Synthesis and Characterization of Polyurethanes crosslinked by Polyrotaxanes consisting of Half-methylated Cyclodextrins and PEGs with different chain lengths

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ABSTRACT

Three polyurethanes (**PRX1500Me-PU**, **PRX4000Me-PU**, and **PRX6000Me-PU**) crosslinked by polyrotaxanes (PRXs), which consist of half-methylated α-cyclodextrins (CyDs) and poly(oxyethylene)glycols with different chain lengths (PEG1500, PEG4000, and PEG6000), were synthesized. The filling ratios of CyD in PRX1500, PRX4000 and PRX6000 are 75, 63 and 37 %, respectively. A polyurethane crosslinked by half-methylated CyD (**CDMe-PU**) was also prepared for comparison of their structure and properties. ATR-FT-IR spectra of the PUs showed that the formation ratio of hydrogen bond between the PU chains around PRXs increased with increase in the filling ratio. DSC and dynamic viscoelastic measurements and tensile tests for the PUs revealed that (i) reorganized-crystallization of the soft segment chains of **PRX1500Me-PU** easily occurred because of formation of a pure phase for them; (ii) the thermal and physical behaviors of **PRX6000Me-PU** are similar to those of **CDMe-PU** because CyDs as the crosslink points disperse in a similar fashion in the PUs; (iii) the PRX4000 with the moderate filling ratio of CyD in **PRX4000Me-PU** makes slow reorganized-crystallization of the soft segment chains in the PU as well as improves the tensile performance among the PUs.

1. INTRODUCTION

Polyurethanes (PUs) are among the most important macromolecules because their applications are widely spread industrially and commercially. The applications are based on their characteristic properties originated from the variation of starting materials, preparation conditions, and *etc.* [1]. The type of crosslink point also plays a critical role for the appearance of elastic properties. Therefore, novel design of the crosslink point should enable us to develop unique PU elastomers.

Recently, supramolecular materials have attracted much attention because of their distinctive features [2]. A rotaxane is a molecule where a ring molecule is interlocked by an axle molecule with bulky terminal cap groups that prevent the ring molecule from release [3]. Among the interesting properties of the rotaxane based on the interlocked structure, free sliding of the ring molecule along the axle molecule is remarkable. The use of the sliding makes it possible to construct molecular machines such as molecular shuttles and switches [4].

Since the first discovery of polyrotaxanes (PRXs) consisting of α-cyclodextrin (CyD) and poly(ethylene glycol) (PEG) by Harada, *et al.* [5], a lot of PRXs have been reported [6]. Ito, *et al.* reported an elegant sliding network gel based on a PRX consisting of α-CyD and PEGs with long chain lengths and their physical properties in

detail [7]. Hadziioannou, *et al.* also reported similar sliding gels [8]. PRXs for medical use were strenuously investigated by Yui, *et al* [9]. Takata, et al. also synthesized a PRX crosslinked by 4,4'-Diphenylmethanediisocyanate [10]. Advanced functional polymers crosslinked by rotaxanes has been summarized in reviews [11].

PRXs modified with a variety of polymers have also been published. Molecular rope curtains based on PRXs reported by Araki, *et al.* shows unique and excellent liquid crystal behaviors [12]. Takeoka, *et al.* synthesized a PRX bearing poly(*N*-isopropylacrylamide) and characterized its sliding-gel property [13]. Ito, *et al.* has published a sliding graft copolymer, in which many linear poly(ε-caprolactone) side chains are bound to cyclodextrin rings of PRX [14].

As described above, studies of various kinds of PRXs have so far been published. Especially, the unique sliding property inspired us with an idea of incorporation of the polyrotaxane as crosslink points instead of the hard segment domains of PUs. Polyurethanes crosslinked by CyDs have been published [15]. However, no report of the polyurethane properties based on the structure of polyrotaxanes as the crosslink points has been published in our best knowledge except our latest report [16]. Therefore, we describe herein the synthesis of three PUs (**PRX1500Me-PU**, **PRX4000Me-PU**, and **PRX6000Me-PU**) crosslinked by PRXs, which consist of

half-methylated α-cyclodextrins (CyDs) and poly(oxyethylene)glycols with different chain lengths (PEG1500, PEG4000, and PEG6000), and their characteristics using the results of the measurements of gel fraction, attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectroscopy, differential scanning calorimetry (DSC), dynamic viscoelastic test and tensile test.

