

## - **Electronic Supplementary Information** -

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

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## 1. Experimental details

### Materials

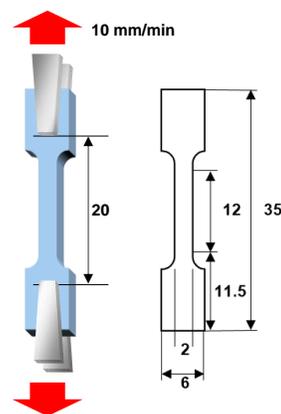
Teracetylated 6-arylamido methylether- $\gamma$ -cyclodextrin (TAc $\gamma$ CDAAmMe) were prepared according to our previous works<sup>1,2</sup>.  $\alpha$ -Thioglycerol, hexamethylene diisocyanate (HDI), dibutyltin diacetate (DBTDA), 2,5-dihydroxy-benzoic acid and silica gel were purchased from Tokyo 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:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 500 MHz with an ECA-500 NMR spectrometer (JEOL) at 25 °C. The 2D  $^1\text{H}$ - $^1\text{H}$  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. S1. Young's modulus was calculated from initial slope of stress-strain curve at a range between 1 - 6% strain.



**Fig. S1.** The dimension of specimen for tensile.

**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.

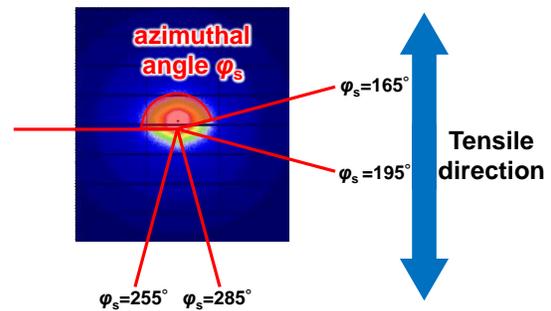
**ATR-FTIR:** The attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) were recorded using JASCO FT/IR-6100 spectrometer in the wavenumber range from 4000 to  $800\text{ cm}^{-1}$  in ATR method.

**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.

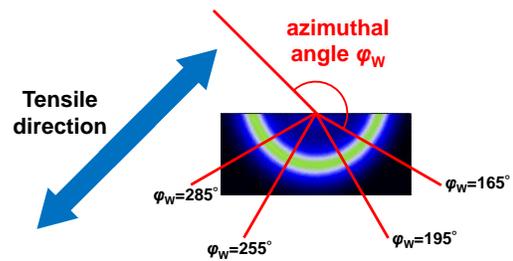
**Gel permeation chromatography (GPC):** GPC measurements were performed in DMSO (0.40 mL·min<sup>-1</sup>, 25 °C), using a TOSOH HLC-8320GPC EcoSEC® (TOSOH) equipped with a TOSOH TSK gel α-M column. Number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ) and polymer dispersity 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  $q = 4\pi \sin \theta/\lambda$  ( $2\theta$  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  $\varphi_s = 255^\circ$ - $285^\circ$  and  $\varphi_s = 165^\circ$ ~ $195^\circ$ , respectively (Fig. SII). WAXS profiles in the tensile directions and vertical directions also were obtained from the 2D patterns, in azimuthal angles  $\varphi =$



**Fig. SII.** Azimuthal angle  $\varphi_s$ .



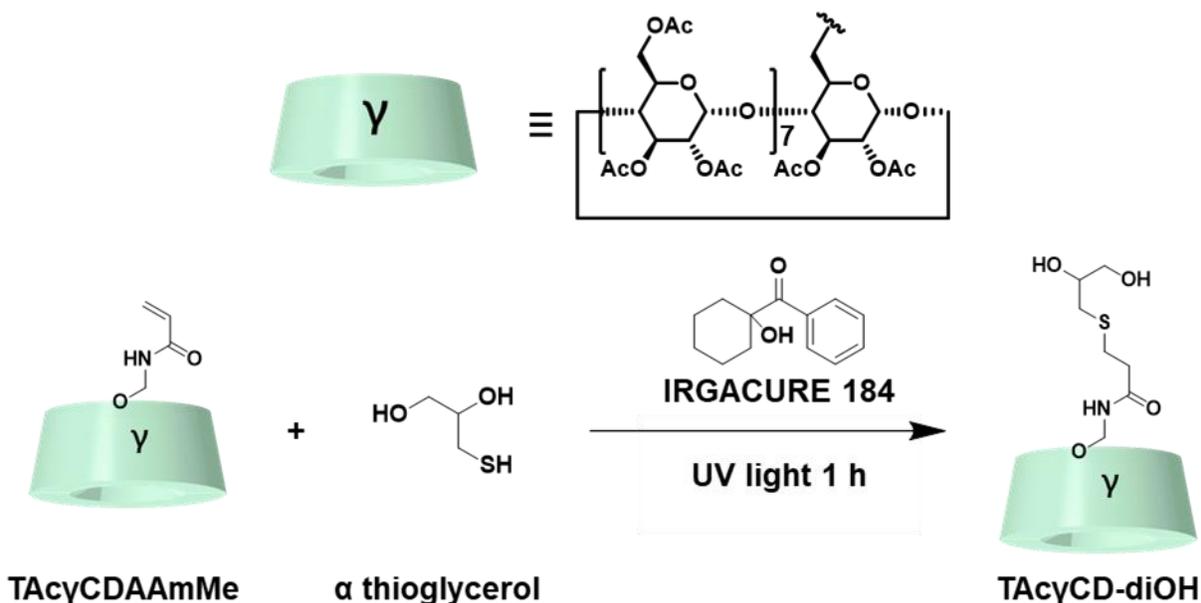
**Fig. SIII.** Azimuthal angle  $\varphi_w$ .

255°~285° and  $\varphi = 165^\circ\sim 195^\circ$ , 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<sub>2</sub> 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<sub>2</sub> 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<sup>st</sup> 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<sup>nd</sup> scan.

## 2. Preparation of teracetylated $\gamma$ CD diol (TAc $\gamma$ CD-diOH)



**Scheme S1.** Preparation of TAc $\gamma$ CD-diOH.

### Preparation of TAc $\gamma$ CD-diOH:

TAc $\gamma$ CDAAmMe (2.3 g, 1 mmol),  $\alpha$  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.  $\lambda = 365$  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).

### $^1\text{H}$ NMR (500 MHz, chloroform-*d*):

$\delta = 7.12$  (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<sub>2</sub>O-), 4.73 (m, 9H, C(2)*H* of CD and -NHCH<sub>2</sub>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<sub>2</sub>OH), 3.59 (m, 1H, HOCH-), 2.89 (dd, 2H, -SCH<sub>2</sub>-), 2.66 (dd, 2H, -CH<sub>2</sub>S-), 2.53 (dd, 2H, -CH<sub>2</sub>CONH-), 2.11 (m, 72H, CH<sub>3</sub> of acetyl).

