Synthesis and Characterization of Polyurethanes Crosslinked by Polyrotaxanes of Two Filling Ratios of α-Cyclodextrin and with Two Modification Ratios of Polyurethane Chain

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Abstract
Four polyurethanes (PUs) crosslinked by polyrotaxanes (PRXs) of two filling ratios of CyD (63% for PRX4000 and 37% for PRX6000) and with modification ratios of 1 and 2 for a PU chain. The PUs were abbreviated as PU6000(1), PU6000(2), PU4000(1), and PU4000(2), in which 4000 and 6000 are the molecular weights of PEGs as an axle molecule of the PRX and the numbers in parentheses are the modification ratios of the PU chain. ATR-FT-IR, DSC, viscoelastic measurements and tensile test were carried out to investigate their thermal and physical properties. The formation of hydrogen bonds between the PU chains increased with increase in the modification ratio of the PU chain. PU4000(2) possessing the half filling ratio of CyD and higher modification ratio of the PU chain made the recrystallization of the soft segment slow. PU6000(2) with the lower filling ratio of CyD and higher modification ratio of the PU chain showed the highest elongation among the PUs, implying that the sliding effect based on the rotaxane structure occurred.

Keywords Polyurethanes, Polyrotaxanes, Crosslinks

Introduction
Polyurethanes (PUs) have been widely used in industrial and commercial goods because of their characteristic properties, which are based on microphase-separated structures that are controlled by variation of starting materials, preparation conditions, and so on.1–9) The microphase-separated structures consist of hard segment and soft segment domains. Especially, the hard segment domains acting as physical crosslink points via hydrogen bonds between the urethanes play a critical role for the appearance of elastic properties. Therefore, development of unique PUs with interesting properties involves novel design of the crosslink point.

Recently, supramolecular materials have spread worldwide because of their distinctive features.10–16) A rotaxane possesses an interlocked structure where a ring molecule and dumbbell shaped axle molecule are interlocked.17) The dumbbell shaped molecule bears bulky end-cap groups which prevent the ring molecule from release. Interestingly, the ring molecule can slide along the axle molecule because of no covalent bond between the ring and axle molecules. The use of the sliding makes it possible to construct molecular machines such as molecular shuttles and switches.18–20) Polyrotaxanes (PRXs) consisting of α-cyclodextrin (CyD) and poly(ethylene glycol) (PEG) were reported first by Harada, et al.21) Since then, a lot of PRXs have been reported.22–28) An elegant sliding network gel based on a PRX consisting of α-CyD and a PEG with long chain lengths was reported by Ito, et al. and they described their physical properties in detail.29–34) Hadziioannou, et al. also reported similar sliding gels.35–37) Yui, et al. strenuously investigated PRXs modified with drugs for medical use.38–41) Takata, et al. synthesized a PRX crosslinked by 4,4'-diphenylmethanediisocyanate.42) Recent study on functional polymers crosslinked by rotaxanes and polyrotaxanes has been summarized in reviews.43, 44) Hybridization of PRXs and a variety of polymers have also been published. Araki, et al. reported molecular rope
curtains, which show unique and excellent liquid crystal behaviors\(^{45-47}\). Synthesis of a PRX modified with poly(N-isopropylacrylamide) and its sliding-gel property were reported by Takeoka, et al.\(^{48}\). Ito, et al. was published a PRX grafted on cyclodextrin rings with many linear poly(ε-caprolactone)\(^{49}\).

As described above, studies of various kinds of PRXs have so far been published. These distinctive properties inspire us with an idea that PRXs instead of the hard segment domains of PUs is introduced. PUs crosslinked by CyDs have been published\(^{50-54}\). However, no report of the polyurethane properties based on the structure of polyrotaxanes as the crosslink points has been published in our best knowledge. Therefore, we describe herein the synthesis of four PUs (PU\(_{4000}(1)\), PU\(_{4000}(2)\), PU\(_{6000}(1)\), and PU\(_{6000}(2)\)) crosslinked by PRXs, which consist of α-cyclodextrins (CyDs) and poly(oxyethylene) glycols with different chain lengths (PEG4000, and PEG6000), and modified with PU chains at \([\text{NCO}]_{\text{total}}/[	ext{OH}]_{\text{total}}=1\) and 2 as well as their characteristics using the results of attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectroscopy, differential scanning calorimetry (DSC), dynamic viscoelastic measurement and tensile test.