2. EXPERIMENTAL

2.1 Materials

α,ω-Bis(aminopropyl)poly(oxyethylene)#1500 (PEG1500; $M_n = ca.$ 1500) was provided by NOF Co., Ltd. and used as received. Poly(oxyethylene)#4000 (PEG4000; $M_n = ca.$ 3100) and poly(oxyethylene)#6000 (PEG6000; $M_n = ca.$ 7500) were purchased from Nacalai Tesque Inc. and dried *in vacuo* prior to use. Polyrotaxanes consisting of the PEGs and α-cyclodextrin were synthesized according to the literature [5, 17]. Form the results of ^{1}H NMR measurements, the numbers of CyDs for PRX1500, PRX4000 and PRX6000 were estimated to be 12, 22 and 31, respectively; the filling ratios of CyDs for PEG1500, PEG4000, and PEG6000 were calculated to be 75, 63, and 37 %, respectively, when close packing for each PEG is defined to be 100 % (see Supporting information). 4,4'-Diphenylmethanediisocyanate (MDI) was provided by

Mitsui Chemical, Co., Ltd. and used as received. Poly(oxytetramethylene) (PTMG) ($M_n = ca.$ 2000) was purchased from Wako Pure Chemical Inc. and dried with nitrogen under reduced pressure prior to use. All other chemicals were of reagent grade. Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and toluene were dried over molecular sieve 4A and distilled under a nitrogen atmosphere prior to use. Solvents used in measurements were of spectral grade. Deuterated solvents were purchased from Euriso-Top SA.

2.2 Design and Synthesis

Three PUs crosslinked by PRXs, in which the filling ratios of CyD as a ring molecule and chain lengths of PEGs as an axle molecule are different, were designed to investigate the influence of the PRX structures on their PU properties. To enhance the solubility of the PRXs, the hydroxyl groups of the threaded CyDs were partially methylated by the treatment with NaH and then iodomethane.

The synthesis of PUs was carried out according to Scheme 1. The PUs were synthesized by a prepolymer method [18]. The prepolymer was prepared with MDI and PTMG2000 with a ratio of [NCO]$_{MDI}$/[OH]$_{PTMG}$ = 3.0 in dry DMF at 95 °C under an argon atmosphere. Subsequently, the prepolymer and partially methylated PRXs

were reacted with a ratio of [NCO]$_{total}$/[OH]$_{total}$ = 2.0 to obtain the PUs. Excess NCO groups were treated by methanol. The prepolymer was also reacted with partially methylated CyD, in which half of the hydroxy groups were methylated, to obtain **CDMe-PU**.

2.2.1 Methylation of PRX1500 (PRX1500Me)

To a solution of PRX1500 (0.29 g, 22 μmol) in dry DMSO (16 mL) was added sodium hydride (60 % dispersion in oil, 0.5 g, 12.5 mmol) at ambient temperature under a nitrogen atmosphere. After waiting for a few minutes until the generation of hydrogen gas finished, iodomethane (2.8 g, 20 mmol) was added to the mixture. After stirring at ambient temperature overnight, the reaction mixture was neutralized by addition of 1.2 M HCl aqueous solution. A solid precipitated was collected by filtration and washed with diethyl ether and then water, followed by drying at 100 °C *in vacuo.* **PRX1500Me** was obtained as a light red solid (90 mg, 28 %). ^{1}H NMR (300 MHz, DMSO-d$_6$, TMS, r.t.) ^{1}H NMR (300 MHz, DMSO-d$_6$, TMS, r.t.) δ 8.8 (m, 2H, ArH), 8.2 (m, 2H, ArH), 7.1 (m, 2H, ArH), 5.64-5.50 (m, 54H, 2OH, 3OH for CyD), 4.96-4.79 (m, 72H, 1CH for CyD), 4.41 (m, 54H, 6OH for CyD), 3.7-2.95 (m, 814H, 3CH, 5CH, 6CH$_2$, 2CH, 4CH for CyD, OCH$_3$, OCH$_3$, OCH$_3$, O*CH$_2$*CH$_2$*CH$_2$*NAr), 3.51

(124H, PEG), 1.76 (bs, 4H, OCH$_2$$CH_2CH_2$NAr) ppm.