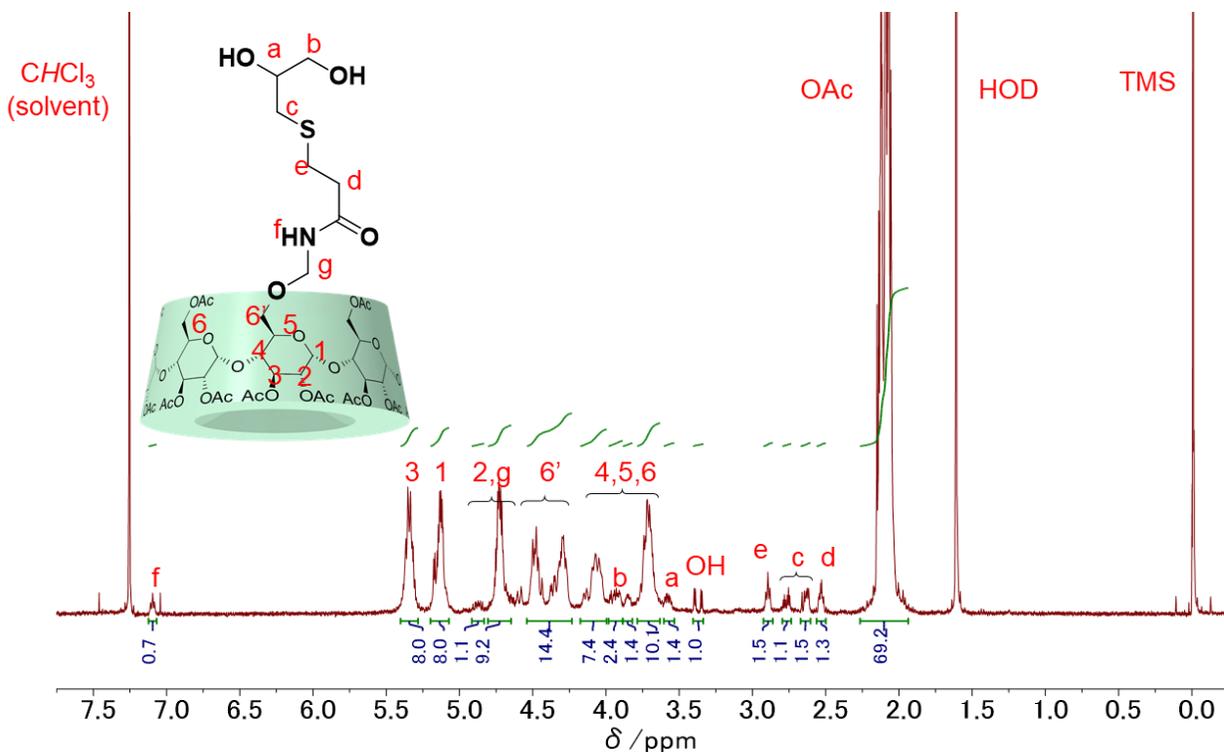
### $^{13}\text{C}$ NMR (125 MHz, chloroform-*d*):

$\delta = 170.7 \sim 169.4$  (CH<sub>3</sub>-CO- in acetyl), 96.3 (C(1)*H* of CD), 75.2  $\sim$  76.6 (C(4)*H* of CD), 71.3  $\sim$  69.7 (C(2, 3, 5)*H* of CD and OHCH-), 66.7 (CH<sub>2</sub>-OH), 65.4 (-NHCH<sub>2</sub>O-), 62.9  $\sim$  62.4 (C(6)*H* of CD), 36.6 (CH<sub>2</sub>S-), 35.9 (CH<sub>2</sub>-CO-), 27.8 (S-CH<sub>2</sub>-), 20.9 (CH<sub>3</sub>-CO- in acetyl).

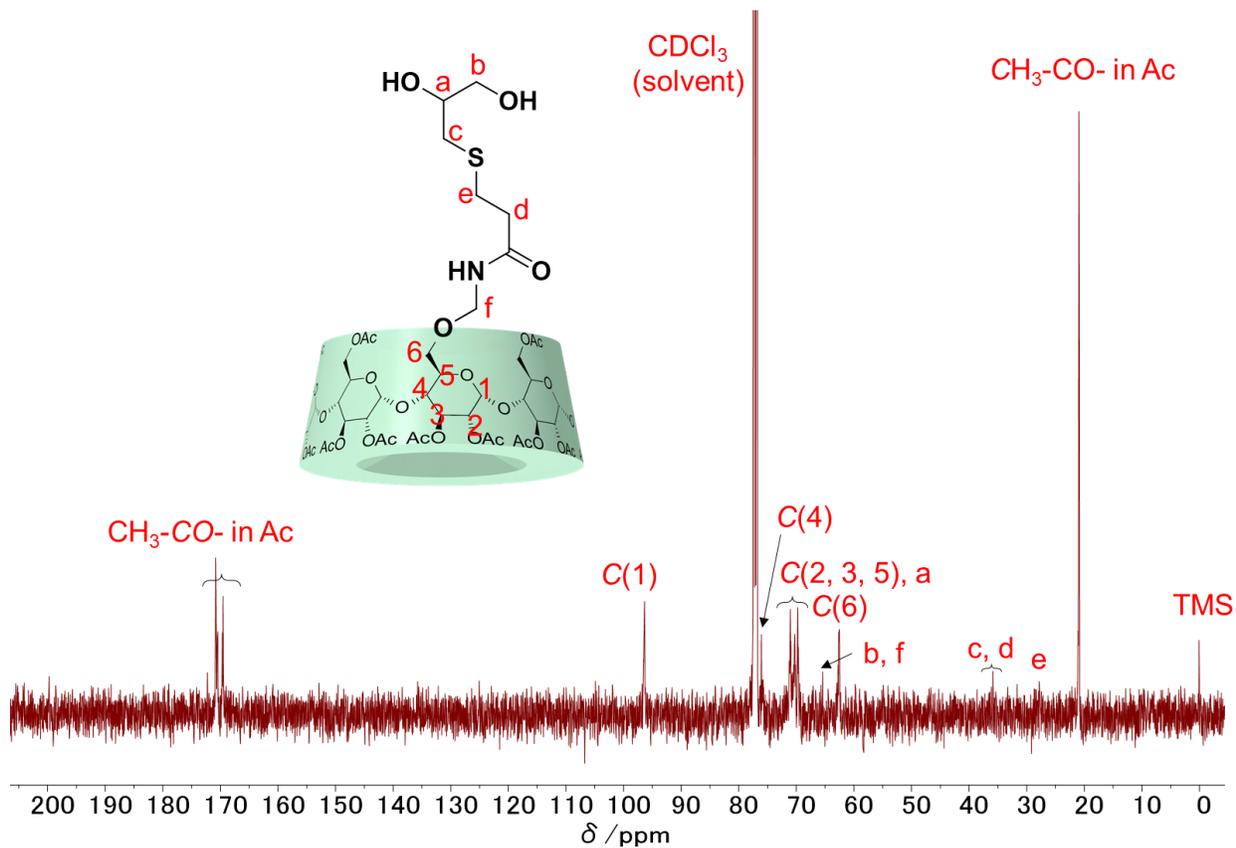
**MALDI TOF MS:**

Calcd for  $[\text{C}_{101}\text{H}_{139}\text{NO}_{66}\text{SNa}]^+$ :  $m/z = 2478.209$ . Found:  $m/z=2478.998$ .

