

ORIGINAL ARTICLE

Synthesis and characterization of a mechanically linked transformable polymer

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A shape-transformable polymer in which the wheel component can move freely along the axle chain was synthesized and characterized. Rotaxane-linked linear poly(δ -valerolactone) was synthesized in one pot via ring-opening polymerization initiated by a *sec*-ammonium/crown ether-type pseudo[2]rotaxane that possessed two initiating hydroxyl groups on both the axle and wheel components; this was followed by an end-capping reaction with a bulky isocyanate. Acetylation of the obtained polymer to remove the interaction between the *sec*-ammonium axle and the crown ether wheel afforded the transformable polymer. The movement of the wheel component bearing a polymer chain was confirmed by weakening the interaction between the axle and the wheel in the rotaxane-linked linear polymer that did not possess a bulky end-cap group. The result clearly supported the mobility of the wheel component bearing a graft chain from one end of the polymeric axle chain to the other end.

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INTRODUCTION

Topologically interacting polymers have been synthesized to discover the specific properties by adjusting the polymerization conditions^{1–4} or using the specially designed initiators^{5–7} and monomers.^{8–13} However, once these polymers have formed their individual structures, the covalently bonded polymers no longer change their structures. The rotaxane structure has attracted considerable attention because of its wide range of utility, resulting from the structural characteristics of its topological bonding and the dynamic nature of its components. With respect to the movability of mechanically linked structures, there have been many reports on the synthesis^{14–29} and application^{30–36} of polymers based on the rotaxane structure in the past two decades. Ito and coworkers³⁷ reported the polyrotaxane that contains graft polymers connected to the wheel components, demonstrating the movement of graft chains along the axle chain. We previously reported a polyrotaxane that contains movable graft chains threaded in the poly(crown ether) as the main chain in which the movement of the graft chains affected the entire shape of the polymer chain.³⁸ Fustin and coworkers reported the synthesis of a mechanically linked block copolymer that contained poly(methyl acrylate) and poly(ethylene oxide) connected to a rotaxane structure using the metal template method to introduce only one wheel component into the polymeric axle chain. This result predicted that transformable block polymers could be synthesized; these polymers are likely to have interesting inter-block mobility, but this has not yet been explored.^{23,39}

We recently developed a synthetic method for preparing macromolecular [2]rotaxanes,⁴⁰ which consist of a polymeric axle chain and a wheel molecule, in one pot with a high purity and high isolated yield. The mobility of the wheel component was also investigated by removing the interaction with the polymeric axle, which enabled the wheel component to travel along the entire axle chain. For the purpose of synthesizing mechanically linked transformable polymers, we have designed a macromolecular [2]rotaxane with a dangling polymer chain on the wheel component. In this paper, a well-defined rotaxane-linked linear polymer, which is a macromolecular [2]rotaxane with a dangling polymer chain on the wheel, was synthesized to convert the mechanically linked transformable polymer by removing the interaction between the wheel component and the polymer chain. The mobility of the wheel component containing a dangling polymer chain was also investigated (Figure 1).

MATERIALS AND METHODS

Materials

Dichloromethane was purchased from Asahi Glass, Tokyo, Japan and was distilled over CaH₂ under a nitrogen atmosphere after being washed with water. δ -Valerolactone (δ -VL; 98%, Tokyo Kasei Kogyo (TKI)), diphenyl phosphate (DPP; 99%, TKI), 3,5-dimethylphenyl isocyanate (98%, TKI) and acetic anhydride (98%, Sigma-Aldrich, St Louis, MO, USA) were used as received. Other reagents and solvents were commercially available and were used without further purification unless otherwise noted. The *sec*-ammonium axle and dibenzo-24-crown-8 wheel bearing a hydroxyl group (**DB24C8-OH**) were synthesized according to the literature (Supplementary Material).

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Synthesis of rotaxane-linked poly(δ -valerolactone)s (2-PVL-OH and 2-PVL_F)

A typical procedure for the polymerization of δ -VL, as shown in Scheme 1, is as follows: DPP (78.0 mg, 0.31 mmol) was added to a sonicated solution of initiator **1** (the axle component⁴⁰ (0.12 g, 0.26 mmol) and **DB24C8-OH** (0.14 g, 0.29 mmol) in CH_2Cl_2 (6.4 ml)). δ -VL (1.32 g, 13.2 mmol) was then added to the solution to initiate polymerization, at room temperature under a nitrogen atmosphere. After 2 h, a small amount of the reaction solution was removed to obtain **2-PVL-OH** as a precursor, and an excess amount of 3,5-dimethylphenyl isocyanate (1.5 ml) was added to the solution and stirred for 12 h to introduce a bulky end-cap group at the terminus of poly(δ -valerolactone) (PVL). The polymer was isolated by reprecipitation from CH_2Cl_2 in ethanol/hexane (1/9, v/v) and purified by preparative gel permeation chromatography (GPC) with CHCl_3 as the eluent to obtain a rotaxane-linked graft polymer bearing PVL as the axle component and graft chain **2-PVL_F** (isolated: 1.34 g).