From the result of the NMR measurement, 38 % of the secondary hydroxy groups and 75 % of the primary hydroxy group still remain as unreacted ones. Resultantly, 50 % of the hydroxy groups remain as the unreacted one (See Supporting Information).

2.2.2 Methylation of PRX4000 (PRX4000Me)

Sodium hydride (60 % dispersion in oil, 60 mg, 1.5 mmol) was added little by little to a solution of PRX4000 (0.2 g, 8.1 μmol) in dry DMSO (14 mL). The clear polyrotaxane solution became a suspension while being accompanied by hydrogen gas generation. After finishing the hydrogen gas generation, iodomethane (0.2 g, 1.5 mmol) was added at once into the suspension. After stirring at ambient temperature for 24 h, the reaction mixture was neutralized by addition of 1.2 M HCl aqueous solution. The solvent was evaporated *in vacuo*. Methanol (20 mL) was added to the residue and an insoluble solid was removed by filtration. The filtrate was added dropwise to diethyl ether (800 mL). The precipitate was collected by centrifugation and dried at 80 °C. This purification procedure was repeated twice. PRX4000Me was obtained as a slight yellow solid (80 mg, 36 %). ^{1}H NMR (400 MHz, DMSO-d$_6$, TMS, r.t.) δ 6.57 (s, 4H, ArH), 6.51 (s, 2H, ArH), 5.76-5.51 (m, 87H, 2OH, 3OH for CyD), 5.00-4.80 (m, 132H, 1CH for CyD), 4.67-4.47 (m, 111H, 6OH for CyD),

3.81-3.39 (m, 1191H, 3CH, 5CH, 6CH$_2$, 2CH for CyD, OCH$_3$, OCH$_3$), 3.51 (m, 280H, PEG), 3.30-2.95 (m, 195H, 2CH for CyD, OCH$_3$), 2.22 (12H, ArCH$_3$) ppm.

From the result of the NMR measurement, 33 % of the secondary hydroxy groups and 84 % of the primary hydroxy group still remain as unreacted ones.   Resultantly, 50 % of the hydroxy groups remain as the unreacted one (See Supporting Information).

2.2.3 Methylation of PRX6000 (PRX6000Me)

Methylation of PRX6000 was conducted by the same manner as that of PRX4000. PRX6000Me was obtained as a slight yellow solid (95 mg, 43 %). ^{1}H NMR (400 MHz, DMSO-d$_6$, TMS, r.t.) δ 6.56 (s, 4H, ArH), 6.48 (s, 2H, ArH), 5.83-5.48 (m, 134H, 2OH, 3OH for CyD), 5.00-4.80 (m, 186H, 1CH for CyD), 4.65-4.45 (m, 145H, 6OH for CyD), 3.80-3.39 (m, 1644H, 3CH, 5CH, 6CH$_2$, 2CH for CyD, OCH$_3$, OCH$_3$), 3.51 (m, 680H, PEG), 3.30-2.95 (m, 309H, 4CH for CyD, OCH$_3$), 2.22 (12H, ArCH$_3$) ppm.

From the result of the NMR measurement, 36 % of the secondary hydroxy groups and 78 % of the primary hydroxy group still remain as unreacted ones.   Resultantly, 50 % of the hydroxy groups remain as the unreacted one (See Supporting Information).

2.2.4 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

the prepolymer.   After cooling to ambient temperature, the prepolymer was dissolved

in dry DMF (10 mL) and then added dropwise into a solution of PRX (PRX1500Me: 68

mg, 4.6 µmol; PRX4000Me: 70 mg, 2.5 µmol; PRX6000Me: 75 mg, 1.8 µmol; CDMe:

61 mg, 56 µmol) in dry DMF (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.   Finally, the PU films were pressed at 100 °C under 1.0 MPa for 10

min with an IMOTO Compact Heating Press IMC-180C.   The PUs were abbreviated

as **PRX1500Me-PU**, **PRX4000Me-PU**, and **PRX6000Me-PU**, in which the numbers

are derived from the PEGs of the PRX units.