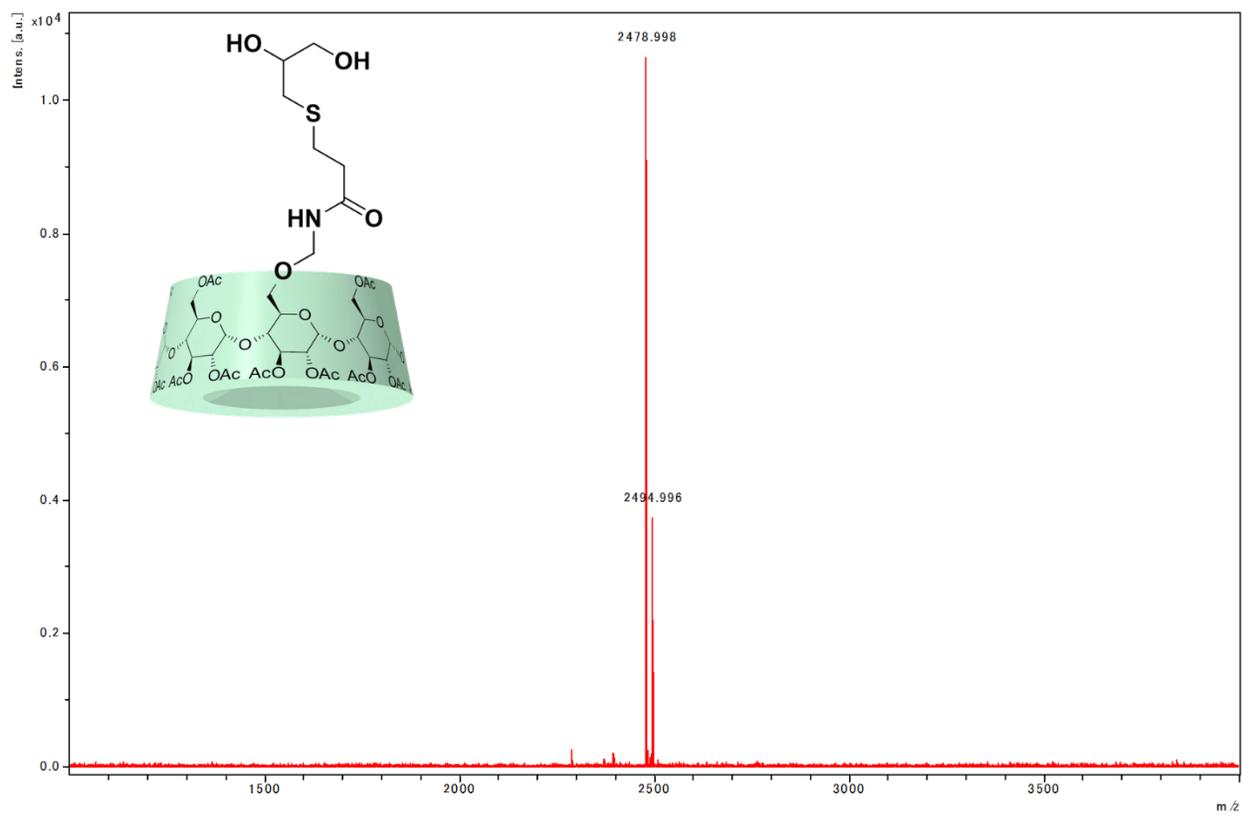
Calcd for  $[\text{C}_{101}\text{H}_{139}\text{NO}_{66}\text{SK}]^+$ :  $m/z = 2494.318$ . Found:  $m/z=2494.996$ .



**Fig. S1.** 500 MHz  $^1\text{H}$ -NMR spectrum of TAc $\gamma$ CD-diOH in chloroform-*d*.

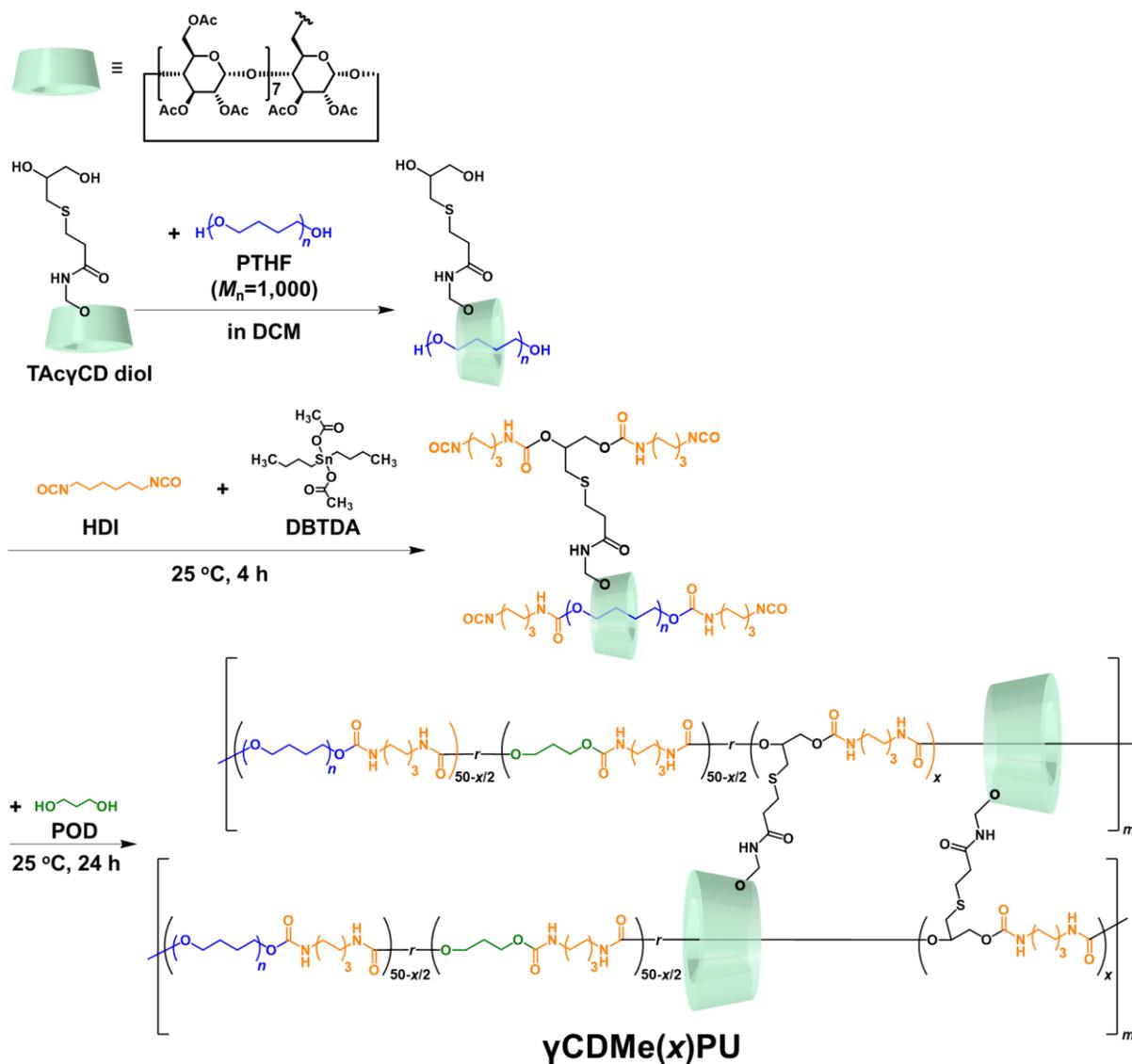


**Fig. S2.** 125 MHz  $^{13}\text{C}$ -NMR spectrum of TAc $\gamma$ CD-diOH in chloroform-*d*.



**Fig. S3.** MALDI TOF mass spectrum of TAc $\gamma$ CD-diOH.

### 3. Preparation of movable cross-linked polyurethane: $\gamma$ CDMe( $x$ )PU



Scheme S2. Preparation of  $\gamma$ CDMe( $x$ )PU.

#### Preparation of the $\gamma$ CDMe( $x$ )PU:

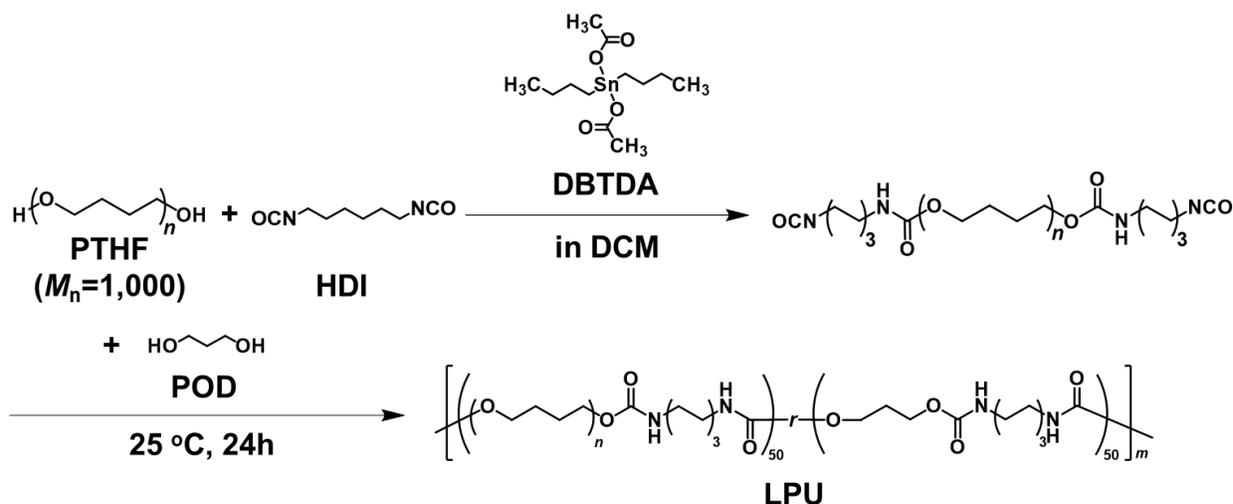
1. Before use, PTHF and POD were respectively heated at 90 °C under vacuum for 2 hours to remove moisture.
2. Dried TAc $\gamma$ CD-diOH powder was added to the solution of PTHF in DCM (5 mL), and the mixture was stirred at room temperature under an N<sub>2</sub> atmosphere.
3. After the dissolution, the DCM was removed by N<sub>2</sub> 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 N<sub>2</sub> 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  $\gamma$ CDMe(*x*)PU.

