

**Synthesis of MDI and PCL-diol-based Polyurethanes
Containing [2] and [3]Rotaxanes and their Properties**

HIROTO MURAKAMI,* RYUTA NISHIIDE, SHINJI OHIRA, AKIKO OGATA,

Division of Materials Science, Graduate School of Engineering, Nagasaki University,

1-14 Bunkyo, Nagasaki 852-8521, Japan

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Corresponding author: Tel.: +81 95 819 2688.

E-mail address: hiroto@nagasaki-u.ac.jp (H. Murakami)

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Abstract

We have successfully synthesized novel polyurethanes where **PU1** contains a [3]rotaxane that consists of *N*-3,5-di-*tert*-butylbenzyl-*N*-3-hydroxypropylammonium hexafluorophosphate (**AOH1**) and *N,N'*-Dimethyl-*N,N'*-bis(dibenzo-24-crown-8)-terephthalamide (**BisC**) as well as **PU2** contains a [2]rotaxane that consists of **AOH1** and dibenzo-24-crown-8 ether. Diphenylmethanediisocyanate (MDI), 1,4-butanediol (BD) and poly(ϵ -caprolactone)diol (PCL) were used as an isocyanate, chain expander, and soft segment, respectively. A polyurethane without any rotaxane structures (**PU0**) were also prepared as a reference polymer. The existence of the rotaxanes in the polyurethanes was confirmed by ^1H NMR spectroscopy and TGA measurement. ATR-FT-IR spectral measurement revealed that the rotaxanes disturb the formation of hydrogen bonding between the polyurethane chains. From the DSC result, the rotaxanes retard the recrystallization of the PCL unit whereas no influence on the glass transition temperatures of the polyurethanes was observed. The retarding effect appeared remarkably with **PU1**. These thermal behaviors of the polyurethanes were also supported by viscoelastic measurement. In tensile test, the tensile strength and break of strain of **PU1** were larger than those of **PU2**.

1. Introduction

Polyurethanes (PUs) are one of the functional macromolecules widely used as sealants, adhesives, fibers, and so on. Their characteristic properties can be controlled by the change of starting materials, preparation conditions, and *etc.* [1]. The PUs are usually synthesized from diisocyanate, α,ω -glycols with a long chain and short one, as well as curing agent. In the raw materials, the chemical structure of the glycols, which play an important role for the PU's properties, can be easily modified. Therefore, novel design of the glycols should enable us to develop unique PUs with interesting properties.

Recently, much attention has been focused on supramolecular materials because of their distinctive features [2]. A rotaxane is an interlocked molecule in which a ring molecule as its constituent is threaded by an axle molecule having bulky terminal cap groups that prevent the ring molecule from release [3]. This unique link style between the ring and axis molecules is called "*mechanical bond*". One of the most interesting properties of the rotaxane based on the mechanical bond is the free movement of the ring molecule along the axle molecule due to the absence of any covalent bond between them [4].

Polyrotaxanes [5] have also attracted world-wide attention since the first discovery of a polyrotaxane consisting of α -cyclodextrin (α -CD) and poly(ethylene glycol) (PEG) by Harada et al [6]. Gibson et al. has prepared many PUs possessing rotaxane structures [7]. For instance, PUs being composed of a PU chain threading many crown ethers were prepared

by polyaddition reaction in melting crown ether [8]. A mechanically linked network structure was also achieved using polyurethanes incorporating crown ethers in their main chain skeletons [9]. Osakada et al. reported the preparation of a PU threaded into permethylated- β -CDs [10]. Studies of interesting polyrotaxane gels have also been published. Ito et al. first realized experimentally a sliding network gel based on a polyrotaxane consisting of α -CD and PEG [11]. Hadziioannou et al. also prepared similar sliding gels [12]. Takata et al. first synthesized a recyclable crosslinked PUs in which PUs incorporating crown ethers in the main chain skeletons were linked by a dumbbell-shaped disulfide using a dynamic covalent bond [13]. Advanced functional polymers with rotaxane-crosslinking points were summarized by Takata and Koyama [14].

As described above, the rotaxanes enable the appearance of the unique and interesting properties of the polymers. Especially, [3]rotaxanes acting as crosslink points inspired us with a new design of the glycol component in PU. It is of interest how introduction of the [3]rotaxane instead of the short glycol partially into an orthodox PU influences its thermal and physical properties. No such report has been published in our best knowledge although a lot of PUs with rotaxane structures have already been published as described above. Therefore, we describe herein the strategy for synthesis of a PU containing a [3]rotaxane that consists of a bis(crown ether) and a (ω -hydroxyalkyl)ammonium derivative (**PU1**) under an equilibrium system. PUs containing a [2]rotaxane that consists of dibenzo-24-crown-8 ether and the

(ω -hydroxyalkyl)ammonium derivative (**PU2**) as well as without any rotaxane structures (**PU0**) were also synthesized by similar manner as a reference. We also describe the properties of these PUs using the results of the measurements of attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic viscoelastic test and tensile test.