The PUs were subjected to the measurements of gel fraction, ATR-FT-IR spectral,

DSC, TGA, viscoelastic measurements and tensile test.

2.3 Measurements

Gel fractions (g) was 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

DMSO and toluene at 30 °C; g was defined as $g = Wg/Wo \times 100$. Degree of swelling (q) was determined from Wg and the weight (Ws) after the sample is swelled to an equilibrium state with toluene at 30 °C; q was defined as $q = Ws/Wg$.

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 -140 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 testing was performed with a TENSILON RTC-1150A at ambient temperature. The initial length and cross-head speed were set to be 10.0 mm and 3.0 mm min^{-1}, respectively. The Young's moduli of the PUs were calculated from the initial slopes on the stress-strain curves.

3. Results and Discussion

3.1 Gel fraction and Degree of Swelling

Gel fractions and degrees of swelling of the PUs were summarized in Table 1. All of the PUs showed similar gel fraction values, indicating that the concentration of urethane linkage between the prepolymer and PRX in the PUs is at the same level. In addition, all of the PUs left their gel components even in DMSO. In the PU synthesis, the isocyanate index was 2. If ideal reaction occurred, no crosslinks between the PRXs be formed. Consequently, the gel fraction results suggest that the crosslinks between the PRXs exist and the degrees of the crosslinks between PRXs in the PUs are almost the same. However, the number of the crosslink would be small because of low mechanical strengths of the gel components.

The degrees of swelling for **PRX4000Me-PU** and **PRX6000Me-PU** were higher than those of **PRX1500Me-PU** and **CDMe-PU**. It seems that the PUs possessing the polyrotaxane structure in which a sufficient sliding space for the CyDs exists provides the higher degree of swelling.

3.2 ATR-FT-IR spectral measurement

Figure 1 shows the ATR-FT-IR spectra of the PUs. The C=O stretching ($\nu_{(C=O)}$)

bands for the urethane bond were observed around 1730 and 1710 cm^{-1}, whose bands are assignable to a free $\nu_{(C=O)}$ and hydrogen bonded $\nu_{(C=O)}$, respectively. These are characteristic bands observed in the IR spectra of typical polyurethanes. For instance, a CyD-free PU consisting of MDI, PTMG2000 and butanediol gave the free $\nu_{(C=O)}$ and hydrogen bonded $\nu_{(C=O)}$ at 1730 and 1705 cm^{-1}, respectively [1h]. The $\nu_{(C=O)}$ band assignable to a urea bond was also observed around 1650 cm^{-1}, because the excess amount of the isocyanate and DMF as the solvent were used for the synthesis of the PUs. The N-H stretching ($\nu_{(N-H)}$) band was observed in the region of 3000 to 4000 cm^{-1} as a broad peak due to the overlapping of the $\nu_{(N-H)}$ bands for the urethane and urea bonds as well as unreacted OH groups of CyD.

Relative intensity ratios of the urethane carbonyl groups ($I_{\nu(C=O)H\text{-bond}}$/ $I_{\nu(C=O)free}$) increased in the following order: **CDMe-PU** < **PRX6000Me-PU** < **PRX4000Me-PU** < **PRX1500Me-PU** (see Supporting Information). This order corresponds to the filling ratios of CyD. It is reasonable because the urethane bonds are crowded around CyDs and tight packing of CyDs makes it easy to form the hydrogen bonding between the urethane bonds.

3.3 Thermal properties of PUs

The thermal properties of the PUs were investigated by DSC measurement (Figure 2). As can be seen, **PRX1500Me-PU**, **PRX6000Me-PU**, and **CDMe-PU** gave a baseline shift, an exothermic and endothermic peaks, assignable to glass transition of the soft segment chains, reorganized-crystallization of the soft segment chains, and melting of the crystallized soft segment chains. In the case of **PRX4000Me-PU**, a baseline shift for the grass transition and an endothermic peak for the melting were observed, but not a reorganized-crystallization peak.

