Synergetic Improvement in the Mechanical Properties of Polyurethanes with Movable Crosslinking and Hydrogen Bonds

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1. Experimental details

Materials

Teracetylated 6-arylamido methylether-γ-cyclodextrin (TAcγCDAAmMe) were prepared according to our previous works\textsuperscript{1,2}. α-Thioglycerol, hexamethylene diisocyanate (HDI), dibutyltin diacetate (DBTDA), 2,5-dihydroxy-benzoic acid and silica gel were purchased from Tokyo Chemical Industries Co. Ltd. Poly(tetrahydrofuran) (PTHF $M_n=1,000$), propan-1,3-diol (POD), triethanolamine (TEA), methanol, dichloromethane (DCM) and chloroform-$d$ were purchased from Wako Pure Chemical Industries. 1-Hydroxy-cyclohexyl-phenyl-ketone (Ciba IRGACURE184) was purchased from BASF Japan Ltd. Water was purified with a Milli-Q system. Other reagents and solvents were used without further purification.
Instruments and Measurements

**Nuclear magnetic resonance (NMR) spectroscopy**: $^1$H and $^{13}$C NMR spectra were recorded at 500 MHz with an ECA-500 NMR spectrometer (JEOL) at 25 °C. The 2D $^1$H-$^1$H nuclear Overhauser effect spectroscopy (NOESY) NMR were performed at 600 MHz with an Agilent VNS600 (mixing time 1000 ms). In all the NMR measurements, chemical shifts were referenced to an internal standard ($\delta = 0$ ppm for tetramethylsilane).

**Mass spectroscopy**: MALDI-TOF-MS measurements were performed using an autoflex maX LRF Bruker speed mass spectrometer using 2,5-dihydroxy-benzoic acid as a matrix.

**Tensile test**: Tensile tests of the polymers were performed using Autograph AG-X plus (Shimadzu) at deformation rate of 10 mm/min. The dimension of dumbbell shaped specimen for tensile test is shown in Fig. SI. Young’s modulus was calculated from initial slope of stress-strain curve at a range between 1 - 6% strain.

**Cyclic tensile test**: Cyclic tensile tests were performed using Autograph AG-X plus (Shimadzu). The test pieces were continuously stretched and recovered without interval, where the maximum strains were set to 50% for 5 times at deformation rate of 10 mm/min.

**Stress relaxation test**: Stress relaxation tests were performed using Autograph AG-X plus (Shimadzu). Test pieces were stretched until 100%. Then, the strains were held, and the stresses were recorded for 3600 seconds.

**ATR-FTIR**: The attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) were recorded using JASCO FT/IR-6100 spectrometer in the wavenumber range from 4000 to 800 cm$^{-1}$ in ATR method.
In-situ FTIR: Infrared measurements of samples during stretching were performed at BL43IR in SPring-8, Nishiharima, Japan, with a Vertex70 FTIR spectrometer and a Hyperion 2000 infrared microscope from Bruker. Test films (10 mm×5 mm×0.01 mm) were stretched at 10 mm/min using TST 350 tensile stage (Linkam; 200 N load cell). The spectra were recorded for the samples at 0% and 300% strains.

Gel permeation chromatography (GPC): GPC measurements were performed in DMSO (0.40 mL·min⁻¹, 25 °C), using a TOSOH HLC-8320GPC EcoSEC® (TOSOH) equipped with a TOSOH TSK gel α-M column. Number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$) and polymer dispersity index (PDI) ($M_w/M_n$) of the samples were calculated based on calibration curves prepared using poly(ethylene glycol) (PEG) standards.

Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) measurements: Internal structures of polymers were determined by SAXS and WAXS at BL40B2 in SPring-8, Nishiharima, Japan. The wavelength of the incident X-ray beams was 0.10 nm. The sample-to-detector length (camera length) for SAXS/WAXS was 2 m. The lengths of the scattering vector $q$ in the SAXS measurements were 0.05–2.5, in the WAXS measurements were 5–30, where $q = 4\pi \sin \theta/\lambda$ (20 and $\lambda$ are the scattering angle and the wavelength, respectively). Test pieces (20 mm×5 mm×1 mm) were stretched at 10 mm/min using a TST 350 tensile stage (Linkam; 200 N load cell). SAXS profiles in the tensile directions and vertical directions were obtained from the 2D patterns in azimuthal angles $\phi_s = 255^\circ$–285° and $\phi_s = 165^\circ$–195°, respectively (Fig. SII). WAXS profiles in the tensile directions and vertical directions also were obtained from the 2D patterns, in azimuthal angles $\phi =$
255°~285° and \( \varphi = 165°~195° \), respectively (Fig. SIII). For easy observation, the detector was tilted 45° clockwise for the WAXS measurement.

**Thermal gravimetric analysis (TGA):** Thermal degradation of the polymers were measured by TGA system (PerkinElmer STA6000). Temperature increased 10 °C/min. from 80 °C to 500 °C with N\(_2\) gas flow (20 mL/min).

**Differential scanning calorimeter (DSC):** measurements for glass transition temperatures \((T_g)\) and Melting points \((T_m)\) of the samples were determined by differential scanning calorimeter (Hitachi High-Technologies Corporation, NEXTA DSC200) with N\(_2\) gas flow (30 mL/min). Thermal transitions were measured in the temperature range of -100 °C to 150 °C heated 10 °C/min. All samples were first cooled to -100 °C and then heated to 150 °C, the curves in this stage were named the \(1^{st}\) scan. After cooled to -100 °C again, all samples were heated to 150 °C again and the curves in this stage were named the \(2^{nd}\) scan.
2. Preparation of teracetylated γCD diol (TAcγCD-diOH)

Preparation of TAcγCD-diOH:

TAcγCDAAmMe (2.3 g, 1 mmol), α thioglycerol (1.1 g, 10 mmol) and IRGACURE 184 (20 mg, 0.1 mmol) were dissolved in methanol (5 mL). The mixture was irradiated by UV light with a Hg lamp (HL100G, HB 100A-1 Seritech Co., Ltd. λ = 365 nm) with stirring for 1 hour. Then the solution was dropped into cold water (1 L) and suction filtered to separate the white precipitate. The obtained solid was dried at 40 °C with blue Silica gel in vacuo for at least 72 hours. The yield is 50% (1.2 g).

$^1$H NMR (500 MHz, chloroform-d):

δ = 7.12 (t, 1H, -CONH-), 5.33 (m, 8H, C(3)H of CD), 5.15 (m, 8H, C(1)H of CD), 4.91 (dd, 1H, -NHCH$_2$O-), 4.73 (m, 9H, C(2)H of CD and -NHCH$_2$O-), 4.45 (m, 14H, C(6')H of CD), 4.00 (m, 18H, C(4, 5, 6)H of CD), 3.86 (t, 2H, -CH$_2$OH), 3.59(m,1H, HOCH-), 2.89(dd, 2H, -SCH$_2$-), 2.66 (dd, 2H, -CH$_2$S-),2.53 (dd, 2H, -CH$_2$CONH-) 2.11 (m, 72H, CH$_3$ of acetyl).

$^{13}$C NMR (125 MHz, chloroform-d):