2. EXPERIMENTAL

2.1 Materials

4,4'-Diphenylmethanediisocyanate (MDI) was provided by Mitsui Chemicals, Inc. and used as received. Poly(ϵ -caprolactone)diol (PCL, average molecular weight = *ca.* 2000), whose trade name is Placel220™, was purchased from Daicel Corp. and used as received. *N,N'*-Dimethyl-*N,N'*-bis(dibenzo-24-crown-8)-terephthalamide (**BisC**) as a ring molecule, *N*-3,5-di-*tert*-butylbenzyl-*N*-3-hydroxypropylammonium hexafluorophosphate (**AOH1**) and *N*-(4-hydroxymethyl)benzyl-*N*-6-hydroxyhexylammonium hexafluorophosphate (**AOH2**) as axle molecules were synthesized according to the literature (see supporting information) [15]. All other chemicals were of reagent grade. Chloroform for the polymer synthesis was dried over calcium chloride and distilled prior to use. Solvents used in measurements were of spectral grade. Deuterated solvents were purchased from Euriso-Top SA.

2.2 Synthesis of Polyurethane

The synthesis of **PU1** containing a [3]rotaxane component is as follows. **BisC** (50.7 mg, 0.047 mmol) and **AOH1** (39.4 mg, 0.093 mmol) were dissolved in dry chloroform (1.0 mL) under an Ar atmosphere and then sonicated briefly to prepare a pseudo[3]rotaxane solution. The pseudorotaxane solution was added all at once to a solution of PCL (1.04 g, 0.52 mmol) in dry chloroform (1.5 mL), followed by the addition of one drop of dibutyltin dilaurate as a catalyst. A solution of MDI (393 mg, 1.57 mmol) in dry chloroform (1.5 mL) was added dropwise to the diol solution at 25 °C under an Ar atmosphere to prepare a prepolymer solution. After stirring for 4 h at the same condition, a solution of 1,4-butanediol (BD, 90.1 mg, 1.00 mmol) in dry chloroform (1.0 mL) was added slowly to the prepolymer solution. The reaction mixture was allowed to stir overnight. The addition of BD resulted in an increase in viscosity of the reaction mixture. Methanol (1.0 mL) was added to the mixture to deactivate unreacted isocyanate groups. After stirring for 24 h, the solvent was evaporated. The gel like residue was washed thoroughly with chloroform and then methanol. The residue was dissolved in THF and then poured into a Teflon vessel, followed by air drying to obtain a thin film: the yield was 1.38 g. **PU2** containing a [2]rotaxane that consists of dibenzo-24-crown-8 ether and **AOH1** as well as **PU0** without any rotaxane structures were prepared by similar manner: the yields were 1.35 g for **PU2** and 1.16 g for **PU0**. Feed amounts of the chemicals for the synthesis of the PUs were summarized in

Supporting Information. All of the PUs dissolve in DMA, DMSO, and THF.

The PUs obtained were subjected to the following measurements without further purification.

2.3 Measurements

The number- and weight-average molecular weights (M_n and M_w) and polydispersity index (M_w / M_n) of the PUs in DMF, an eluent, were obtained by GPC (Shodex[®] KD-803 and KD-805, Showa Denko K.K.) at 40 °C using a calibration plot constructed from polystyrene standards.

The existence of the rotaxanes in the PUs were confirmed by NMR spectroscopy. The ¹H NMR spectra of the PUs dissolved in deuterated dimethyl sulfoxide (DMSO-d₆) were measured with a Varian Gemini-300 (300 MHz).

The state of hydrogen bond in the PUs was determined by ATR-FT-IR spectroscopy. The ATR-FT-IR spectra measurements for the PU films were performed on a Thermo Nicolet NEXUS 670 equipped with a Spectra-Tech Foundation Thunder dome with a Ge crystal at ambient temperature under the air; 32 scans and a resolution of 4 cm⁻¹.

Thermal properties were measured by DSC and TGA. The PUs cooled from 200 to -100 °C at a cooling rate of -10 °C min⁻¹ under a nitrogen atmosphere were used as the measurement samples. The DSC thermograms were collected on a Shimadzu DSC-60 and

from -100 to 200 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The TGA curves were obtained with a Shimadzu TGA-50 and from room temperature to 500 °C at a heating rate of 10 °C min^{-1} under the air.

Temperature dependence of dynamic mechanical properties was measured with an RSA II solid analyzer (Rheometrics, Co., Ltd.) in a tension mode. The measurement was performed from -100 to 120 °C at a heating rate of 2 °C min^{-1} under a nitrogen atmosphere. The imposed strain and frequency were set to be 0.05 % and 10 Hz, respectively.

Tensile testing was performed with a TENSILON RTC-1150A at room temperature. The initial length and cross-head speed were set to be 10.0 mm and 3.0 mm min^{-1} , respectively.

3. Results and Discussion

3.1 Formation of Rotaxane Complex

The synthesis of the PU containing the [3]rotaxane involves the formation of the pseudo[3]rotaxane consisting of **BisC** and **AOH** in advance. The formation of pseudorotaxane is an equilibrium reaction and often confirmed by ^1H NMR spectroscopy. Therefore, the ^1H NMR measurement was conducted for chloroform solutions of **BisC** and **AOH** with a molar ratio of $[\text{BisC}]:[\text{AOH1}] = 1:2$. The ^1H NMR spectra of **AOH1** and the mixture of **BisC** and **AOH1** are shown in Figure 1a and 1b, respectively. The signal