Samples	PTHF		TAc $\gamma$ CD-diOH		POD		HDI		DBTDA
	mg	mmol	mg	mmol	mg	mmol	mg	mmol	mg
$\gamma$ CDMe(9)PU	1000	1	470	0.2	76	1	388	2.3	2.5
$\gamma$ CDMe(13)PU	1000	1	705	0.3	76	1	406	2.4	2.5

#### 4. Preparation of the linear polyurethane: LPU



Scheme S3. Preparation of the LPU.

#### Preparation of the LPU:

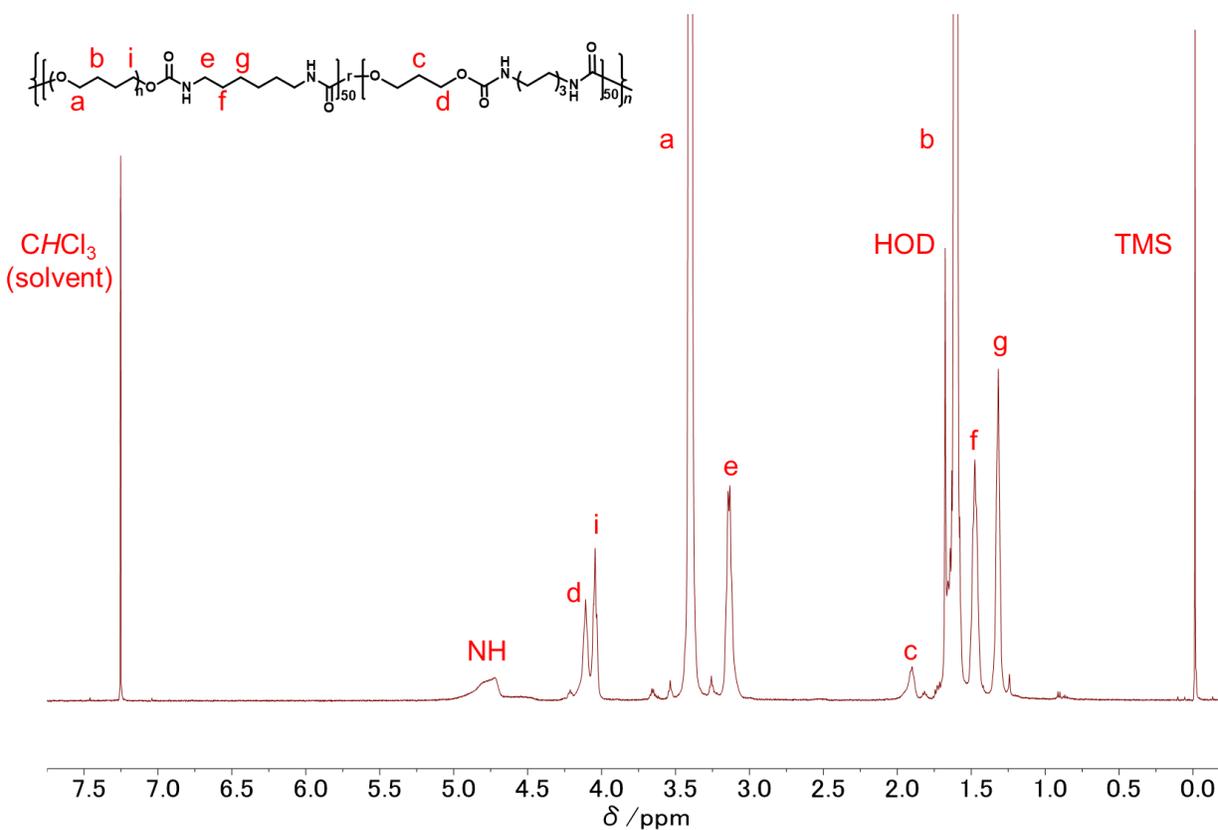
1. Before use, PTHF and POD were respectively heated at 90 °C under vacuum for 2 hours to remove moisture.
2. A mixture of HDI and DBTDA was added to the solution of PTHF and stirred to obtain homogeneous solution.
3. The solution was kept stirred at room temperature under an N<sub>2</sub> atmosphere 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.

Sample	PTHF		POD		HDI		DBTDA
	mg	mmol	mg	mmol	mg	mmol	mg
LPU	1000	1	76	1	353	2.1	2.5

**<sup>1</sup>H NMR (500 MHz, chloroform-*d*):**

$\delta = 5.10 \sim 4.60$  (CO<sub>2</sub>-NH-), 4.11 (-CH<sub>2</sub>-CO<sub>2</sub>-), 4.05 (-CH<sub>2</sub>-O-), 3.40(-O-CH<sub>2</sub>-), 3.14 ~ 3.13 (-NH-CH<sub>2</sub>-), 1.90 (-CH<sub>2</sub>-CH<sub>2</sub>-O-), 1.60 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-), 1.47 (-NH-CH<sub>2</sub>-CH<sub>2</sub>-), 1.32 (-NH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-).



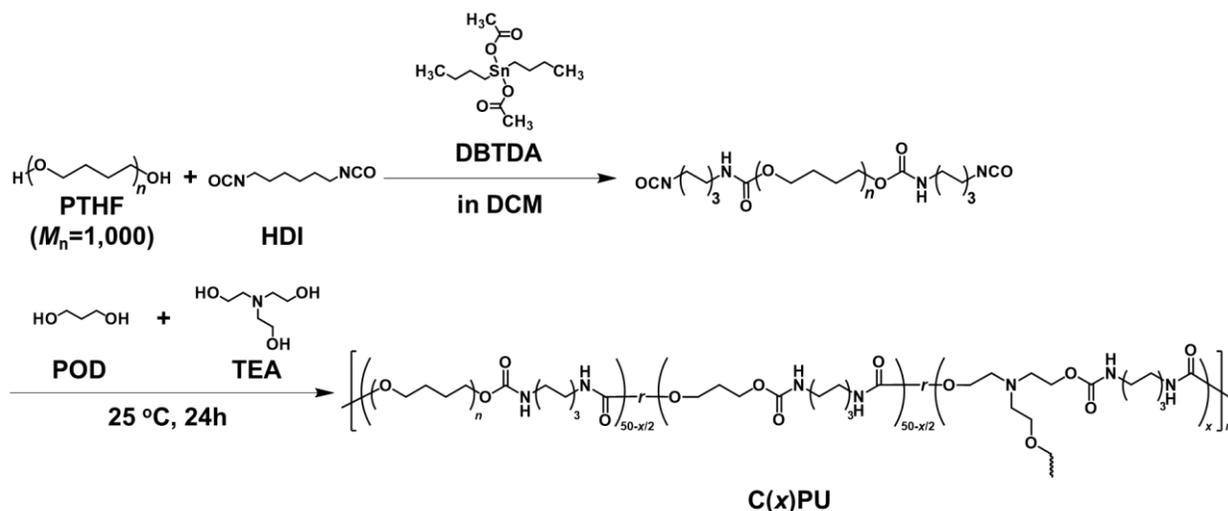
**Fig. S4.** 500 MHz <sup>1</sup>H-NMR spectrum of LPU in chloroform-*d*.