δ = 170.7 ~ 169.4 (CH$_3$-CO- in acetyl), 96.3 (C(1)H of CD), 75.2 ~ 76.6 (C(4)H of CD), 71.3 ~ 69.7 (C(2, 3, 5)H of CD and OHCH-), 66.7 (CH$_2$-OH), 65.4 (-NHCH$_2$O-), 62.9 ~ 62.4 (C(6)H of CD), 36.6 (CH$_2$S-), 35.9 (CH$_2$-CO-), 27.8 (S-CH$_2$-), 20.9 (CH$_3$-CO- in acetyl).
MALDI TOF MS:
Calcd for [C\textsubscript{101}H\textsubscript{139}NO\textsubscript{66}SNa]\textsuperscript{+}: \textit{m/z} = 2478.209. Found: \textit{m/z} = 2478.998.
Calcd for [C\textsubscript{101}H\textsubscript{139}NO\textsubscript{66}SK]\textsuperscript{+}: \textit{m/z} = 2494.318. Found: \textit{m/z} = 2494.996.
**Fig. S1.** 500 MHz $^1$H-NMR spectrum of TAcγCD-diOH in chloroform-$d$.

**Fig. S2.** 125 MHz $^{13}$C-NMR spectrum of TAcγCD-diOH in chloroform-$d$. 

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Fig. S3. MALDI TOF mass spectrum of TAcγCD-diOH.
3. Preparation of movable cross-linked polyurethane: γCDMe(x)PU

![Scheme S2. Preparation of γCDMe(x)PU.](image)

**Preparation of the γCDMe(x)PU:**

1. Before use, PTHF and POD were respectively heated at 90 °C under vacuum for 2 hours to remove moisture.
2. Dried TAcγCD-diOH powder was added to the solution of PTHF in DCM (5 mL), and the mixture was stirred at room temperature under an N₂ atmosphere.
3. After the dissolution, the DCM was removed by N₂ gas flow.
4. After the solvent was completely removed, DCM (10 mL) was added to dissolve the inclusion complex again.
5. A mixture of HDI and DBTDA was added to the solution and stirred to obtain homogeneous solution.
6. The solution was kept stirred at room temperature under an N₂ atmosphere for 2 hours (pre-polymerization).
7. The solution of POD in DCM (1 mL) was added and the mixture was stirred at room temperature for 24 hours (polymerization).
8. After the polymerization, the mixture was poured into Teflon mold (size: 50mm × 50 mm × 20 mm) and dried at 25 °C at least 16 hours.

Table S1. Feed ratios for \(\gamma\text{CDMe}(x)\text{PU}\).

<table>
<thead>
<tr>
<th>Samples</th>
<th>PTHF</th>
<th>TAcγCD-\text{diOH}</th>
<th>POD</th>
<th>HDI</th>
<th>DBTDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg</td>
<td>mg</td>
<td>mg</td>
<td>mg</td>
<td>mg</td>
</tr>
<tr>
<td>(\gamma\text{CDMe}(9)\text{PU})</td>
<td>1000</td>
<td>1</td>
<td>470</td>
<td>0.2</td>
<td>76</td>
</tr>
<tr>
<td>(\gamma\text{CDMe}(13)\text{PU})</td>
<td>1000</td>
<td>1</td>
<td>705</td>
<td>0.3</td>
<td>76</td>
</tr>
</tbody>
</table>
4. Preparation of the linear polyurethane: LPU

![Scheme S3. Preparation of the LPU.](image)

**Preparation of the LPU:**

1. Before use, PTHF and POD were respectively heated at 90 °C under vacuum for 2 hours to remove moisture.
2. A mixture of HDI and DBTDA was added to the solution of PTHF and stirred to obtain homogeneous solution.
3. The solution was kept stirred at room temperature under an N₂ atmosphere for 2 hours (pre-polymerization).
4. The solution of POD in DCM (1 mL) was added and the mixture was stirred at room temperature for 24 hours (polymerization).
5. After the polymerization, the mixture was poured into Teflon mold (size: 50mm × 50 mm × 20 mm) and dried at 25 °C at least 16 hours.