assignable to the methylene proton of the benzyl group in **AOH1** without **BisC** appeared at 4.21 ppm (Figure 1a). In contrast, the signal in the presence of **BisC** shifted to 4.52 ppm (Figure 1b). This lower magnetic field shift is the evidence for the formation of the pseudorotaxane consisting of **BisC** and **AOH1** [16]. The concentration dependence measurement of the ^1H NMR spectra was carried out with the constant molar ratio of $[\text{BisC}]:[\text{AOH1}] = 1:2$. The chloroform solution with the concentration of 4 mM of **BisC** and 8 mM of **AOH1** gave the signal for the methylene at 4.52 ppm. No lower magnetic field shift of the signal was observed even the concentration was further increased. This results suggest that the equilibrium shifted to the formation of the pseudo[3]rotaxane. Dilution of the solution to 2 mM of **BisC** and 4 mM of **AOH1**, however, caused the upper magnetic field shift of the signal, which was observed at 4.27 ppm (see Supporting Information), suggesting the dissociation of the pseudo[3]rotaxane. As the result, it was found that **BisC** and **AOH1** forms a 1:2 complex with the pseudo[3]rotaxane structure in the chloroform solution of at least 4 mM of **BisC** and 8 mM of **AOH1**. The temperature stability of the pseudo[3]rotaxane was also investigated (see Supporting Information). The signal for the methylene observed at 4.52 ppm at 25 °C was appeared at 4.26 ppm at 50 °C, suggesting the disassociation of the pseudorotaxane. Therefore, the PU synthesis should be done at 25 °C or below.

The complexation of **BisC** and **AOH2** was carried out in a mixed solution of

chloroform and acetonitrile with a volume ratio of 1:1, because of the poor solubility of **AOH2** in chloroform. In the case of 4 mM of **BisC** and 8 mM of **AOH2** in the mixed solution, two signals assignable to the free benzyl proton by the hydroxyl group and complexed ones by the hydroxyl and ammonium groups in **AOH2** were observed at 4.63 and 4.50 ppm, respectively. The integration ratio of the signals at 4.63 and 4.50 ppm was 1:1; the complexation ratio was calculated to be *ca.* 33 % (see Supporting Information). The use of the mixed solvent, especially acetonitrile, would be one of causes for the low complex formation.

Poly(oxytetramethylene)2000 (PTMG2000) is commonly used as a soft segment of polyurethanes. Consequently, the influence of PTMG2000 on the pseudorotaxane formation was investigated. The result is shown in Figure 1c. The addition of PTMG2000 to the chloroform solution of **BisC** and **AOH1** caused upper magnetic field shift of the signal for the methylene from 4.52 to 4.21 ppm. The chemical shift at 4.21 ppm was the same as that of the signal for the methylene of free **AOH1**, suggesting that the formation of the pseudo[3]rotaxane was disturbed. This is because the ether units of PTMG and **BisC** compete for the interaction with the ammonium unit of **AOH1**. PCL is also one of the soft segment components for polyurethanes and possesses a hydrophobic and biodegradable properties compared with PTMG. Hence, the influence of PCL on the pseudorotaxane formation was investigated. The ¹H NMR spectrum of the chloroform solution of **BisC** and

AOH1 in the presence of PCL showed the signal for the methylene at 4.52 ppm (Figure 1d). The chemical shift was the same as that of the signal for the complexed **AOH1**, indicating that PCL does not disturb the formation of the pseudo[3]rotaxane. From these results, **BisC** as the ring molecule, **AOH1** as the axle molecule and PCL as the soft segment were picked out for the synthesis of the polyurethane.

3.2 Synthesis of Polyurethanes containing rotaxanes

Rigid and bulky structures of the [3]rotaxane affect the physical properties of the PU. In fact, the PUs prepared with molar ratios of [pseudo[3]rotaxane] / [BD] = 2:1 and 1:1 were waxy and brittle. This is because of the difference of the molecular weights and volumes of those; the molecular weights of the pseudo[3]rotaxane and BD are 1932 and 90, respectively. Therefore, **PU1** was prepared with a weight ratio of [pseudo[3]rotaxane] / [BD] = 1:1, in which the content of the [3]rotaxane component is *ca.* 3 mol%.

The synthesis of the **PU1** containing the [3]rotaxane was conducted according to a urethane end-capping protocol reported by Takata [15b]: the synthesis route of the **PU1** can be shown in Supporting Information. A prepolymer was prepared with MDI, PCL and the pseudorotaxane with a ratio of $[\text{NCO}]_{\text{MDI}} / [\text{OH}]_{\text{PCL,rotaxane}} = 3.0$ in dry chloroform containing 1 drop of a tin catalyst under an Ar atmosphere. The reaction temperature was set at 25 °C to hold the pseudo[3]rotaxane formation as mentioned in the previous section. Finally, the

prepolymer and BD were reacted with a ratio of $[\text{NCO}]_{\text{prepolymer}}/[\text{OH}]_{\text{BD}} = 1.0$ to obtain the PUs. **PU2** containing a [2]rotaxane, which consists of dibenzo-24-crown-8 ether and **AOH1**, were also prepared by the similar manner: the synthesis route of the **PU2** can be shown in Supporting Information. The content of the [2]rotaxane component in **PU2** is *ca.* 3 mol%. **PU0**, which did not contain any rotaxane structure, was prepared only by MDI, PCL, and BD. The possible structures of the PUs are shown in Figure 2.

The number-average and weight-average molecular weights as well as polydispersity estimated by GPC measurements were 34.8, 60.2 kDa and 1.6 for **PU0**, 30.5, 62.2 kDa and 2.0 for **PU1** and 36.2, 82.6 kDa and 2.3 for **PU2**, respectively.