Synthesis of 2-PVL_M

In a screw-capped test tube, a mixture of **2-PVL_F** (120 mg, 0.0210 mmol), acetic anhydride (110 mg, 1.08 mmol) and triethylamine (210 mg, 2.08 mmol) in tetrahydrofuran (THF) (3.0 ml) was stirred for 24 h at 40 °C. The solution was diluted with CH_2Cl_2 and washed with brine, dried over magnesium sulfate, evaporated in vacuo and purified by preparative GPC with CHCl_3 as the eluent to obtain **2-PVL_M** (isolated: 90 mg) as a red solid.

Acetylation of 2-PVL-OH

A mixture of **2-PVL-OH** and triethylamine (1.31 g, 13.0 mmol) in THF (5.0 ml) was stirred for 12 h. An excess amount of 3,5-dimethylphenyl isocyanate

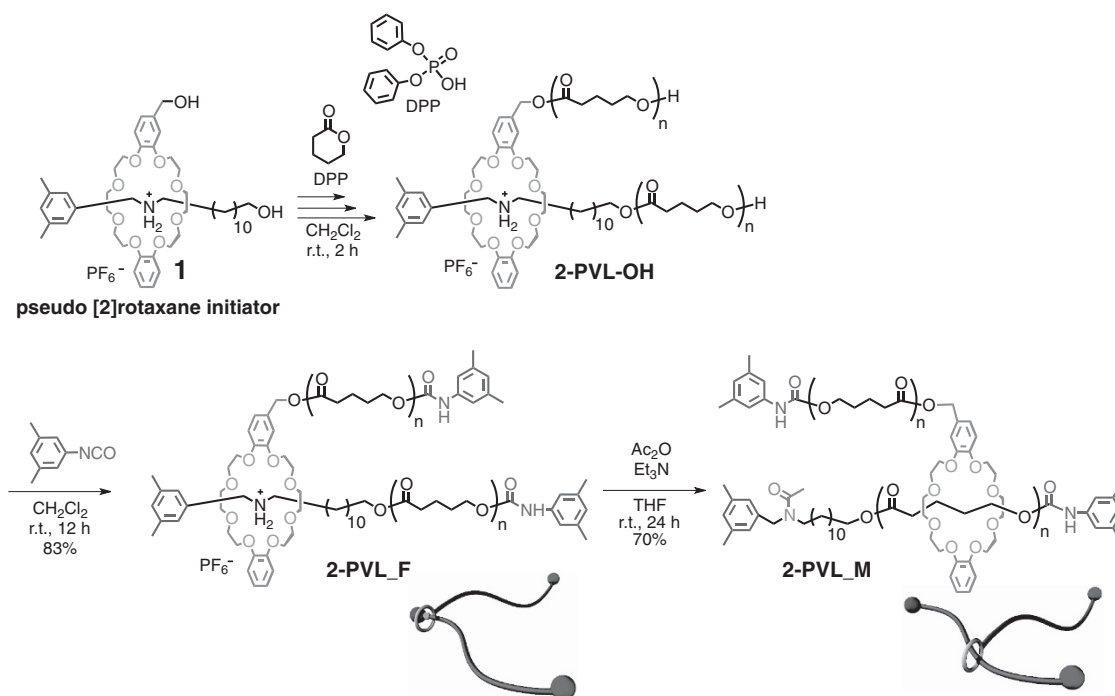
(1.5 ml) was then added to the solution and stirred for an additional 12 h to introduce a bulky end-cap group at the terminus of the polymer. The polymer was isolated by reprecipitation from CH_2Cl_2 in ethanol/hexane (1/9, v/v) and purified by preparative GPC with CHCl_3 as the eluent (isolated: 0.70 g).