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

Sample	$M_n^a$	$M_w^a$	PDI <sup>a</sup>
LPU	$8 \times 10^3$	$14 \times 10^3$	1.7

<sup>a</sup>Determined by GPC using PEG standards for calibration in DMSO as an eluent.

## 5. Preparation of chemical crosslinked polyurethane: C(x)PU



**Scheme S4.** Preparation of C(x)PU.

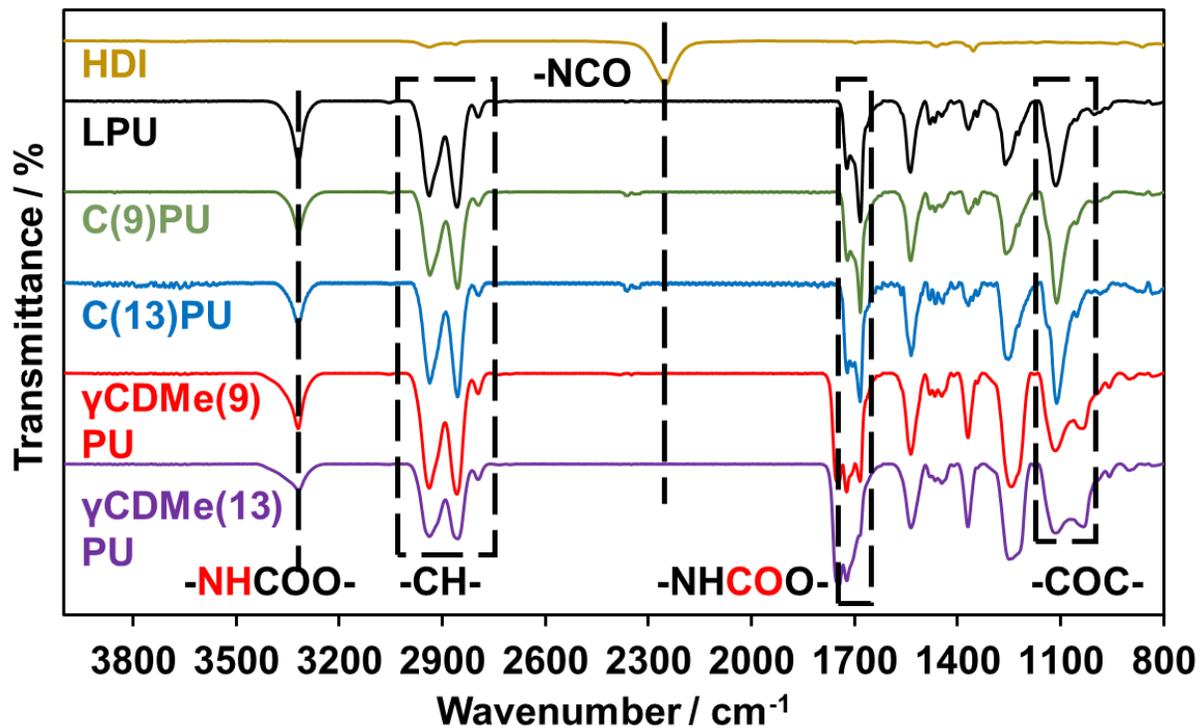
### Preparation of C(x)PU:

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 N<sub>2</sub> 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.

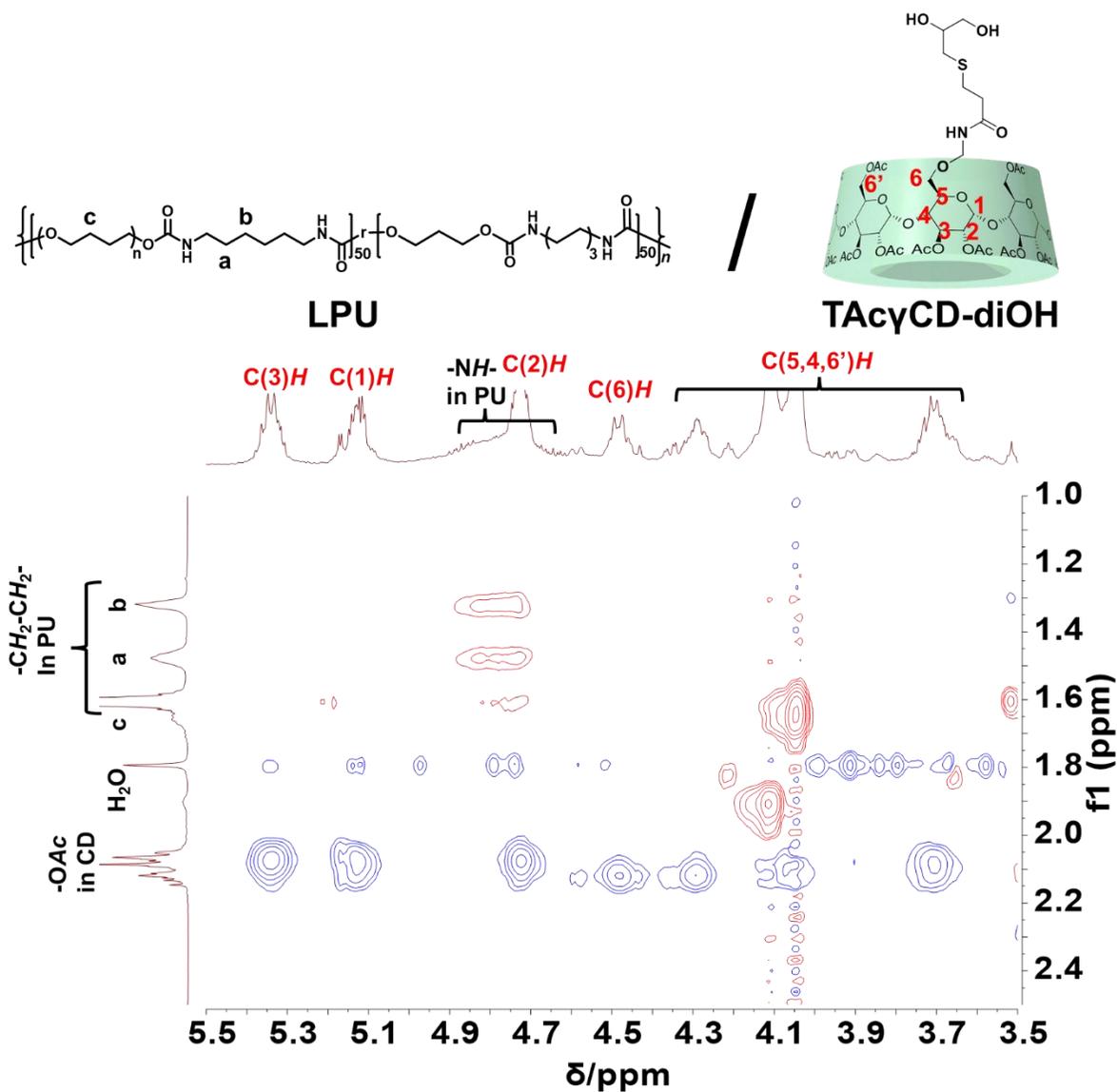
Samples	PTHF		TEA		POD		HDI		DBTDA
	mg	mmol	mg	mmol	mg	mmol	mg	mmol	mg
C(9)PU	1000	1	30	0.2	76	1	406	2.4	2.5
C(13)PU	1000	1	45	0.3	76	1	432	2.6	2.5