**Experimental**

**Materials**

Poly(ethylene glycol)#4000 (Nacalai; PEG4000, \(M_n=ca. 3100\)) and poly(ethylene glycol)#6000 (Nacalai; PEG6000, \(M_n=ca. 7500\)) were dried in vacuo prior to use. PRXs consisting of the PEGs and α-cyclodextrin were synthesized according to the literature\(^{55}\). 1H NMR measurements of the PRXs reveal that the numbers of CyD for PRX4000 and PRX6000 were estimated to be 22 and 31, respectively (see Supporting Information): the filling ratios of CyDs for PRX4000 and PRX6000 were estimated to be 63 and 37%, respectively, when close packing for each PEG is defined to be 100%. 4,4’-Diphenylmethanediisocyanate (MDI) was provided by Mitsui Chemical, Co., Ltd. and used as received. Poly(tetramethylene glycol) (PTMG) (Wako, PTMG2000; \(M_n=ca. 2000\)) was dried by a bubbling with dry nitrogen under slight reduced pressure prior to use. All other chemicals were of reagent grade.

**Synthesis of Polyurethanes**

Typical procedure is as follows. Dry PTMG2000 (1.0 g, 0.5 mmol) and MDI (0.38 g, 1.5 mmol) were reacted at 95°C under an argon atmosphere overnight to obtain a prepolymer\(^{56}\). After cooling to ambient temperature, the prepolymer was dissolved in a dry DMAc solution containing 9 wt% LiBr (10 mL) and then added dropwise into a solution of PRX (PRX4000: 31 mg, 1.3 \(\mu\)mol; PRX6000: 37 mg, 0.9 \(\mu\)mol; CyD: 27 mg, 28 \(\mu\)mol) in a dry DMAc solution containing 9 wt% LiBr (10 mL). The reaction mixture was stirred at 80°C overnight under an argon atmosphere. Methanol (5.0 mL) was added into the reaction mixture to deactivate the excess isocyanates. After stirring for 2 h, the reaction mixture was concentrated to 10 mL, poured into a Teflon vessel and dried at 40°C for 24 h and then 80°C for 24 h. The films obtained were washed with toluene, methanol and then water. This washing procedure was repeated three times. Finally, the PU films were pressed at 100°C under 1.0 MPa for 10 min with an IMOTO Compact Heating Press IMC-180C.

**Measurements**

Gel fractions (g) were determined from the original weight (Wo) and the weight (Wg) of which the sample was dried after it is swelled to an equilibrium state with toluene and DMSO at 30°C; \(g\) was defined as \(g=W_g/W_o \times 100\).

The formation of hydrogen bond between the PU chains was estimated by attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectroscopy. The ATR-FT-IR measurements 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\(^{-1}\).

DSC thermograms were collected on a Shimadzu DSC-60 from −100 to 200°C at a heating rate of 10°C min\(^{-1}\) under a nitrogen atmosphere.

Temperature dependence of dynamic viscoelastic properties was measured with an RSA II solid analyzer (Rheometrics, Co., Ltd.) in a tension mode. The measurement was performed from −120 to 200°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 test was performed with a TENSILON RTC-1150A at ambient temperature. The initial length and cross-head speed were set to be 20.0 mm and 5.0 mm min\(^{-1}\), respectively.

**Results and Discussion**

**Design and Synthesis**

To investigate the influence of the PRX structures on their PU properties PRXs consisting of PEG4000 with 64% filling ratio of CyD and PEG6000 with 37% one were
used as the crosslinker. Two modification ratios of a PU chain, \([\text{NCO}]_{\text{total}}/\text{[OH]}_{\text{total}}=1.0\) and 2.0, were also chosen to obtain PU films with a sufficient strength. In fact, PUs prepared with the modification ratios of 0.67 and 0.5 were of flake.

The synthesis of PUs was carried out according to Scheme 1. The PUs were synthesized by a prepolymer method\textsuperscript{56}. The prepolymer is a mixture of free MDI, and \(\alpha,\omega\)-diisocyanato-oligomers. The PUs with the modification ratio of 2 have naturally many dangling PU chains compared to the PUs with the modification ratio of 1. The NCO groups of the dangling PU chains and unreacted ones were treated by methanol. PUs crosslinked by CyD were also prepared as reference PUs. The PUs crosslinked by PRXs were abbreviated as \(\text{PU}_x(y)\) in which \(x\) and \(y\) are the molecular weights of the PEGs and the modification ratios, respectively: \(\text{PU}_{4000}(1), \text{PU}_{4000}(2), \text{PU}_{6000}(1),\) and \(\text{PU}_{6000}(2)\). The reference PUs were also abbreviated as \(\text{PU}_0(1)\) and \(\text{PU}_0(2)\).

**Scheme 1.** Synthesis routes of PUs crosslinked by PRXs and CyD.

Gel fraction

Gel fractions of the PUs were summarized in Table 1. The PUs with the same modification ratio gave similar gel fractions, indicating that the concentrations of the modified...
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prepolymers on CyDs in the PUs with the same modification ratio are at the same level. Meanwhile, the gel fractions of PUx(2) were slightly higher than those of PU(1). This is reasonable because of the higher modification ratio for PUx(2). All of the PUs also left gel components in DMSO, suggesting the existence of crosslinks between PRXs and between the CyDs. The concentration of the crosslink will be discussed in Mechanical Properties.