Characterization

^1H - (400 MHz) and ^{13}C - (100 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a JEOL AL-400 spectrometer using CDCl_3 as the solvent. The spectra were referenced to residual undeuterated solvent and tetramethylsilane as the internal standard. IR spectra were recorded on a JASCO (Tokyo, Japan) FT/IR-230 spectrometer. Melting points were measured on a SMP3 melting point apparatus (Stuart Scientific, Staffordshire, UK). FAB (Fast Atom Bombardment) and ESI HR-MS (Electrospray Ionization High Resolution Mass Spectrometry) were obtained at the Center for Advanced Material Analysis, Tokyo Institute of Technology, on request. Size exclusion chromatography (GPC) was performed at 30 °C in CHCl_3 (0.5 ml min⁻¹) using a JASCO Gulliver system equipped with Shodex GPC K-805L column. The number-average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity indices (M_w/M_n) of the polymers were calculated based on a calibration with polystyrene. Preparative GPC was performed using a HPLC LC-918 instrument from the Japan Analytical Industry equipped with a Megapak-Gel 201C. Matrix-assisted laser desorption/ionization–time of flight–mass spectrometry (MALDI–TOF–MS) were recorded on a Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser ($\lambda = 337 \text{ nm}$) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV using the linear-positive ion mode. The sample polymer solution (1 mg ml⁻¹) was prepared in THF or CHCl_3 , and the matrix (dithranol) and cationizing



Figure 1 Transformable polymer based on a rotaxane structure. A full color version of this figure is available at *Polymer Journal* online.



Scheme 1 Synthesis of mechanically linked PVL. A full color version of this figure is available at *Polymer Journal* online.

agent (sodium trifluoroacetate) were dissolved in THF (10 mg and 1 mg ml⁻¹, respectively). The polymer solution and the matrix solution were mixed, and a 1 μ l aliquot of the mixture was deposited onto a sample target plate and allowed to dry in air at room temperature. Mass values were calibrated by the two-point method with insulin β plus H⁺ at 3497.96 and R-cyanohydroxy cinnamic acid dimer plus H⁺ at 379.35.

RESULTS AND DISCUSSION

Synthesis of mechanically linked PVL

A rotaxane-linked linear polymer consisting of two polymer chains connected to the axle and the wheel molecules was designed, in which the attractive interaction between the axle and the wheel components is located at the end of the axle molecule. To ensure that the polymer chains in the synthesized rotaxane-linked linear polymer were the same length, a bifunctional initiator was employed. The reaction scheme is depicted in Scheme 1. The complex **1** between the axle having the *sec*-ammonium moiety with a hydroxyl group and the wheel having a hydroxyl group (**DB24C8-OH**), is the key initiator to introduce the mechanically linked structure into the polymer. The DPP-catalyzed living ring-opening polymerization of δ -VL with initiator **1** ([VL]₀/[initiator]₀/[DPP]₀ ratio of 50/1.0/1.2) was performed for 2 h at room temperature. The polymerization was quenched by the addition of 3,5-dimethylphenyl isocyanate for end-capping the living end as a bulky stopper. The obtained polymer was purified by reprecipitation and preparative GPC to afford the mechanically linked poly(δ -valerolactone) **2-PVL_F** (suffix F indicates a 'Fixed' wheel on the *sec*-ammonium moiety) in a one-pot reaction with a high isolated yield (83%).

A rotaxane-linked linear polymer without a urethane end-capping group (**2-PVL-OH**) was also isolated by precipitation into an ethanol/hexane (1/9, v/v) mixed solvent. The formation of **2-PVL-OH** indicates the excellent stability of the *sec*-ammonium/DB24C8 complex on the initiator, that is, no deslipping of the wheel component occurred during the isolation of the polymer. The interaction of the ammonium moiety in **2-PVL_F** with the wheel component bearing a polymer chain was then neutralized by acetylation with excess

amounts of acetic anhydride and triethylamine to release the wheel component bearing a graft chain. This acetylation afforded the topologically transformable polymer **2-PVL_M** (suffix M indicates a 'Movable' wheel), in which the grafted chain might travel from one end of the polymeric axle component to the other end.