The temperatures of glass transition (T_g), reorganized-crystallization (T_c), and melting (T_m) were summarized in Table 2. It is well-known that the formation of hydrogen bond influences the T_g value [1f]. The T_gs of the PUs were lower than that of the CyD-free PU, whose T_g was observed around -60 °C [18]. In addition, there was no correlation between the T_gs and the formation of hydrogen bond described in section 3.2. Consequently, the T_gs would be subjected by the numbers of the end groups of the PU chains rather than the formation of hydrogen bond near the PRX unit. Remarkably, **PRX1500Me-PU** showed sharp exo- and endothermic peaks attributable to the reorganized-crystallization and melting peaks for the soft segment chains, respectively. The melting of the crystallized soft segment chains in **PRX1500Me-PU** was observed at 20 ºC, which is the same as the melting point of a raw PTMG2000,

suggesting that the soft segment chains form a lamella structure similar to that of the raw PTMG2000.   In addition, the reorganized crystallization of the soft segment chains in **PRX1500Me-PU** was observed at −40 ºC which is lower than those of the other PUs and those of CyD-free-PUs [19].   PRX1500Me is more rigid and shorter than the other PRXs.   Therefore, we expect that PRX1500 and the soft segment chains would be clearly separated.   In other word, a pure phase for the soft segment would be formed and the formation of the pure segment would enhance the easy reorganized crystallization of the soft segment chains.

In contrast, the T_cs and T_ms of **PRX6000Me-PU** and **CDMe-PU** were close and the DSC curves were similar.   **PRX6000Me-PU** possesses the loosest filling of CyD and the longest axle chain of the PRX unit among the PUs.   The CyDs in **PRX6000Me-PU** could disperse at almost the same level as those in **CDMe-PU**.   Therefore, the thermal behavior of **PRX6000Me-PU** is not affected by the rotaxane structure.   As described above, the T_c of **PRX4000Me-PU** was unclear.   The reason is described below.

Figure 3 shows the temperature dependence of the storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) of the PUs.   All the PUs gave a peak around −70 °C in the tan δ curves, attributable to an α relaxation that corresponds to the glass transition of the soft segment.   The E's and tan δ curves of **PRX1500Me-PU**,

PRX6000Me-PU, and **CDMe-PU** showed a hump and small peak, respectively, in the temperature region (−50 to 20 °C), indicating that the reorganized-crystallization and melting of the soft segment chains occurred around the temperature region. In contrast, the E' of **PRX4000Me-PU** monotonically decreased in the temperature region. The unclear reorganized-crystallization behavior is in good agreement with the result of the DSC measurement. Note that the tan δ curve showed the second broad peak around 10 °C without the decrease of the tan δ value in the temperature region. This result suggests that the slowest reorganized-crystallization of the soft segment chains in the broad temperature region and the earliest melting of the crystallized soft segment chains among the PUs occur in the temperature region. The moderate filling of CyDs would provide the structure where loosely filled CyD part and tightly filled one are mixed in the PRX unit. This unique structure would influence the mobility of the soft segment in **PRX4000Me-PU**. Similar thermal behavior was also observed in the case of PUs crosslinked by non-methylated PRX4000 and modified by the prepolymer with different isocyanate indexes of 1 and 2 [16].

Rubbery plateau regions were observed in the E's of the PUs from around 20 °C. Interestingly, the terminal temperature of the rubbery plateau region of **PRX1500Me-PU** is much higher than those of **PRX4000Me-PU**, **PRX6000Me-PU**,

and **CDMe-PU**.　This would be because gathering of CyDs gives reasonable cohesion to **PRX1500Me-PU**.

3.4 Mechanical properties

Figure 4 shows the stress-strain curves for the PUs.　Magnitudes of Young's Modulus, tensile strength, and strain at break of the PUs were summarized in Table 3. As a reference, the data of CyD-free PU cited from reference 18 were also added in Table 3.　Young's moduli for the PUs increased in the following order: **PRX1500Me-PU** < **PRX4000Me-PU** < **PRX6000Me-PU** < **CDMe-PU**.　This order is in good agreement with the filling ratios of CyD of the PRX units.　That is, the Young's moduli are subject to the dispersion degree of CyDs as the crosslink points in the PUs. The Young's modulus of the CyD-free PU was *ca.* 10 MPa [18], which was an average of those of the PUs.