3.3 Structure of Polyurethanes

To examine the existence of the rotaxanes in the PUs, ^1H NMR spectral measurements were carried out. Figure 3 shows the ^1H NMR spectra of **PU1** and **PU2** in DMSO- d_6 . In the Figure, the signals assignable to **AOH1** and the crown ethers were clearly observed. The signals for the methylene proton of benzyl group in **AOH1** were observed at 4.5 ppm (filled circles in Figure 3), indicating that the rotaxane structure was still maintained in the PUs. The ratio of the intensities of the signal for the methylene proton in **AOH1** to that for the aromatic protons in **BisC** was 2:7, indicating that **BisC** and **AOH1** exist with 1:2 ratio in **PU1**. In the case of **PU2**, the intensity ratio was 2:8, that dibenzo-24-crown-8 ether and **AOH1**

exist with 1:1 ratio in **PU2**. These results suggest that almost all **AOH1** molecules forms the [3]rotaxane in **PU1** and the [2]rotaxane in **PU2**.

ATR-FT-IR spectra measurements were carried out to evaluate the formation of hydrogen bond (H-bond) between NH of urethane bonds and C=O of urethane and/or ester bonds in the PU chains. The C=O stretching ($\nu(\text{C=O})$) band regions of the ATR-FT-IR spectra for the PUs were used, because the N-H stretching ($\nu(\text{N-H})$) bands of the urethane bond and ammonium moiety of **AOH1** were overlapped in the $\nu(\text{N-H})$ band region. Figure 4 shows the ATR-FT-IR spectra of the $\nu(\text{C=O})$ band regions for the urethane and ester bonds. A free C=O band ($\nu(\text{C=O})_{\text{free}}$) at 1725 cm^{-1} and hydrogen bonded one ($\nu(\text{C=O})_{\text{H-bond}}$) at 1709 cm^{-1} were observed for **PU0**. This characteristic H-bond is well observed in the IR spectra of typical polyurethanes. In contrast, the hydrogen bonded C=O band was hardly observed in the spectra of **PU1** and **PU2**. Introduction of a few wt% of the rotaxane component seems to induce the break of the H-bonds. This may be due to the steric hindrance by the bulky rotaxane.

3.4 Thermal properties of PUs

DSC and TGA measurements were performed in order to examine the thermal properties of the PUs. Figure 5 shows DSC thermograms of the PUs. At the first heating, all the PUs show only an endothermic peak from melting of the crystallized PCL (see

supporting information). At the second heating, T_g , T_c , and T_m were obviously observed. The T_g s of **PU0**, **PU1** and **PU2** were observed at 50, 50 and 47 °C, respectively; there were no significant difference in the T_g values. In contrast, the crystalline temperatures for the PCL of **PU0**, **PU1** and **PU2** were observed at -6, 13 and 3 °C, respectively. This difference of the T_c s indicates that the sterically bulky rotaxane unit at the PU chain terminal leads to inhibition of the packing for the crystallization of the PCL unit. In addition, the T_c for **PU2** is lower than that for **PU1**. This may be because the mobility of the PU chain terminals is inhibited by the [3]rotaxane structure.

To evaluate thermal decomposition of the PUs the temperature of 5 % weight loss (T_d) was obtained from the TGA curves (Figure 6). The T_d for **PU0**, **PU1** and **PU2** were at 295, 286 and 281 °C, respectively. The descent of T_d values for **PU1** and **PU2** compared with that for **PU0** would be due to the increment of the terminal groups; the [3]rotaxane unit in **PU1** may be also regarded as the terminal groups. **PU1** and **PU2** showed the remarkable shoulder peak around 350-450 °C whereas no such peak was observed in the TGA curve for **PU0**. It is expected that the shoulder peak is based on the rotaxane unit. This result is also an indirect evidence for the existence of the rotaxane component in the PUs.

3.5 Mechanical properties of PUs

Figure 7 shows the temperature dependence of the storage modulus (E'), loss modulus

(E'') and loss tangent ($\tan \delta$) of the PUs. Starting temperatures of the decreasing E' and onset temperatures of $\tan \delta$ curves showed similar magnitude compared with the DSC results. E' s of the PUs gradually decreased and $\tan \delta$ curves showed broad peaks in the temperature region (-50 to 50 °C), because the glass transition, recrystallization and melting of the PCL continuously occurred in the temperature region. Change in E' for the recrystallization of the soft-segment in **PU1** and **PU2** was clearly observed around 0 °C, but not for **PU0**. The T_c for the PCL of **PU0** is lower than those of **PU1** and **PU2** as mentioned in the DSC section, leading to the broad change in E' . Unfortunately, no rubbery plateau regions were observed in all the PUs. As mentioned in the IR section, this is because the low formation ratio of the hydrogen bonds in the PUs results in the lack of physical crosslinks to form a 3D structure.