The chemical structures of **2-PVL_F** and **2-PVL_M** were characterized by ¹H-NMR and MALDI-TOF-MS. In the ¹H-NMR spectra shown in Figures 2a and b, the multiplet signals at approximately 4.5 and 3.1 p.p.m. (signals *d* and *e*), which were observed both before and after polymerization, are the characteristic peaks of the benzylic protons and methylene protons adjacent to the *sec*-ammonium moiety surrounded by DB24C8 through hydrogen bonding, indicating that the *sec*-ammonium/crown ether-type complex was retained during polymerization. The peak X at approximately 4.6 p.p.m. due to the methylene proton in the benzylic position of the DB24C8 was shifted to 5.0 p.p.m. after the polymerization, suggesting that polymerization was also initiated from the benzyl alcohol moiety on the wheel. The degree of polymerization (DP) of **2-PVL_F** was calculated to be 47 from the ¹H-NMR spectrum.

After acetylation, the characteristic signals (*d* and *e*) were observed to change into two series of split peaks (*d* and *e*), as shown in Figure 2c, revealing the complete acetylation of the *sec*-ammonium moiety to convert **2-PVL_F** to **2-PVL_M**, which has a movable graft chain along the axle chain. Figures 3a and b present the MALDI-TOF-MS of the mechanically linked PVLs before and after acetylation. A series of peaks with an interval of 100.05 Da can be observed in Figure 3a, which correspond to the molecular weights of the PVLs possessing both the pseudo[2]rotaxane initiating group and 3,5-dimethylphenylurethane as the end-capping group. Figure 3b shows a series of peaks with the same interval that are shifted from the spectrum in (a) to approximately 65 Da due to the mass of the acetyl group and sodium added. These results are consistent with the DPP-catalyzed ring-opening polymerization and the subsequent end-capping reaction proceeding successfully to afford **2-PVL_F** with a high isolated yield, and acetylation also proceeded without any side reactions to afford the pure transformable polymer **2-PVL_M**.

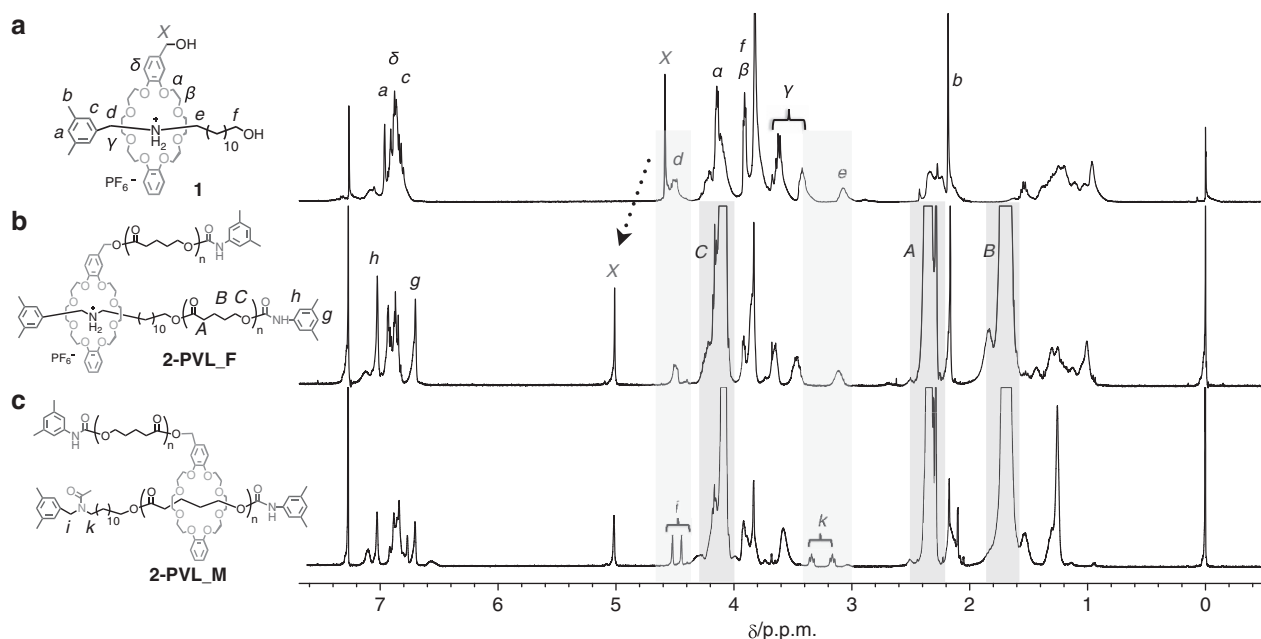


Figure 2 ¹H-NMR spectra of (a) initiator **1**, (b) **2-PVL_F** and (c) **2-PVL_M** in CDCl₃ (400 MHz, 298 K). A full color version of this figure is available at *Polymer Journal* online.

