end group of macromolecular pseudo[2]rotaxane was then capped with 3,5-dimethyl- and 3,5-bis(trifluoromethyl)phenyl isocyanates to afford PCL-containing macromolecular [2]rotaxanes **4** (R = CH_3, 80% yield) and **5** (R = CF_3, 75% yield), respectively. The capping reaction has another important role besides adding an end-cap; it enables the introduction of a carbamate station at

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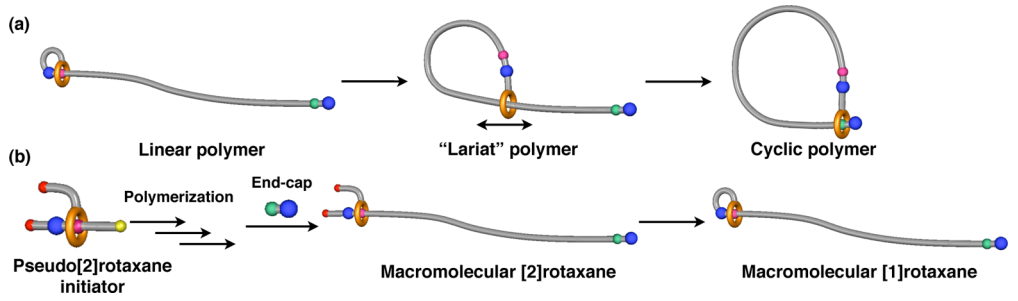
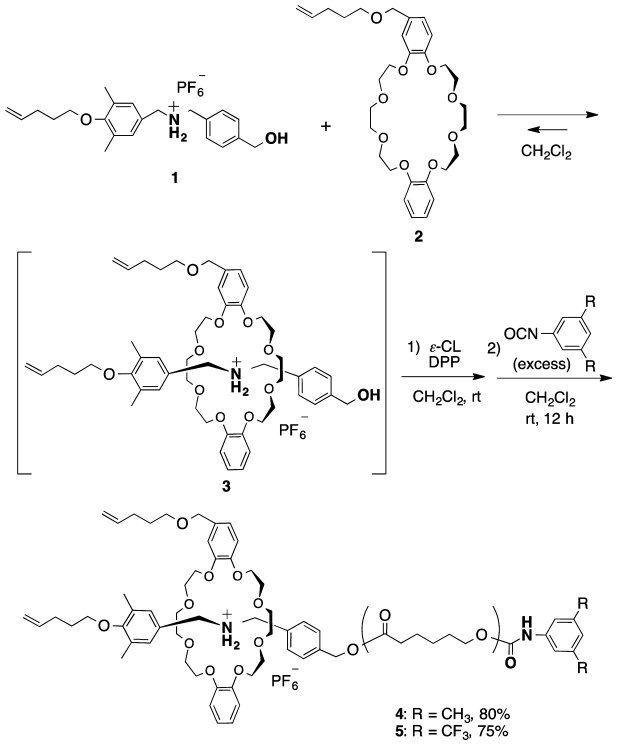
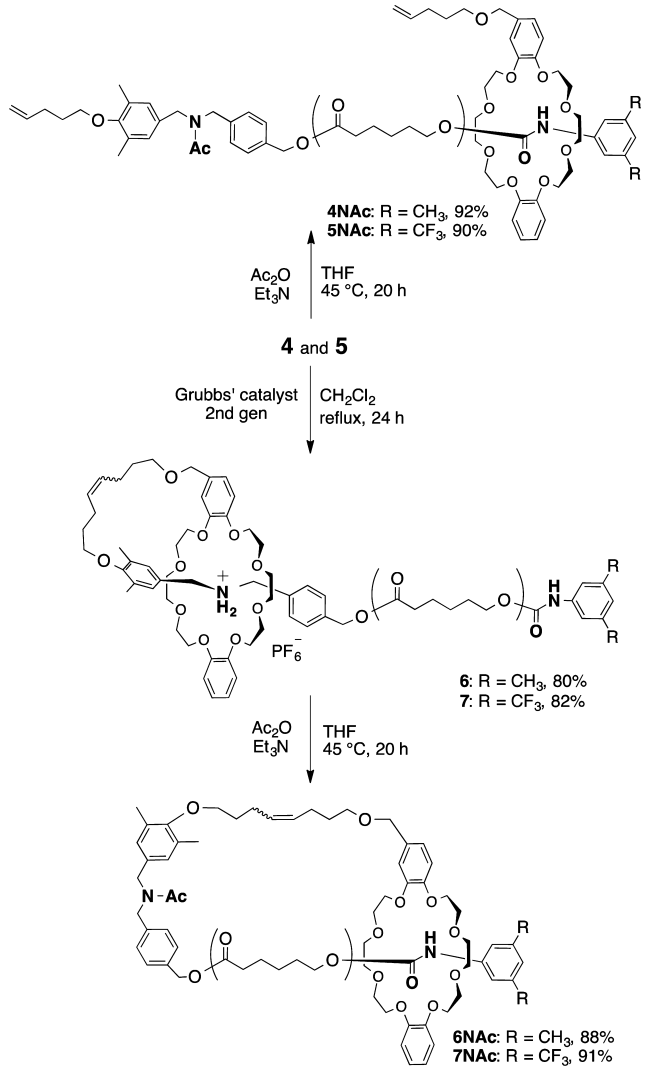