Stress-strain curves for the PUs were measured at 15 and 30 °C. The PUs at 15 °C behaved as a hard plastic because of the crystallized PCL component (see supporting information). Figure 8 shows the stress-strain curves for the PUs at 30 °C. Young's Modulus, tensile strength, and strain at break of the PUs were summarized in Table 1. The young moduli of the PUs seem to depend on the measurement temperature rather than their chemical structure, because the melting of the PCL unit in **PU0** was already started at the measurement temperature of 30 °C, but not for **PU1** and **PU2**. The tensile strength and break of strain of **PU1** were higher than those of **PU2**. As the reason, we considered a sliding effect of the rotaxane ring molecule and entanglement of the PU chains. We

expected, however, that contribution of the sliding effect is very small because the rotaxane moiety is located at the terminals of the PU chains and the interaction between the ammonium group in **AOH1** and oxygen atoms of **BisC** is still remained. It is likely that the entanglement of the PU chains influences the mechanical property of **PU1**. The [3]rotaxane moiety forms both a crankshaft structure and U-figured structure. The U-figured structure could enhance entanglement of the PU chains. In addition, the sterically bulky and rigid structure of the [3]rotaxane provides a sufficient space to encourage the entanglement. Consequently, the mechanical properties of **PU1** were higher than those of **PU2**.

4. Conclusions

We have demonstrated the synthesis strategy of the PUs containing the [3]rotaxane that consists of **BisC** and **AOH1**, and containing the [2]rotaxane that consists of dibenzo-24-crown-8 ether and **AOH1** under the equilibrium system. It was found that PCL can be used in this system rather than PTMG as the soft segment, because the ether units of the PTMG inhibit the pseudorotaxane formation between **BisC** and **AOH1**. The existence of the rotaxane units in the PUs was confirmed by the ¹H NMR spectroscopy and TGA measurement. The influence of the rotaxane structures on the thermal and mechanical properties of the PUs were as follows. The rotaxanes in the PUs disturb the formation of the hydrogen bond between the PU chains as well as recrystallization of the PCL component. It

is likely that the U-figured [3]rotaxane structure enhances the mechanical property due to the entanglement of the PU chains encouraged by sterically bulky and rigid structure of the [3]rotaxane. Further improvement of the properties of the PUs containing the [3]rotaxane unit as a rubber material is in progress in our laboratory.

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References

- [1] a) Petrović ZS, Ferguson J *Prog Polym Sci* 1991;16:695-836;
b) Ng HN, Allegrezza AE, Seymour RW, Cooper SL. *Polymer* 1973;14:255-261;
c) Koberstein JT, Russell TP *Macromolecules* 1986;19:714-720;
d) Leung LM, Koberstein JT *J Polym Sci Part B Polym Phys* 1985;23:1883-1931;
e) Kojio K, Fukumaru T, Furukawa M *Macromolecules* 2004;37:3287-3291;
f) Kojio K, Nakamura S, Furukawa M *Polymer* 2004;45:8147-8152;
g) Kojio K, Nonaka Y, Furukawa M *J Polym Sci Part B Polym Phys* 2004;42:4448-4458;
h) Kojio K, Nakashima S, Furukawa M *Polymer* 2007;48:997-1004;
i) Kojio K, Kugumiya S, Uchiba Y, Nishino Y, Furukawa M *Polym J* 2009;41:118-124.
- [2] a) Grossel MC. In: Rao CNR, Mürller A, Cheetham AK, editors. *Nanomaterials Chemistry*. Weinheim: Wiley-VCH; 2007. pp. 319-355;
b) Loeb SJ *Chem Soc Rev* 2007;36:226-235;
c) Saha S, Stoddart JF *Chem Soc Rev* 2007;36:77-92;
d) Balzani V, Credi A, Silvi S, Venturi M *Chem Soc Rev* 2006;35:1135-1149;
e) Ballardini R, Balzani V, Credi A, Gandolfi MT, Venturi M *Acc Chem Res* 2001;34:445-455;
f) Balzani V, Credi A, Raymo FM, Stoddart JF *Angew Chem Int Ed* 2000;39:3248-3391.
- [3] In: Sauvage J-P, Dietrich-Buchecker CO, Editors. *Molecular Catenanes, Rotaxanes and Knots*. Weinheim: Wiley-VCH; 1999.
- [4] a) Murakami H, Kawabuchi A, Matsumoto R, Ido T, Nakashima N *J Am Chem Soc* 2005;127:15891-15899;
b) Murakami H, Kawabuchi A, Kotoo K, Nakashima N *J Am Chem Soc* 1997;119:7605-7605;
c) Anelli PL, Spencer N, Stoddart JF *J Am Chem Soc* 1991;113:5131-5133.
- [5] a) Li J, Loh XJ *Adv Drug Delivery Rev* 2008;60:1000-1017;
b) Harada A *J Polym Sci Part A Polym Chem* 2006;44:5113-5119;
c) Takata T *Polym J* 2006;38:1-20;
d) Takata T, Kihara N, Furusho Y *Adv Polym Sci* 2005;171:1-75;
e) Benjamin Beck J, Rowan SJ. In: Ciferri A, Editor. *Supramolecular Polymers*. Boca Raton: Taylor & Francis; 2005. pp. 257-299;
f) Huang F, Gibson H *Prog Polym Sci* 2005;30:982-1018;
g) Harada A *Acta Polym* 1998;49:3-17.
- [6] Harada A, Li J, Kamachi M *Macromolecules* 1990;23:2821-2823.
- [7] Gibson HW, Marand H *Adv Mater* 1993;5:11-21.