**Table S2. Feed ratio for LPU.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>PTHF</th>
<th>POD</th>
<th>HDI</th>
<th>DBTDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg</td>
<td>mg</td>
<td>mg</td>
<td>mg</td>
</tr>
<tr>
<td></td>
<td>mmol</td>
<td>mmol</td>
<td>mmol</td>
<td></td>
</tr>
<tr>
<td>LPU</td>
<td>1000</td>
<td>76</td>
<td>353</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>
$^1$H NMR (500 MHz, chloroform-$d$):

$\delta = 5.10 \sim 4.60$ (CO$_2$-NH$-$), 4.11 (-CH$_2$-CO$_2$-), 4.05 (-CH$_2$-O-), 3.40(-O-CH$_2$-), 3.14 \sim 3.13$ (-NH-CH$_2$-), 1.90 (-CH$_2$-CH$_2$-O-), 1.60 (CH$_2$-CH$_2$-CH$_2$-), 1.47 (-NH-CH$_2$-CH$_2$-), 1.32 (-NH-CH$_2$-CH$_2$-CH$_2$-).

**Table S3.** Molecular weight and distribution of LPU by GPC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n^a$</th>
<th>$M_w^a$</th>
<th>PDI$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPU</td>
<td>$8 \times 10^3$</td>
<td>$14 \times 10^3$</td>
<td>1.7</td>
</tr>
</tbody>
</table>

$^a$Determined by GPC using PEG standards for calibration in DMSO as an eluent.

**Fig. S4.** 500 MHz $^1$H-NMR spectrum of LPU in chloroform-$d$. 
5. Preparation of chemical crosslinked polyurethane: C(x)PU

Preparation of C(x)PU:
1. Before use, PTHF, POD and TEA were respectively heated at 90 °C under vacuum for 2 hours to remove moisture.
2. A mixture of HDI and DBTDA was added to the solution of PTHF and stirred to obtain homogeneous solution.
3. The solution was kept stirred at room temperature under an N₂ atmosphere for 2 hours (pre-polymerization).
4. The mixed solution of POD and TEA in DCM (2 mL) was added and the mixture was stirred at room temperature for 24 hours (polymerization).
5. After the polymerization, the mixture was poured into Teflon mold (size: 50mm × 50 mm × 20 mm) and dried at 25 °C at least 16 hours.

Table S4. Feed ratios for C(x)PU.

<table>
<thead>
<tr>
<th>Samples</th>
<th>PTHF</th>
<th>TEA</th>
<th>POD</th>
<th>HDI</th>
<th>DBTDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg</td>
<td>mmol</td>
<td>mg</td>
<td>mmol</td>
<td>mg</td>
</tr>
<tr>
<td>C(9)PU</td>
<td>1000</td>
<td>1</td>
<td>30</td>
<td>0.2</td>
<td>76</td>
</tr>
<tr>
<td>C(13)PU</td>
<td>1000</td>
<td>1</td>
<td>45</td>
<td>0.3</td>
<td>76</td>
</tr>
</tbody>
</table>
6. ATR-FTIR spectra of polyurethane (PU) materials

Fig. S5. ATR-FTIR spectra of γCDMe(α)PU, C(α)PU, and LPU. ATR-FTIR spectrum of HDI was shown in Figure. as a reference.
7. 2D NOESY NMR spectrum of LPU and TAcγCD diOH mixture solution

Fig. S6. 600 MHz 2D NOESY NMR spectrum of the mixture of LPU and TAcγCD diOH in chloroform-\(d\). There was no NOE correlation signal between the TAcγCD units and PU main chains.
8. Swelling tests of PU materials

![Swelling ratio graph](image)

**Fig. S7.** Swelling ratios of γCDMe(x)PU and C(x)PU for chloroform. x were 0, 9, and 13.

The swelling ratios were determined by the following equation:

\[
\text{Swelling ratio} = \frac{W - W_0}{W_0} \times 100\%
\]

where \( W \) is the weight of the swollen PU, and \( W_0 \) is the initial weight of PU before the immersion. The \( W_0 \) of all samples were 20 ± 5 mg and immersed in 10 mL DCM for 24 h at 25 °C.
9. DSC curves of PU materials