Figure 1. (a) Structural transformation and (b) synthetic strategy using the rotaxane-from method of macromolecular [1]rotaxane.

Scheme 1



Scheme 2



the other polymer terminus, with which the crown ether wheel has an attractive interaction.

Subsequent ring-closing metathesis of the terminal rotaxane moiety of **4** and **5** yielded the corresponding macromolecular [1]rotaxanes **6** (R = CH_3, 80% yield) and **7** (R = CF_3, 82% yield), respectively (Scheme 2). The high efficiency of the cyclization can be accounted for by the proximity effect of the reactive olefin groups, which are forced into close contact by the ammonium/crown ether interaction. The present high-yielding synthesis of macromolecular [1]rotaxane via selective intramolecular cyclization mostly prevents intermolecular oligomerization, which results in tedious purification while performing gram-scale synthesis. Cyclization of the linear polymer was carried out with **6** and **7** by treating with acetic anhydride and triethylamine, according to our previous reports[24,25] to give the cyclic polymers **6NAc** (88%) and **7NAc** (91%), respectively. This was accomplished by removing the strong attractive interaction between the *sec*-ammonium group and the crown ether wheel, which causes the wheel to move from the ammonium station to the carbamate station, that is, from one polymer end to the other.[20−22] Similar treatment of macromolecular [2]rotaxanes **4** and **5** with a mixture of acetic anhydride and triethylamine gave the corresponding isomeric structures, **4NAc** and **5NAc**, in high yields, as the linear counterpart models for **6NAc** and **7NAc** (Scheme 2).

The products were fully characterized by MALDI-TOF-MS and other spectroscopic analyses. The MALDI-TOF-MS spectra provided concrete evidence for the proposed chemical structures of the macromolecular rotaxanes **4**−**7** and **4NAc**−**7NAc**. The observed m/z values matched the calculated values within the experimental error (Figures 2a and S27−S34).