Deslipping of 2-PVL-OH

The most intriguing property of mechanically linked **2-PVL_M** is the dynamic nature of the components, that is, the translational topology change of the polymer that depends on the location of the wheel component. To confirm the mobility of the wheel component bearing a polymer chain, we removed the interaction between the *sec*-ammonium/crown ether couple from the **2-PVL-OH** that was obtained before the end-capping reaction (Scheme 2).

To the **2-PVL-OH** solution in THF, triethylamine was added as a base to decompose the complex to separate the axle polymer and the graft polymer, in which the interaction between *sec*-ammonium and crown ether becomes weak because of the polarity of THF. After 12 h, 3,5-dimethylphenyl isocyanate was added to the solution and stirred for an additional 12 h to introduce a bulky end-cap group at the terminus of the polymer, preventing the wheel component from being accidentally threaded. The reaction

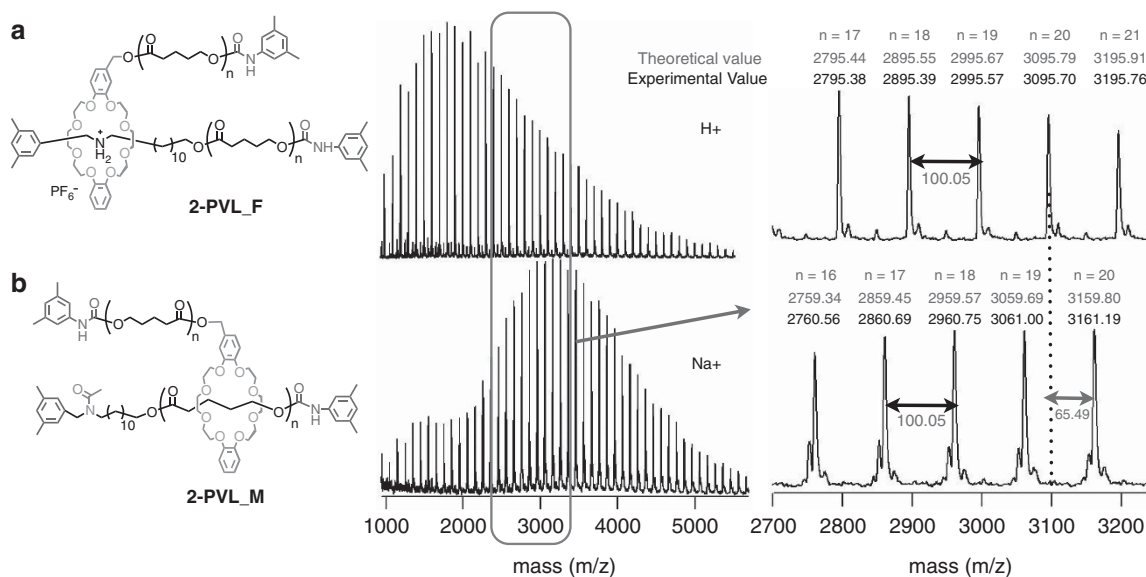
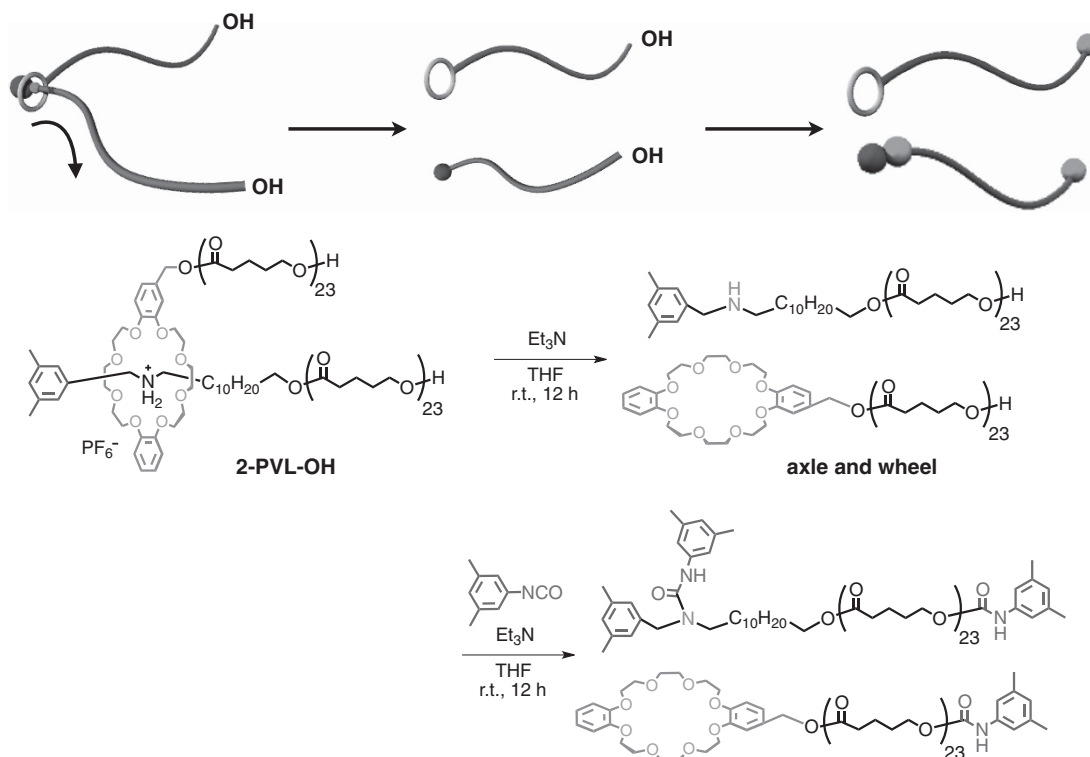