- [8] a) Shen YX, Gibson HW *Macromolecules* 1992;25:2058-2059;
b) Shen YX, Xie D, Gibson HW *J Am Chem Soc* 1994;116:537-538;
c) Marand H, Hu Q, Gibson HW, Veytsman B *Macromolecules* 1996;29:2555-2562;
d) Gong C, Gibson HW *Angew Chem Int Ed* 1997;36:2331-2333;
e) Gong, C, Glass TE, Gibson HW *Macromolecules* 1998;31:308-318;
f) Gong, C.; Ji Q, Subramaniam C, Gibson HW *Macromolecules* 1998;31:1814-1818.
- [9] a) Gong C, Gibson HW *J Am Chem Soc* 1997;119:8585-8591;
b) Gong C, Gibson H W *Macromol Chem Phys* 1998;199:1801-1806.
- [10] a) Yamaguchi I, Takenaka Y, Osakada K, Yamamoto T *Macromolecules* 1999;32:2051-2054;
b) Yamaguchi I, Osakada K, Yamamoto T *Chem Commun* 2000;1335-1336.
- [11] a) Okumura Y, Ito K *Adv Mater* 2001;13:485-487;
b) Ito K *Polym J* 2007;39:489-499.
- [12] a) Fleury G, Schlatter G, Brochon C, Hadziioannou G *Polymer* 2005;46:8494-8501;
b) Fleury G, Schlatter G, Brochon C, Hadziioannou G *Adv Mater* 2006;18:2847- 2851;
c) Fleury G, Schlatter G, Brochon C, Travelet C, Lapp A, Lindner P, Hadziioannou G *Macromolecules* 2007;40:535-543.
- [13] Oku T, Furusho Y, Takata T *Angew Chem Int Ed* 2004;43:966-969.
- [14] a) Takata T, Arai T, Kohsaka Y, Shioya M, Koyama Y. In: Harada A, editor. In: *Supramolecular Polymer Chemistry*. Weinheim: Wiley-VCH; 2012. pp. 331-346;
b) Koyama Y *Polym J* 2014; 46:315-322.
- [15] a) Sohgawa Y-H, Fujimori H, Shoji J, Furusho Y, Kihara N *Chem Lett* 2001;774- 774;
b) Furusho Y. Sasabe H, Nattsui D, Murakawa K, Takata T, Harada T *Bull Chem Soc Jpn* 2004;77:179-185;
c) Takata T, Kawasaki H, Asai S, Kihara N, Furusho Y *Chem Lett* 1999;111-112.
- [16] a) Ashton PR, Campbell PJ, Chrystal EJT, Glink PT, Menzer S, Philp D, Spencer N, Stoddart JF *Angew. Chem. Int. Ed. Eng.* 1995;34:1865-1869;
b) Furusho Y, Oku T, Hasegawa T, Tsuboi A, Kihara N, Takata T *Chem. Eur. J.* 2003;9:2895-2903;
c) Lee Y-G, Koyama Y, Yonekawa M, Takata T *Macromolecules* 2010;43:4070- 4080;
d) Sato T, Takata T *Macromolecules* 2008;41:2739-2742.
- [17] Furukawa M, Hamada Y, Kojio K *J Polym Sci Part B Polym Phys* 2003;41:2355- 2363.

Table 1. Young's Modulus, tensile strength, and strain at break of the PUs.

	Young's Modulus / MPa	tensile strength / MPa	strain at break
PU0	0.1	0.36	6.7
PU1	0.3	0.92	5.5
PU2	0.3	0.64	4.0

Figure captions

Figure 1. ^1H NMR spectra of (a) **AOH1**, (b) **BisC** + **AOH1**, (c) **BisC** + **AOH1** + PTMG2000, and (d) **BisC** + **AOH1** + PCL in CDCl_3 : $[\text{AOH1}] = 8 \text{ mM}$, $[\text{BisC}] = 4 \text{ mM}$, $[\text{PTMG2000}] = [\text{PCL}] = 36 \text{ mM}$. The arrows indicate the signal for the methylene proton of the benzyl group in **AOH1**.

Figure 2. Possible structures of **PU0**, **PU1**, and **PU2**.

Figure 3. ^1H NMR spectra of (a) **PU1** and (b) **PU2** in DMSO-d_6 . Filled circles and open circles indicate the signals for the methylene proton of the benzyl group in **AOH1** and for aromatic protons of crown ethers, respectively.

Figure 4. ATR-FT-IR spectra of (a) **PU0**, (b) **PU1**, and (c) **PU2**.

Figure 5. DSC thermograms of (a) **PU0**, (b) **PU1**, and (c) **PU2**.

Figure 6. TGA curves of **PU0** (solid line), **PU1** (dotted line), and **PU2** (dashed line).

Figure 7. Temperature dependence of storage modulus (a), loss modulus (b), and loss tangent (c) for **PU0** (solid line), **PU1** (dotted line), and **PU2** (dashed line).

Figure 8. Stress-strain curves of (a) **PU0**, (b) **PU1**, and (c) **PU2** at $30 \text{ }^\circ\text{C}$.