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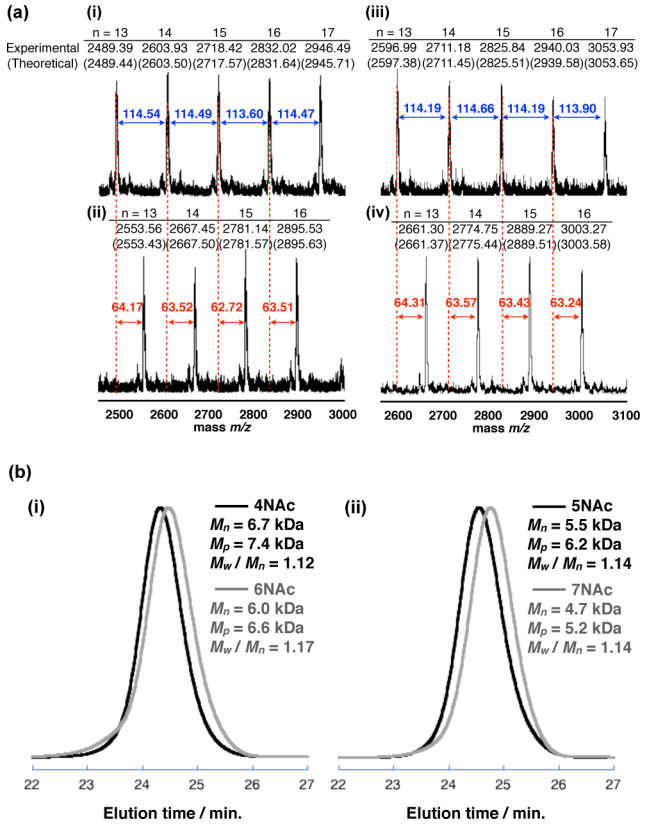

Figure 2. (a) MALDI-TOF-MS spectra of macromolecular [1]-rotaxanes (i) **6**, (ii) **6NAc**, (iii) **7**, and (iv) **7NAc**; (b) SEC profiles of (i) **4NAc** vs **6NAc** and (ii) **5NAc** vs **7NAc** (eluent: $CHCl_3$).

The solution properties of the polymers were investigated to confirm the structural transformation by transposition of the crown ether wheel resulting from *N*-acetylation. Cyclic polymers generally show smaller hydrodynamic volume when compared with their linear counterparts.[1] As shown in Figure 2b, the SEC results of the polymer couples **4NAc** versus **6NAc** and **5NAc** versus **7NAc** in $CHCl_3$ demonstrated that the hydrodynamic volume decreased upon transformation from macromolecular [2]rotaxane to [1]rotaxane, despite their quasi-similar composition. The SEC molecular weight ratio of **4NAc** to **6NAc** was calculated as about 0.89 by comparing their peak top values (M_p). This suggests that the polymer structure changed from linear (**4NAc**) to cyclic (**6NAc**) according to the movement of the wheel component to the carbamate station at the other polymer terminus.[26,27] Similarly, the ratio of **5NAc** to **7NAc** was calculated as about 0.84, which was closer to the reported value of 0.78.[28,29] The structure-dependent change in hydrodynamic volume reveals that **7NAc** should have a higher level of cyclic structure than **6NAc**, although **6NAc** is also mainly cyclic. The difference in degree of cyclization can be readily explained from the difference in hydrogen bonding strength between the electron-donating methyl-substituted and electron-withdrawing trifluoromethyl-substituted carbamates. Figure 1a shows that **6NAc** may also adopt a freely movable lariat-like structure.[30,31] Similarly, the intrinsic viscosity ratios η_{6NAc}/η_{4NAc} and η_{7NAc}/η_{5NAc} were found to be 0.81 and 0.73, respectively (Figures S35 and S36), calculated by the SEC universal calibration theory.[32] As the reported theoretical and experimental viscosity ratios of $\eta_{cyclic}/\eta_{linear}$ 0.66[32] and 0.77,[33] respectively, the cyclic structure of **7NAc** was strongly supported.

The detailed structures, including the local position of the wheel component, were confirmed by NMR spectral analyses. Figure 3 shows the ^{1}H NMR spectra of macromolecular