Figure 3 Matrix-assisted laser desorption/ionization–time of flight–mass spectrometry of **2-PVL_F** and **2-PVL_M** (linear mode). A full color version of this figure is available at *Polymer Journal* online.



Scheme 2 Deslipping of mechanically linked pseudo-PVL. A full color version of this figure is available at *Polymer Journal* online.

mixture was directly subjected to MALDI-TOF-MS and GPC measurements.

Two series of peaks with the same interval (approximately 100 Da) were observed in the MALDI-TOF-MS, as shown in Figure 4, and one series of peaks corresponded to the PVL with the wheel component and the other corresponded to the axle component, indicating that the wheel component bearing a polymer chain could travel from the location of the ammonium to the open end to afford the individual PVLs. In the GPC profiles of the decomposed **2-PVL-OH**, which are shown in Figure 5a, a unimodal peak was obtained and the elution time was consistent with the model polymer (DP=22, Figure 5b), indicating the ideal polymerization of δ -VL from two hydroxyl groups.

The MALDI-TOF-MS and GPC profile results confirmed the successful polymerization of δ -VL from the two initiating groups to

form two mechanically linked PVLs with the same DP. The dangling chain on the wheel was able to move from one end to the other along the axle chain when the interaction between *sec*-ammonium and crown ether became weak, indicating that the graft chain of **2-PVL_M** in which *sec*-ammonium was converted to an acetyl group was movable on the whole axle chain as in **2-PVL-OH**.

Topological transformation of mechanically linked PVL

Although it is very interesting to elucidate where the wheel component is localized on the axle chain, the $^1\text{H-NMR}$ data of **2-PVL_M** did not reveal the specific correlation with the axle component. It was expected from this result that the wheel component was delocalized among the axle polymer chain, that is, the shape of **2-PVL_M** was a randomly branched structure. In general, branched polymers have a smaller hydrodynamic volume