**Formation of Hydrogen bond**

To evaluate the formation of hydrogen bond (H-bond) between the urethane bonds ATR-FT-IR measurement was carried out. The C=O stretching (ν(C=O)) band regions of the ATR-FT-IR spectra for the PUs were used because the N-H stretching (ν(N-H)) bands of the urethane bond and O-H ones of the remaining OH groups on CyD were overlapped in the ν(N-H) band region. The ATR-FT-IR spectra of the ν(C=O) band regions for the PUs were shown in Figure 1. A free ν(C=O) around 1730 cm⁻¹ and hydrogen bonded ν(C=O) around 1710 cm⁻¹ were observed. These are characteristic bands observed in the IR spectra of typical polyurethanes.

Relative intensity ratios of the carbonyl groups ($I_{\nu(C=O)\text{free}}/I_{\nu(C=O)\text{bond}}$) for the PU4000s and PU6000s were increased with increase in the modification ratio of the PU chain (Figure 1 and see Supporting Information). This is reasonable because the number of the urethane bond increased with increase in the modification ratio. The influence of the H-bond formation on the filling ratios was slight, suggesting that the rotaxane structure barely influences the H-bond formation. On the contrary, the H-bond formation ratio of PU0(1) was obviously higher than that of PU0(2). This result seems to be attributable to the steric congestion at the CyD crosslink points rather than the number of the urethane bond. Most of the H-bonds would form near the CyD crosslink points because the MDI units of the PU chains gather there. In addition, the CyD crosslink points with the PU modification ratio of 1 and without the rotaxane structure can provide enough space to form the H-bond at their neighborhood. Therefore, the H-bond formation of PU0(1) would be more enhanced than that of PU0(2).

**Thermal properties**

DSC results are shown in Figure 2. The temperatures of glass transition ($T_g$), recrystallization ($T_c$), and melting

| Table 1. Gel fractions of the PUs. |
|----------------------------------|
|   | Toluene [%]a | DMSO [%]b |
| PU0(2) | 99.2 | 70 |
| PU4000(2) | 99.5 | 66 |
| PU6000(2) | 99.5 | 75 |
| PU0(1) | 99.3 | 72 |
| PU4000(1) | 99.3 | 71 |
| PU6000(1) | 99.5 | 66 |

a) The errors were within ±0.5%.
b) The errors were within ±5.0%.

Figure 1. ATR-FT-IR spectra of the PUs: (a) PU4000(1) (red line), PU6000(1) (blue line), and PU0(1) (green line); (b) PU4000(2) (red line), PU6000(2) (blue line), and PU0(2) (green line).

Figure 2. DSC thermograms of (a) PU0(1), (b) PU4000(1), (c) PU6000(1), (d) PU0(2), (e) PU4000(2), and (f) PU6000(2).
were summarized in Table 2. It is well-known that the H-bond formation influences the $T_g$. However, the $T_g$s of the PUs were almost the same. As described in the previous section, most of the H-bonds would form near the CyD crosslink points. Consequently, the glass transition of the soft segment would be also unsusceptible to the H-bond formation.

The DSC thermograms of the PUs except that of PU4000(2) showed the recrystallization and melting of the soft segments around $-40$ and $0^\circ C$, respectively. Meanwhile, PU4000(2) gave an unclear recrystallization peak and small melting peak. Similar behavior was also observed in the DSC result of a PU crosslinked by half methylated RRX4000 and with the same modification ratio of the PU chain.

Figure 3 shows the temperature dependence of the storage modulus ($E'$) and loss tangent (tan $\delta$) of the PUs (see Supporting Information). In the tan $\delta$ curves, a peak attributable to an $\alpha$ relaxation that corresponds to the glass transition of the soft segment was observed around $-60^\circ C$. The $E'$s and tan $\delta$ curves of PU6000(2), RU6000(1), PU4000(1), PU0(2), and PU0(1) showed shoulder peaks in the temperature region of $-50$ to $0^\circ C$. These peaks indicate that the recrystallization and melting of the soft segment occurred around the temperature region. In contrast, a slight shoulder peak was barely observed in the $E'$ of PU4000(2). This unnoticeable recrystallization behavior is in good agreement with the results of the DSC measurement. This result could be due to a slow recrystallization in the broad temperature region. PU4000(2) possesses the half filling ratio of CyD and middle length of the PEG4000 axle. In addition, the number of crosslinks between PRX4000s is low because of the higher modification ratio. Therefore, the structure of PU4000(2) could be suitable to the slow recrystallization of the soft segment.

| PU       | $T_g$ $[^\circ C]$ | $T_c$ $[^\circ C]$ | $T_m$ $[^\circ C]$ |
|----------|--------------------|--------------------|--------------------|
| PU0(2)   | $-81$              | $-45$              | $2$                |
| PU4000(2)| $-82$              | $-45$              | $2$                |
| PU6000(2)| $-81$              | $-40$              | $2$                |
| PU0(1)   | $-83$              | $-45$              | $1$                |
| PU4000(1)| $-83$              | $-40$              | $1$                |
| PU6000(1)| $-83$              | $-35$              | $3$                |

a) The starting temperatures of the decrease of DSC curves were considered to be $T_g$.  