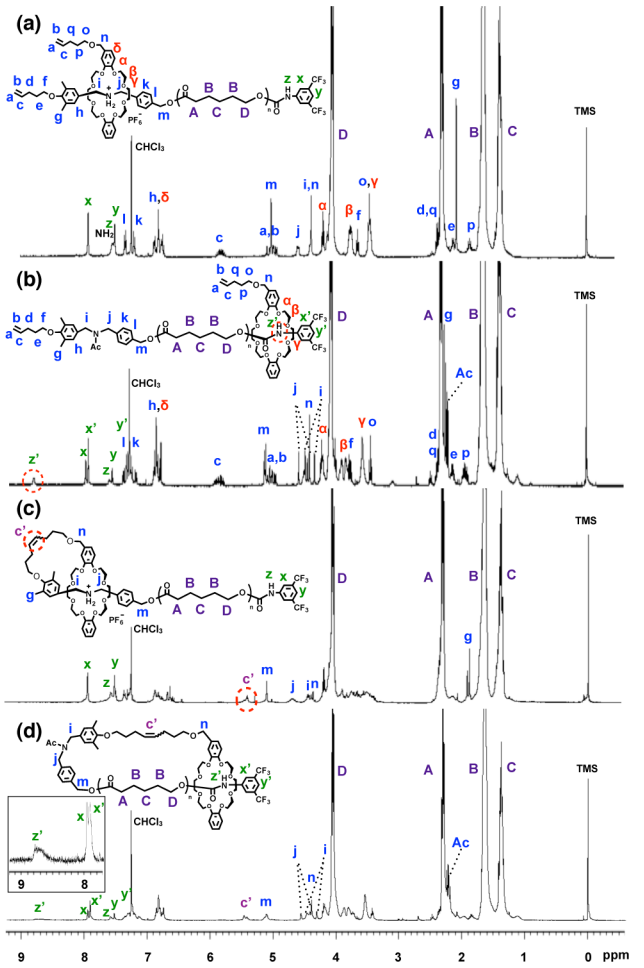

Figure 3. ^{1}H NMR spectra of (a) **5**, (b) **5NAc**, (c) **7**, and (d) **7NAc** (400 MHz, $CDCl_3$).

[2]rotaxanes **5** (Figure 3a) and **5NAc** (Figure 3b), and the corresponding [1]rotaxanes **7** (Figure 3c) and **7NAc** (Figure 3d) end-capped with 3,5-bis(trifluoromethyl)phenyl isocyanate. The peaks corresponding to *O*-benzylic proton H_m and PCL H_{A-D} appeared at reasonable chemical shifts, indicating the polymerization of ε-CL from the terminal OH group of pseudo[2]rotaxane initiator **3**. The peaks corresponding to the 3,5-bis(trifluoromethyl)phenyl end-cap group were also observed at 7.96 ppm (H_x) and 7.54 ppm (H_y) in an appropriate ratio, supporting the structure of **5**. In the ^{1}H NMR spectrum of **5NAc**, the *N*-acetyl proton (H_{Ac}) signal was observed at 2.15 ppm, while the *N*-benzyl proton signals (H_i and H_j) at 4.42 and 4.62 ppm changed from characteristic multiplets to a set of sharp signals based on the amide isomers, indicating the *N*-acetyl moiety is free from the wheel.[24,25] The appearance of the signal at 8.78 ppm, which can be assigned to the carbamate NH ($H_{z'}$) adjacent to the 3,5-bis-(trifluoromethyl)phenyl end,[34] is important for the cyclic structure formation.

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To clarify the stability of the hydrogen bond between the phenylcarbamate moiety and the crown ether wheel along with the local position of the crown ether wheel in rotaxane skeleton, we newly prepared model rotaxanes **S4** and **S4NAc** (R = CH_3, model for **4**/**4NAc** and **6**/**6NAc**) and **S5** and **S5NAc** (R = CF_3, model for **5**/**5NAc** and **7**/**7NAc**). Their spectral data are shown in Figures S37−S46 in the Supporting Information, which well corresponded to their structures. In ^{1}H NMR spectra, remarkably downfield shifted carbamate NH signals of **S4NAc** and **S5NAc** observed at 8.7−8.8 ppm (Figures S37 and S38) indicated the clear positional change of the wheel from *sec*-ammonium moiety to phenylcarbamoyl moiety. Namely, the appearance of the characteristic signal at 8.7−8.8 ppm reveals the encapsulation of the carbamate moiety with the crown ether wheel. The signals with similar chemical shifts observed for **5NAc** and **7NAc** (Figure 3), but not for **4NAc** and **6NAc** (Figures S13 and S15), coincides with the occurrence of the encapsulation of the carbamate moiety with the crown ether wheel in the corresponding polymer systems, too. In addition, the 1D NOESY spectrum of **5NAc** (Figure S17) shows only the correlation between the Hγ signal (wheel component) and the $H_{x'}$ and $H_{z'}$ signals (axle polymer end). Meanwhile, no such correlation was observed for **4NAc**, undoubtedly suggesting the weaker hydrogen bonding ability of the 3,5-dimethylphenylcarbamate moiety than that of 3,5-bis(trifluoromethyl)phenyl moiety. The crucial difference in stability of the threaded structure between these two carbamate groups would reasonably explain the difference in polymer structure, that is, cyclic or lariat-like conformation. Besides the hydrogen bonding, the donor−acceptor interaction between the aromatic rings of the wheel component and the aryl carbamate moiety may also affect the stability of the cyclic polymer structure. On the basis of this discussion, NMR, and SEC results, it was concluded that the structure of **6NAc** has a lariat-like structure, whereas **7NAc** adopts a cyclic structure (Figure 1a).