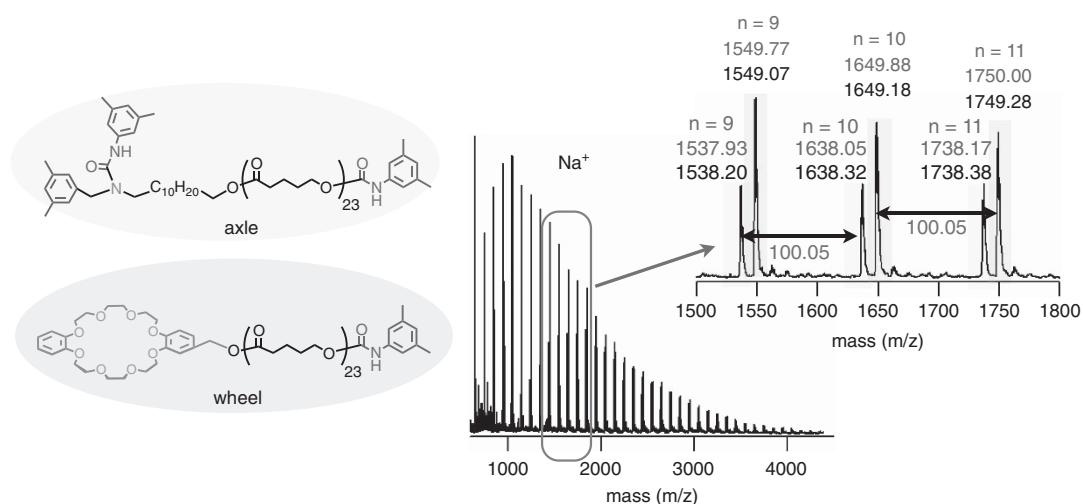


Figure 4 Matrix-assisted laser desorption/ionization-time of flight-mass spectrometry of the acetylated **2-PVL-OH**. A full color version of this figure is available at *Polymer Journal* online.

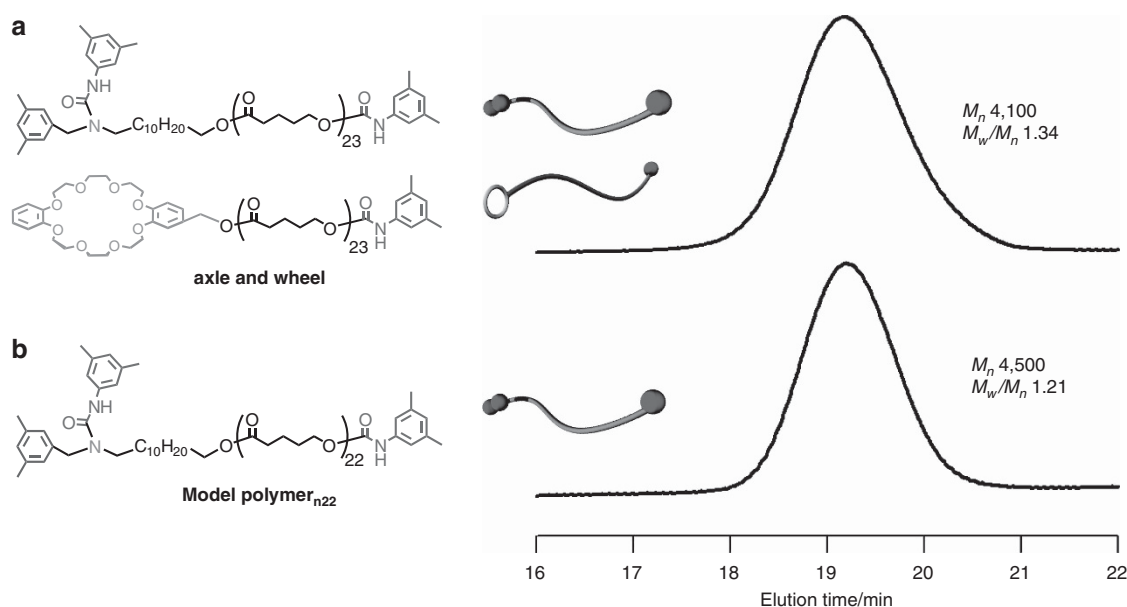


Figure 5 Gel permeation chromatography profiles of (a) acetylated **2-PVL-OH** and (b) model polymer. A full color version of this figure is available at *Polymer Journal* online.