Figure 3. Temperature dependence of storage modulus (upper panel) and loss tangent (lower panel) for the PUs: (a) PU4000(2) (red line), PU6000(2) (blue line), and PU0(2) (green line); (b) PU4000(1) (red line), PU6000(1) (blue line), and PU0(1) (green line).
Rubbery plateau regions were observed in the $E$’s of PU6000(2), RU6000(1), PU4000(2), PU4000(1), and PU0(1) from around 10°C; however, the $E$’s gradually decreased with increase in temperature. The starting $E$’s values of the rubbery plateau regions for the PUs with the modification of 1 were higher than those of the PUs with the modification ratio of 2. PU4000(1) was hard to flow compared to PU4000(2). PU0(2) became a fluid without a rubbery plateau region. These results indicate that the modification ratio of 1 makes more crosslinks between the PRXs and between the CyDs than that of 2. The number of the dangling PU chains would also influence the thermal behavior of the plateau region. Interestingly, the degree of decrease in the $E$’s of PU6000(1) and PU6000(2) was almost the same. It would be due to increase in entanglement of the PU chains. That is, the probability to form the entanglement of the PU chains in PU6000s increases because PRX6000 consists of PEG6000 with longer chain length and CyDs with looser filling ratio of 37%.

**Mechanical properties**

Figure 4 shows stress-strain curves of the PUs. Magnitudes of Young’s Modulus, tensile strength, and elongation of the PUs were summarized in Table 3. The Young’s modulus of PU6000(1) was ca. 2–3 times higher than those of the other PUs. As described in the previous section, the highest Young’s modulus of PU6000(1) is due to the increase in the crosslinks between PRX6000s and the entanglement of the PU chains.

The tensile strengths of PUx(1)s were higher than those of PUx(2)s. Most likely, the number of the crosslinks between the PRXs and between the CyDs in the PUs with the modification ratio of 1 are larger than those in the PUs with the modification ratio of 2. PU4000(1) showed the highest tensile strength among the PUs, attributable to not only the number of crosslinks between PRX4000s but also the higher filling ratio of CyD.

PU6000(2) showed the highest elongation among the PUs. PU4000(2) also showed the second highest elongation among the PUs. Both the PUs possess the low number of crosslinks between the PRXs and the rotaxane structures. Therefore, the sliding effect based on the rotaxane structure could appear in the elongations of PU6000(2) and PU0(2).

### Conclusion

We have demonstrated the synthesis and characterization of four PUs crosslinked by PRXs of two filling ratios of CyD and with two modification ratios of the PU chains as well as two PUs crosslinked by CyD as the reference PUs. The results are follows. In the ATR-FT-IR measurements of the PUs, the H-bond formation between the PU chains is affected by the modification ratios of the PU chains. The results of DSC measurements indicate that the glass transitions of the soft segments in the PUs are unsusceptible to the H-bond formations. The DSC behaviors of the PUs were almost the same except those of PU4000(2) in which the recrystallization of the soft segment was unclear. The viscoelastic measurements suggest that the structure of PU4000(2) seems to make the recrystallization slow. The influences of the crosslinks between the PRXs as well as the dangling chains in the PUs appears in the rubbery plateau regions of the $E$’s and in the tensile strengths of the stress-strain curves. The higher elongations of PU6000(2) and PU4000(1) could be based on the sliding effect of the rotaxane structure. Further characterization is currently in progress in our laboratory.

**Table 3. Mechanical properties of PUs.**

| Young’s modulus [MPa] | Tensile strength [MPa] | Elongation [%] |
|-----------------------|------------------------|----------------|
| PU0(2)                | 2.5                    | 3.8            | 1350           |
| PU4000(2)             | 9.4                    | 16.2           | 1530           |
| PU6000(2)             | 5.7                    | 22.9           | 1940           |
| PU0(1)                | 7.3                    | 13.3           | 1380           |
| PU4000(1)             | 9.2                    | 33.5           | 1350           |
| PU6000(1)             | 24                     | 24.2           | 1350           |

![Stress-strain curves of PUs](image-url)
Supporting Information

Syntheses of PRXs and Additional data for PUs are available in Supplementary materials.

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