Fig. S8. DSC curves of 2\textsuperscript{nd} scan for γCDMe(x)PU, C(x)PU and LPU. The temperature range was from -100 °C to 150 °C, the heating rate was 10 °C/min.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_m$ / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>γCDMe(9)PU</td>
<td>96.8</td>
</tr>
<tr>
<td>γCDMe(13)PU</td>
<td>93.7</td>
</tr>
<tr>
<td>C(9)PU</td>
<td>87.4</td>
</tr>
<tr>
<td>C(13)PU</td>
<td>82.9</td>
</tr>
<tr>
<td>LPU</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table S5. $T_m$ of 2\textsuperscript{nd} scan for all PU materials.
Fig. S9. DSC curves of 1\textsuperscript{st} scan for γCDMe(x)PU, C(x)PU and LPU before (light line) and after (dark Line) cyclic stretching to 50\% strain 5 times. The temperature range was from -100 °C to 150 °C, the heating rate was 10 °C/min.
**Table S6.** $T_m$ of 1st scan for all PU materials.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_m / ^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$CDMe(9)PU</td>
<td>48.7 85.0 111.5</td>
</tr>
<tr>
<td>$\gamma$CDMe(13)PU</td>
<td>61.0 91.7 122.3</td>
</tr>
<tr>
<td>C(9)PU</td>
<td>45.4 89.4</td>
</tr>
<tr>
<td>C(13)PU</td>
<td>95.5 120.9</td>
</tr>
<tr>
<td>LPU</td>
<td>-5.5 50.9 89.6 124.1</td>
</tr>
</tbody>
</table>

**Table S7.** $T_m$ of 1st scan for all PU materials after cyclic stretching to 50% strain 5 times.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_m / ^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$CDMe(9)PU</td>
<td>47.7 84.5 110.2</td>
</tr>
<tr>
<td>$\gamma$CDMe(13)PU</td>
<td>58.1 91.1 121.1</td>
</tr>
<tr>
<td>C(9)PU</td>
<td>46.4 89.5</td>
</tr>
<tr>
<td>C(13)PU</td>
<td>100.7 121.0</td>
</tr>
<tr>
<td>LPU</td>
<td>-9.4 51.7 91.3 124.4</td>
</tr>
</tbody>
</table>
10. TGA curves of PU materials

Fig. S10. TGA curves of PU materials. The temperature range was from 80 °C to 500 °C, the heating rate was 10 °C/min.
11. Stress-Strain Curves of $\gamma$CDMe(13)PU and C(13)PU

![Stress-strain curve](image)

**Fig. S11.** Stress-strain curves of $\gamma$CDMe(13)PU and C(13)PU
12. Cyclic Stress-Strain Curves of C(13)PU and γCDMe(13)PU

(a) [Graph showing cyclic stress-strain curve for C(13)PU]

(b) [Graph showing cyclic stress-strain curve for γCDMe(13)PU]

**Fig. S12.** The cyclic stress-strain curves with fixed strain (50%) of (a) C(13)PU and (b) γCDMe(13)PU. The cycles were performed 5 times.
13. SAXS measurements of LPU

Fig. S13. 2D SAXS patterns of (a-c) LPU with 0%, 100% and 200% strains. The direction of tensile is shown by the arrow. SAXS profiles of LPU with 0%, 100% and 200% strains in (d) tensile and (e) vertical directions.
14. WAXS measurements of $\gamma$CDMe(9)PU, C(9)PU and LPU

Fig. S14. 2D WAXS patterns of (a-c) C(9)PU, (d-f) $\gamma$CDMe(9)PU and (h-j) LPU with 0%, 100% and 200% strains. The direction of tensile is shown by the arrow.
Fig. S15. WAXS profiles of (a-b) C(9)PU, (c-d) γCDMe(9)PU and (e-f) LPU with 0%, 100% and 200% strains in tensile and vertical directions.