The linear-cyclic polymer structural transformation was further strengthened by comparing the diffusion coefficient (D) measured by NMR spectroscopy (Figures S47−S54). The ratio of D values were D_6/D_{6NAc} = 0.93 (D_6 = 3.10 × 10^{-10}, D_{6NAc} = 3.34 × 10^{-10} m^2/s) and D_7/D_{7NAc} = 0.89 (D_7 = 3.44 × 10^{-10}, D_{7NAc} = 3.86 × 10^{-10} m^2/s). Cyclic polymers have smaller D values than their linear counterparts, with the reported D value ratio (D_{linear}/D_{cyclic}) being about 0.85.[35−39] Therefore, the obtained ratios clearly indicate that **7NAc** has a close to cyclic structure.

The polymer structure in the solid state was also investigated using DSC (Figure 4). In the cooling scans, **5**, **5NAc**, and **7** showed exotherm peaks (T_c) that could be attributed to the crystallization of PCL. Meanwhile, **7NAc** showed only T_g at −40 °C without T_c, suggesting significantly lowered crystallinity.[40−43] This dramatic change in crystallinity, despite localization of the wheel component at the polymer terminus, seems to reveal the chain organization for the crystallization was prevented by the cyclic PCL structure.

In conclusion, we have demonstrated a novel, effective synthetic method of a cyclic polymer from a linear polymer using macromolecular [1]rotaxane. This method can be characterized by three points: (i) the rotaxane-from method for the polymer axle synthesis performed without an excess of the rotaxane moiety, (ii) highly efficient cyclization of [2]rotaxane to [1]rotaxane attained through the proximity effect, and (iii) the rotaxane protocol for quantitative cyclic

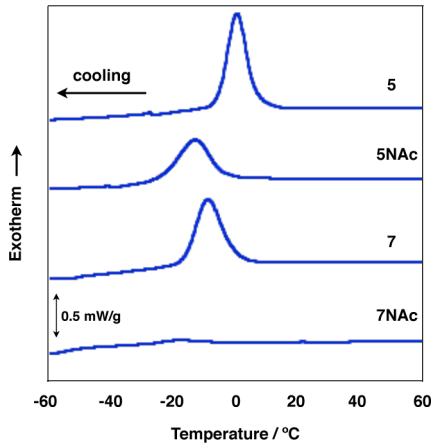

Figure 4. DSC exotherm of **5**, **5NAc**, **7**, and **7NAc** (scan rate: 10 °C/min).

polymer formation from a linear polymer accomplished by moving the wheel component to the other polymer terminus. In addition, the polymer terminus capped with an electron withdrawing group worked efficiently as the station for the wheel by increasing the attractive interaction. SEC, NMR spectroscopy, 2D DOSY, inherent viscosity, and thermal property or crystallinity changes strongly indicated the formation of the cyclic polymer. We have obtained more than 2 g (92% isolated yield) of this "cyclic polymer" via an easy one-pot reaction through the present method, suggesting its usefulness for cyclic polymer synthesis.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, their spectra, and SEC data used for the present study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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