## 6. ATR-FTIR spectra of polyurethane (PU) materials



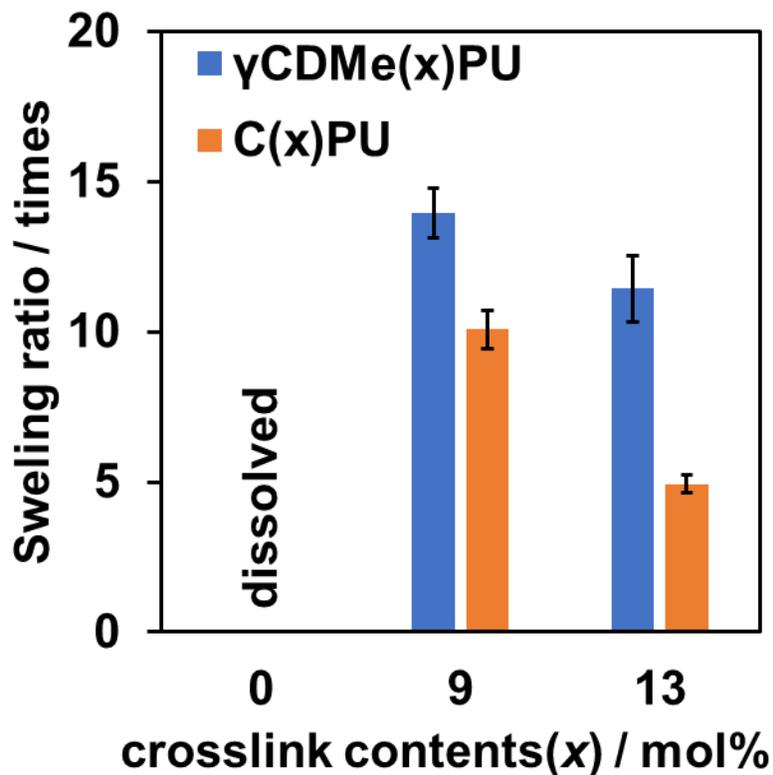
**Fig. S5.** ATR-FTIR spectra of  $\gamma$ CDMe(*x*)PU, C(*x*)PU, and LPU. ATR-FTIR spectrum of HDI was shown in Figure. as a reference.

## 7. 2D NOESY NMR spectrum of LPU and TAc $\gamma$ CD diOH mixture solution



**Fig. S6.** 600 MHz 2D NOESY NMR spectrum of the mixture of LPU and TAc $\gamma$ CD diOH in chloroform-*d*. There was no NOE correlation signal between the TAc $\gamma$ CD units and PU main chains.

## 8. Swelling tests of PU materials



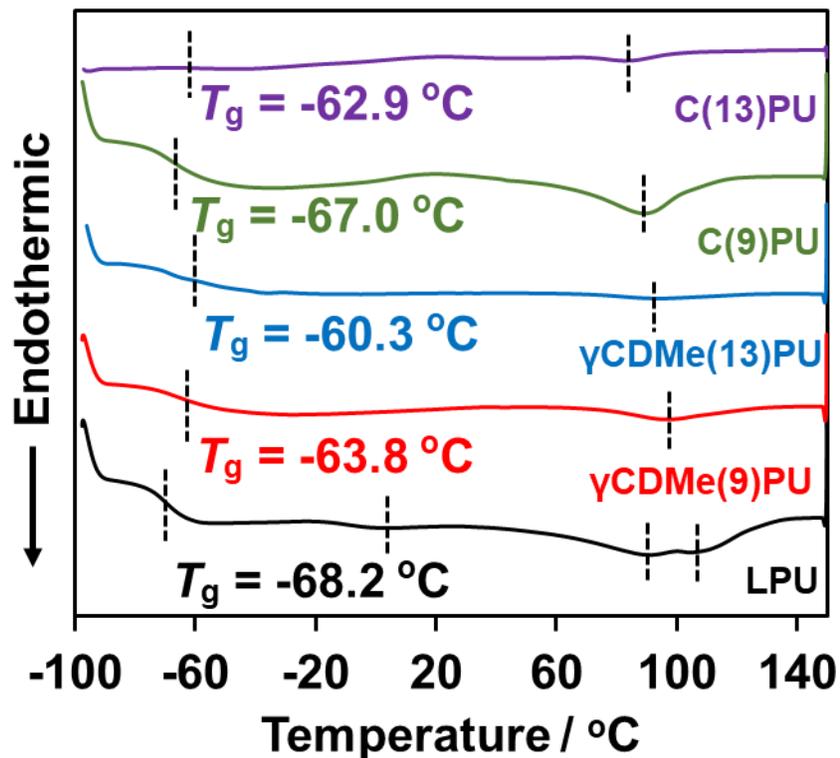
**Fig. S7.** Swelling ratios of  $\gamma$ CDMe(x)PU and C(x)PU for chloroform.  $x$  were 0, 9, and 13.

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  $20 \pm 5$  mg and immersed in 10 mL DCM for 24 h at 25 °C.

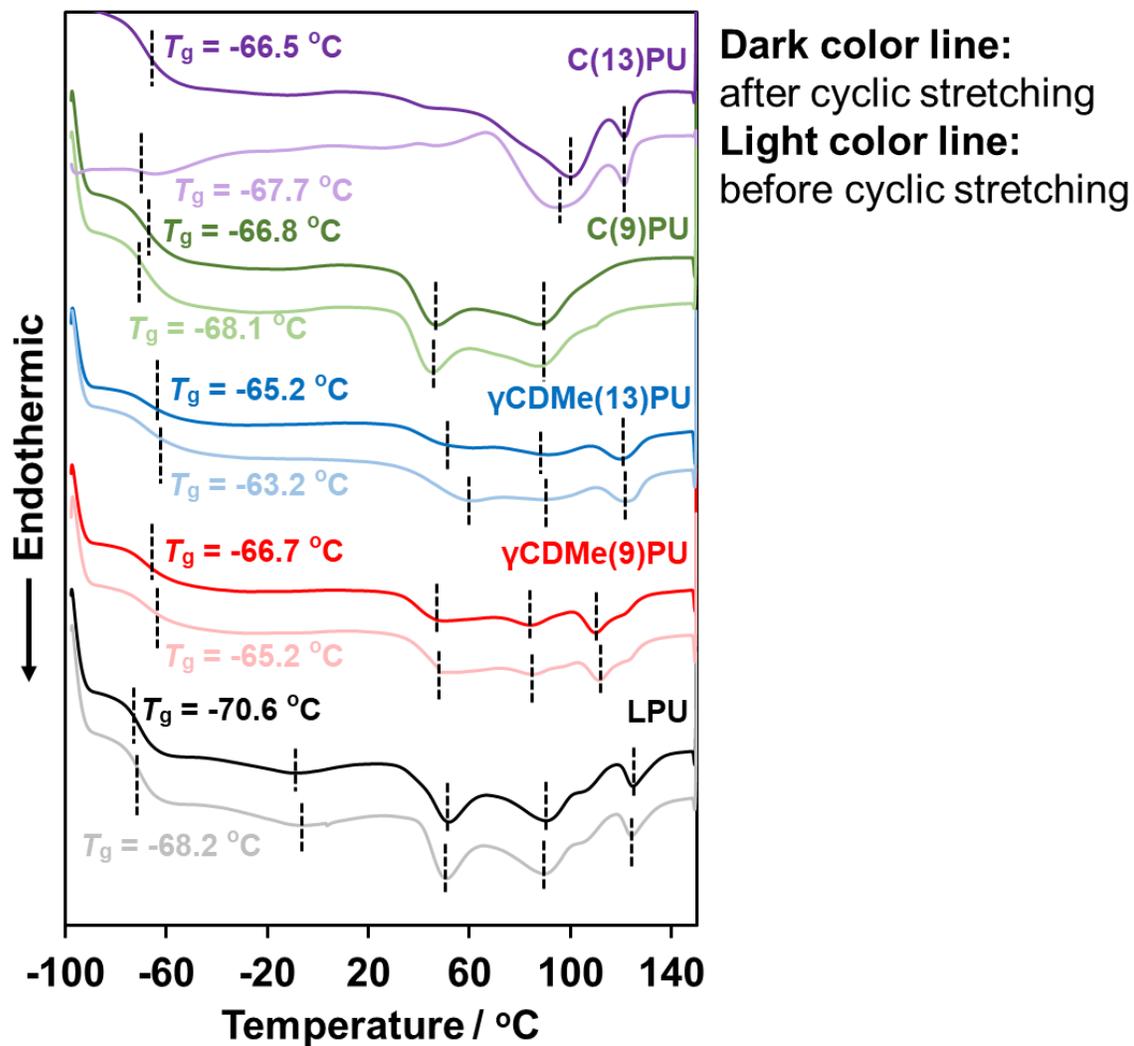
## 9. DSC curves of PU materials



**Fig. S8.** DSC curves of 2<sup>nd</sup> scan for  $\gamma$ CDMe( $x$ )PU, C( $x$ )PU and LPU. The temperature range was from -100 °C to 150 °C, the heating rate was 10 °C/min.