PRX1500Me-PU has the highest filling ratio of CyD, in which the mobility of CyDs is inhibited.　As the result, **PRX1500Me-PU** showed the lowest tensile strength among the PUs.　The mobility of the CyDs in **PRX6000Me-PU** is basically similar to that in **CDMe-PU**; the tensile strengths are similar.　The tensile strength of the CyD-free PU was *ca.* 17 MPa [18], which was the highest value among the PUs.　This

is due to the formation of a large amount of the hydrogen bond between the urethane bonds to build up the hard segment cosslink.

Interestingly, elongations of the PUs are larger than that of the CyD-free PU, whose elongation was *ca.* 500 % [18]. The best elongation was observed in **PRX4000Me-PU**: the elongation is tow times larger than that of the CyD-free PU. This performance would be due to the moderate filling rotaxane structure, which affects the mechanical properties under the tension load. It might be possible to interconvert between the loosely filled CyDs and tightly filled CyDs under the tension load.

4. Conclusion

We have demonstrated the synthesis and characterization of three PUs crosslinked by PRXs consisting of half-methylated CyDs and PEGs with different chain lengths. The results are follows. PRX1500Me with the higher filling ratio of CyD and shorter length of the axle enhances the reorganized-crystallization of the soft segment chains because of the formation of the pure domain for the soft segment chains. The CyDs of PRX6000Me with the lower filling ratio of CyD and longer length of the axle act as individually dispersed crosslink points because the thermal and physical properties of **PRX6000Me-PU** are similar to those of the PU crosslinked by the half-methylated CyD.

PRX4000 with the moderate filling ratio of CyD and middle length of the axle makes

slow reorganized-crystallization of the soft segment chains in the PU as well as

improves the tensile performance among the PUs. Further characterization of the

unique properties of **PRX4000Me-PU** and study on PUs crosslinked by PRXs having

the different filling ratios of CyD with same molecular weight PEG are currently in

progress in our laboratory.

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Table 1. Gel fraction and degree of swelling of PUs.

	Gel fraction (%)		Degree of swelling [a]
	toluene	DMSO	toluene
PRX1500Me-PU	99.6	63.4	1.23
PRX4000Me-PU	99.5	65.1	1.54
PRX6000Me-PU	99.3	61.6	1.41
CDMe-PU	99.5	65.0	1.25

a) The gel samples with sufficient strength were not obtained in DMSO.

Table 2. Thermal properties of PUs.

	T_g [°C]	T_c [°C]	T_m [°C]
PRX1500Me-PU	−77	−48	20
PRX4000Me-PU	−75	-	0
PRX6000Me-PU	−73	−36	8
CDMe-PU	−73	−38	3

Table 3. Mechanical properties of PUs.

	Young's modulus [MPa]	Tensile strength [MPa]	Strain at break [%]
PRX1500Me-PU	6.5	6.9	790
PRX4000Me-PU	7.5	14.0	1080
PRX6000Me-PU	13.3	12.6	900
CDMe-PU	14.0	11.7	890
CyD-free-PU[a]	*ca.* 10.0	*ca.* 17.0	*ca.* 500

a) The data were cited from reference 17.

Figure captions

Figure 1. ATR-FT-IR spectra of (a) **PRX1500Me-PU**, (b) **PRX4000Me-PU**, (c) **PRX6000Me-PU**, and (d) **CDMe-PU**.

Figure 2. DSC thermograms of (a) **PRX1500Me-PU**, (b) **PRX4000Me-PU**, (c) **PRX6000Me-PU**, and (d) **CDMe-PU**.

Figure 3. Temperature dependence of (a) storage modulus, (b) loss modulus, and (c) loss tangent for **PRX1500Me-PU** (solid line), **PRX4000Me-PU** (dotted line), **PRX6000Me-PU** (dashed line), and **CDMe-PU** (dashed-dotted line), respectively.