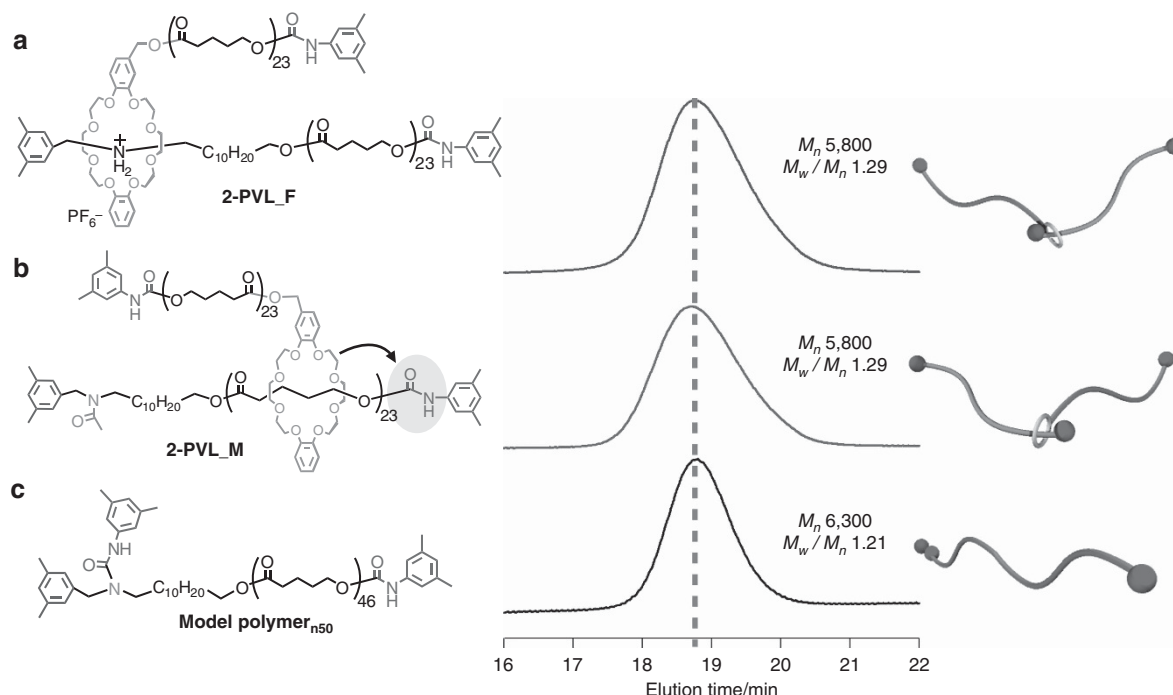


Figure 6 Gel permeation chromatography profiles of (a) **2-PVL_F**, (b) **2-PVL_M** and (c) model polymer (DP=46). A full color version of this figure is available at *Polymer Journal* online.

compared with their linear counterparts with the same molecular weight. This theory motivated us to compare the GPC profiles between **2-PVL_F** and **2-PVL_M**. In non-polar solvents such as CH_2Cl_2 or CHCl_3 , the interaction between *sec*-ammonium and crown ether was strong enough to fix the wheel component, as confirmed by the $^1\text{H-NMR}$ spectrum of **2-PVL_F** shown in Figure 2, indicating that the shape of **2-PVL_F** is a linear structure. In contrast, **2-PVL_M** was expected to behave as a branched polymer as described previously. Figures 6a and b show the GPC profiles of **2-PVL_F** and **2-PVL_M** in CHCl_3 as a non-polar eluent.

No significant shift from before and after acetylation was observed, implying that both polymers have the same hydrodynamic volume. To confirm that the **2-PVL_F** coincides with the linear-shaped polymer, the model polymer (DP=46) was prepared (Supplementary Material) as shown in Figure 6c. All three peaks were perfectly observed in the same elution time, implying that **2-PVL_F** and **2-PVL_M** possessed the same linear topology. Considering this result, the urethane linkage at the end of the polymer chain in **2-PVL_M** might have interacted with the crown ether to make the **2-PVL_M** linear-shaped polymer. Gibson and colleagues⁴¹ reported the synthesis of polyrotaxanes consisting of an axle polyester or polyurethane and crown ethers in which the number of crown ethers threaded with polyurethane was considerably greater than that threaded with polyester. They also reported that the threading efficiency was lower with the polyester due to the lack of a strong attractive force between the ester linkage and the crown ether.^{42–45} Furthermore, the presence of hydrogen bonding between the NH group of the polyurethane and the crown ether results in a significant thermodynamic driving force for threading.⁴³

Consequently, the acetylation of the rotaxane-linked linear polymer **2-PVL_F** afforded the topologically transformable **2-PVL_M** in which the wheel component connected to a graft chain located at the ω -end of the polymeric axle by interacting with the urethane linkage/crown

ether through hydrogen bonding, indicating that the entire polymer topologies of both **2-PVL_M** and **2-PVL_F** were linear structures; however, the positions of the graft chain were different.

CONCLUSIONS

In conclusion, we demonstrated a new synthetic method for preparing transformable polymers through the introduction of a rotaxane structure into the polymer chain linkage position.

The interaction between a *sec*-ammonium and a dibenzo-24-crown-8-ether was the key for the synthesis of mechanically linked PVL without deslipping of the wheel component during polymerization. After acetylation of the ammonium moiety, the dangling polymer chain was able to move along the axle polymer to reach the urethane linkage at the ω -end in a non-polar solvent.

Topologically transformable polymers, such as star-to-linear or linear-to-cyclic polymers, obtained utilizing the present protocol will be reported in the near future.

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