**Table S5.**  $T_m$  of 2<sup>nd</sup> scan for all PU materials.

Samples	$T_m / \text{°C}$		
$\gamma$ CDMe(9)PU	96.8		
$\gamma$ CDMe(13)PU	93.7		
C(9)PU	87.4		
C(13)PU	82.9		
LPU	3.8	90.2	106.1



**Fig. S9.** DSC curves of 1<sup>st</sup> scan for  $\gamma$ CDMe(*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.

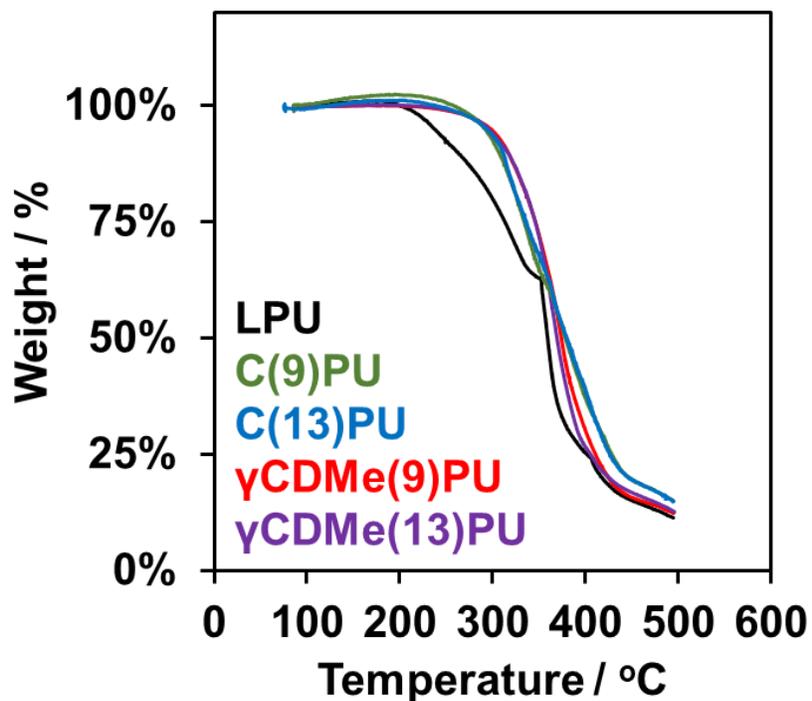
**Table S6.**  $T_m$  of 1<sup>st</sup> scan for all PU materials.

Samples	$T_m / ^\circ\text{C}$			
$\gamma$ CDMe(9)PU	48.7	85.0	111.5	
$\gamma$ CDMe(13)PU	61.0	91.7	122.3	
C(9)PU	45.4	89.4		
C(13)PU	95.5	120.9		
LPU	-5.5	50.9	89.6	124.1

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

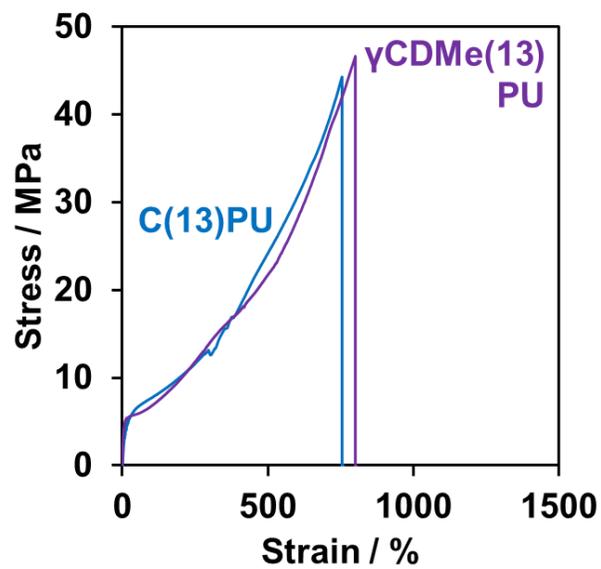
Samples	$T_m / ^\circ\text{C}$			
$\gamma$ CDMe(9)PU	47.7	84.5	110.2	
$\gamma$ CDMe(13)PU	58.1	91.1	121.1	
C(9)PU	46.4	89.5		
C(13)PU	100.7	121.0		
LPU	-9.4	51.7	91.3	124.4

## 10. TGA curves of PU materials



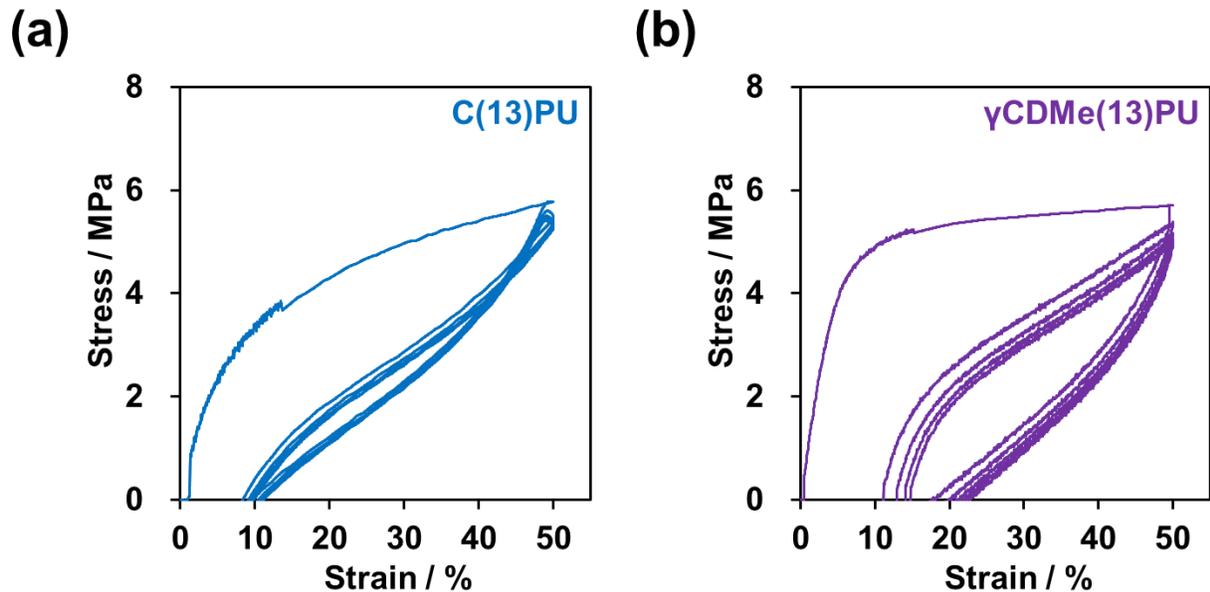
**Fig. S10.** TGA curves of PU materials. The temperature range was from 80 °C to 500 °C, the heating rate was 10 °C/min.