Figure 4. Stress-strain curves of **PRX1500Me-PU** (solid line), **PRX4000Me-PU** (dotted line), **PRX6000Me-PU** (dashed line), and **CDMe-PU** (dashed-dotted line) at 25 °C.

PRX1500: *ca.* x, 6; y, 7.

PRX4000: *ca.* x, 11; y, 25.
PRX4000: *ca.* x, 16; y, 106.

CD

1) NaH
2) MeI   DMSO

1) NaH
2) MeI   DMSO

1) NaH
2) MeI   DMSO

PRX1500Me

PRX4000Me
PRX6000Me

CDMe

Prepolymer   [NCO] / [OH] = 2.0
DMF, 80 °C

Prepolymer   [NCO] / [OH] = 2.0
DMF, 80 °C

Prepolymer   [NCO] / [OH] = 2.0
DMF, 80 °C

PRX1500Me-PU

PRX4000Me-PU
PRX6000Me-PU

CDMe-PU
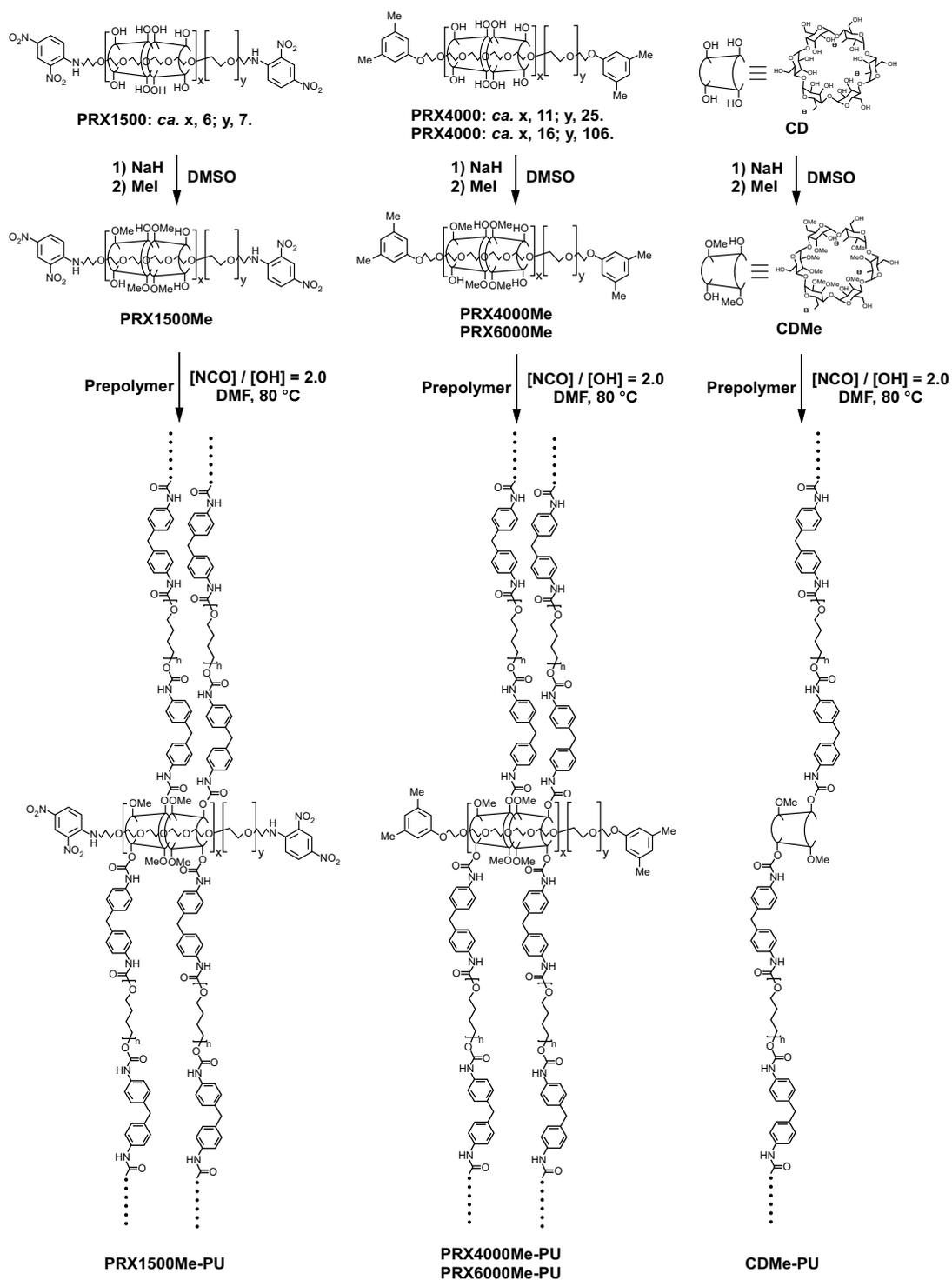
Scheme 1.
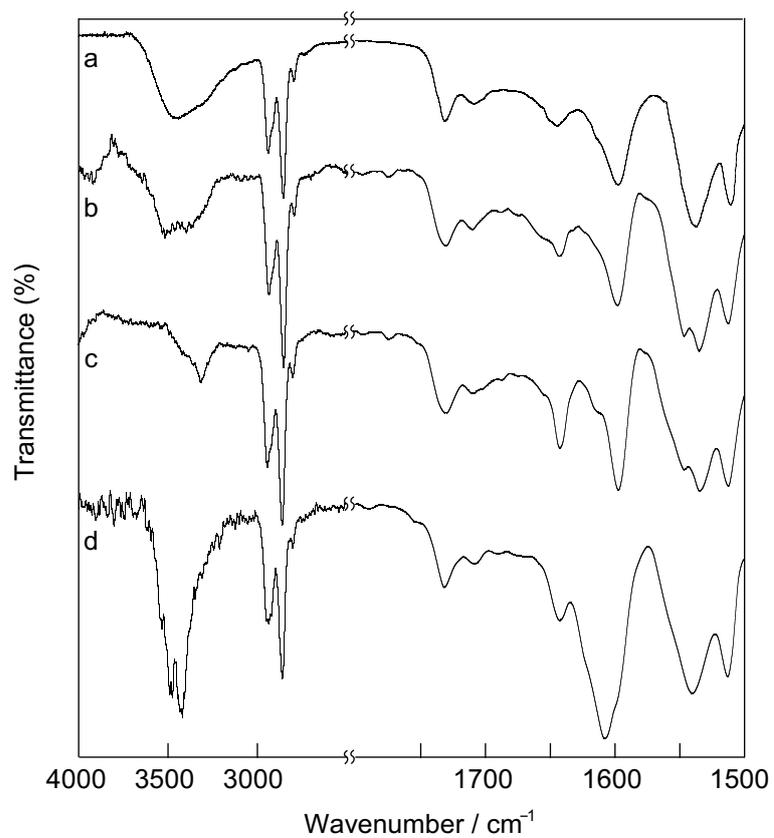
H. Murakami, et al.