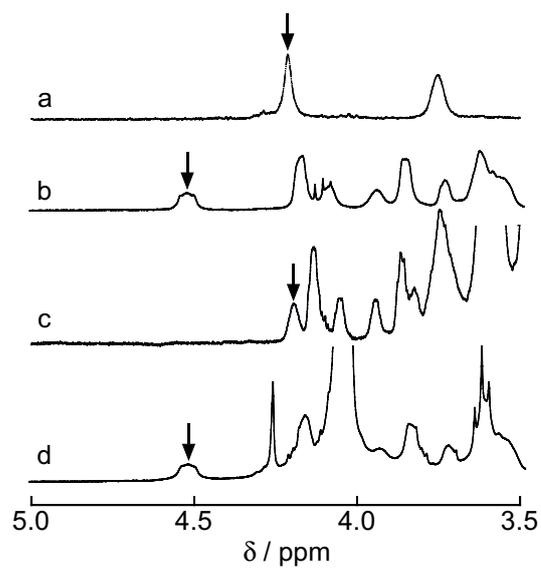
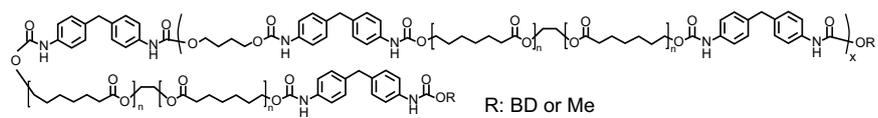
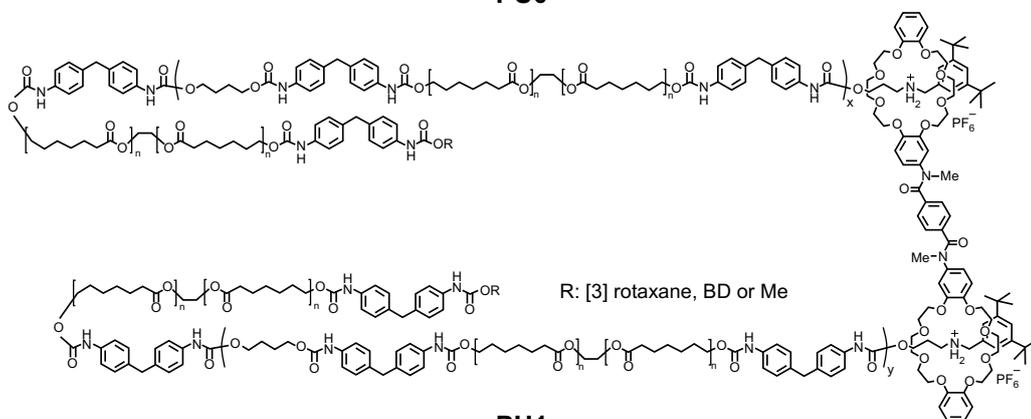


Figure 1

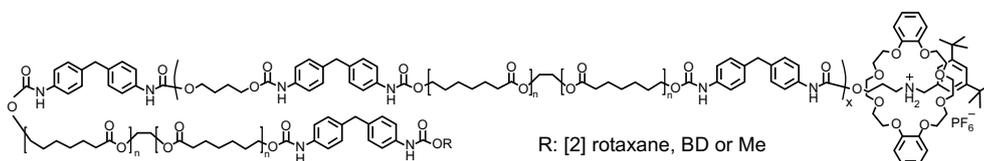
H. Murakami, et al.



PU0



PU1



PU2

Figure 2

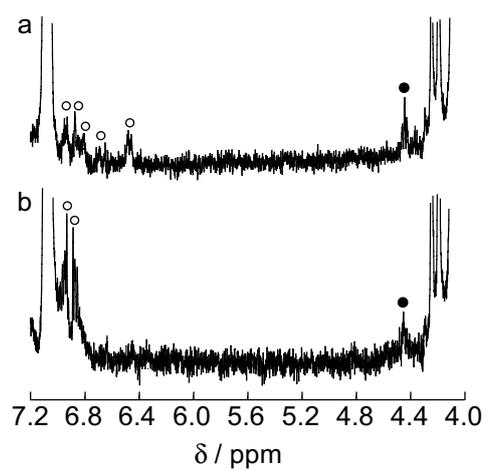


Figure 3

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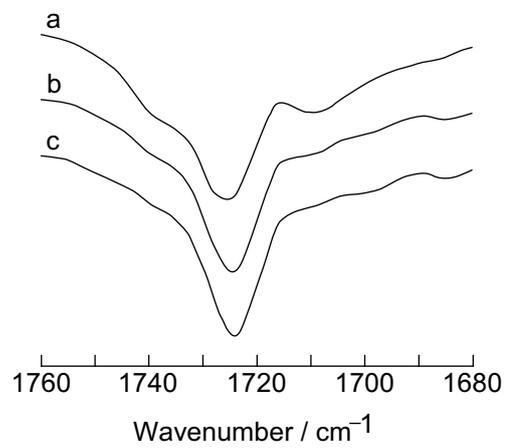


Figure 4

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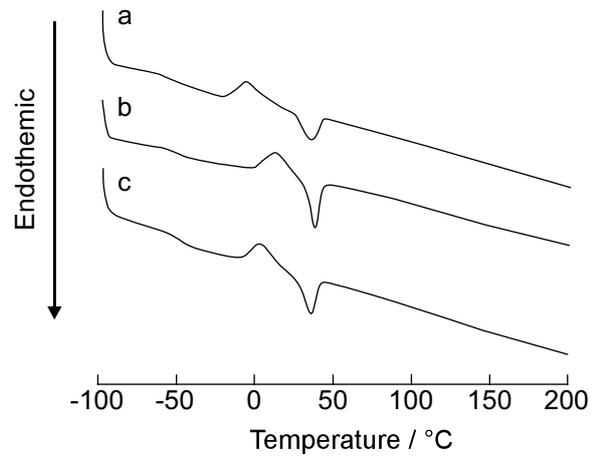


Figure 5

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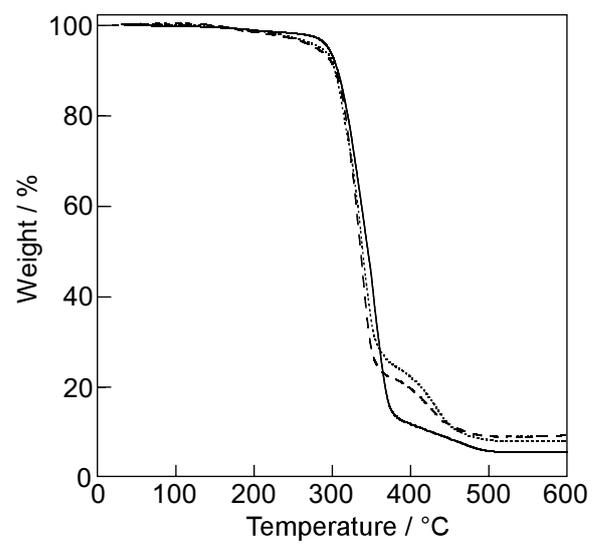


Figure 6

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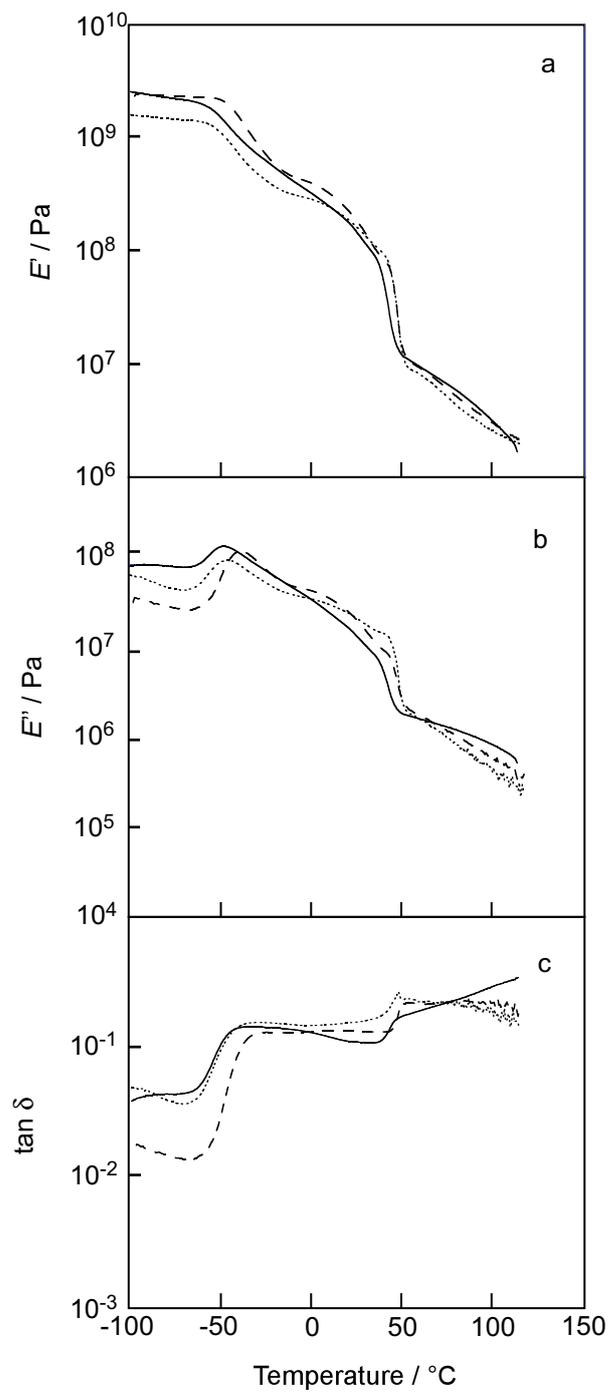


Figure 7

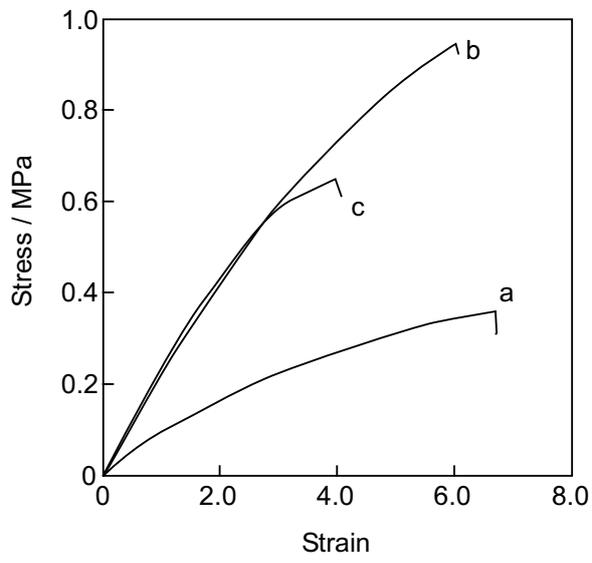


Figure 8

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