Figure 1.

H. Murakami, et al.
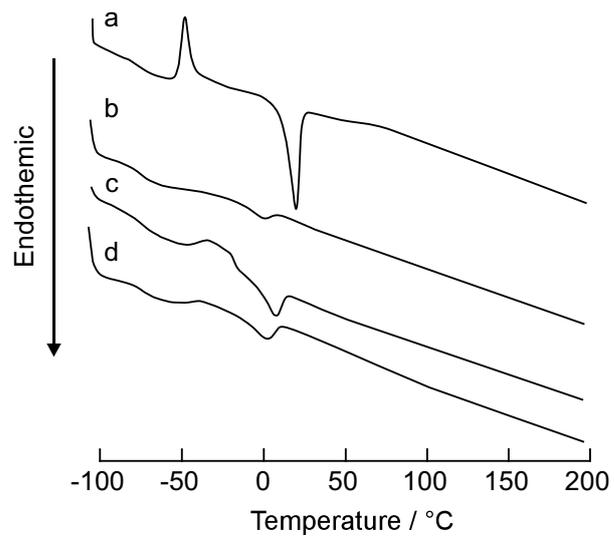
Figure 2.

H. Murakami, et al.

Figure 3.

H. Murakami, et al.

Figure 4.

H. Murakami, et al.