## 11. Stress-Strain Curves of $\gamma$ CDMe(13)PU and C(13)PU



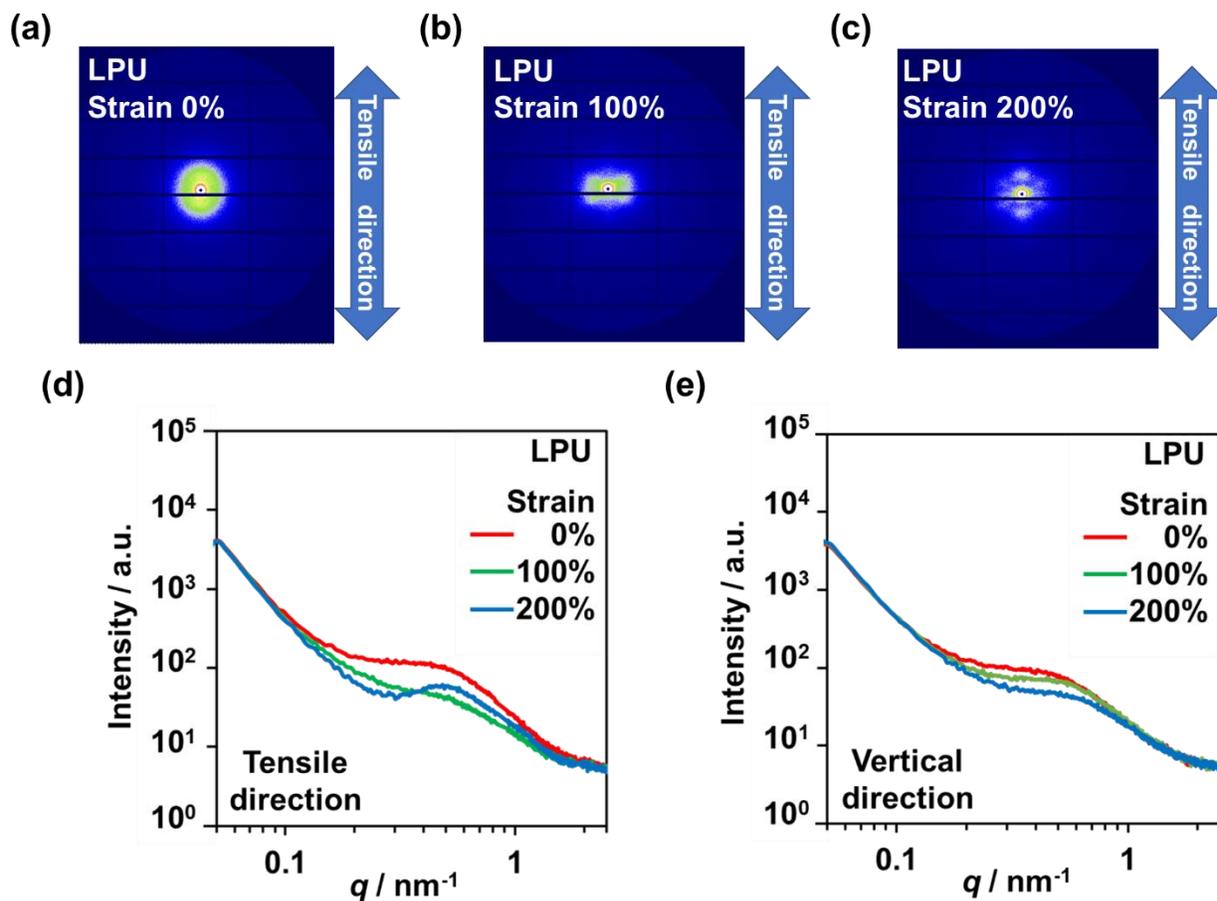
**Fig. S11.** Stress-strain curves of  $\gamma$ CDMe(13)PU and C(13)PU

## 12. Cyclic Stress-Strain Curves of C(13)PU and $\gamma$ CDMe(13)PU



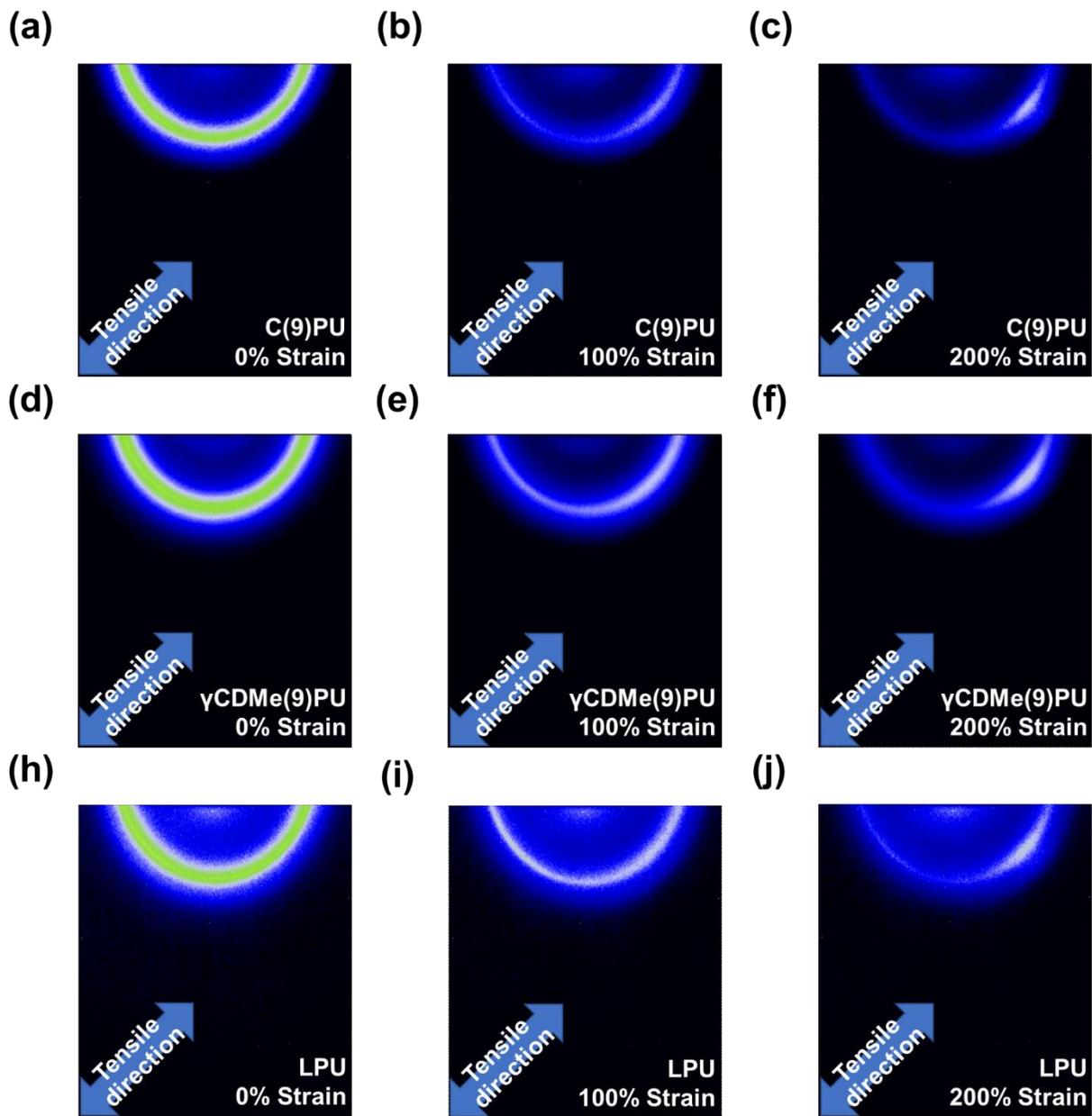
**Fig. S12.** The cyclic stress-strain curves with fixed strain (50%) of (a) C(13)PU and (b)  $\gamma$ CDMe(13)PU. The cycles were performed 5 times.

### 13. SAXS measurements of LPU

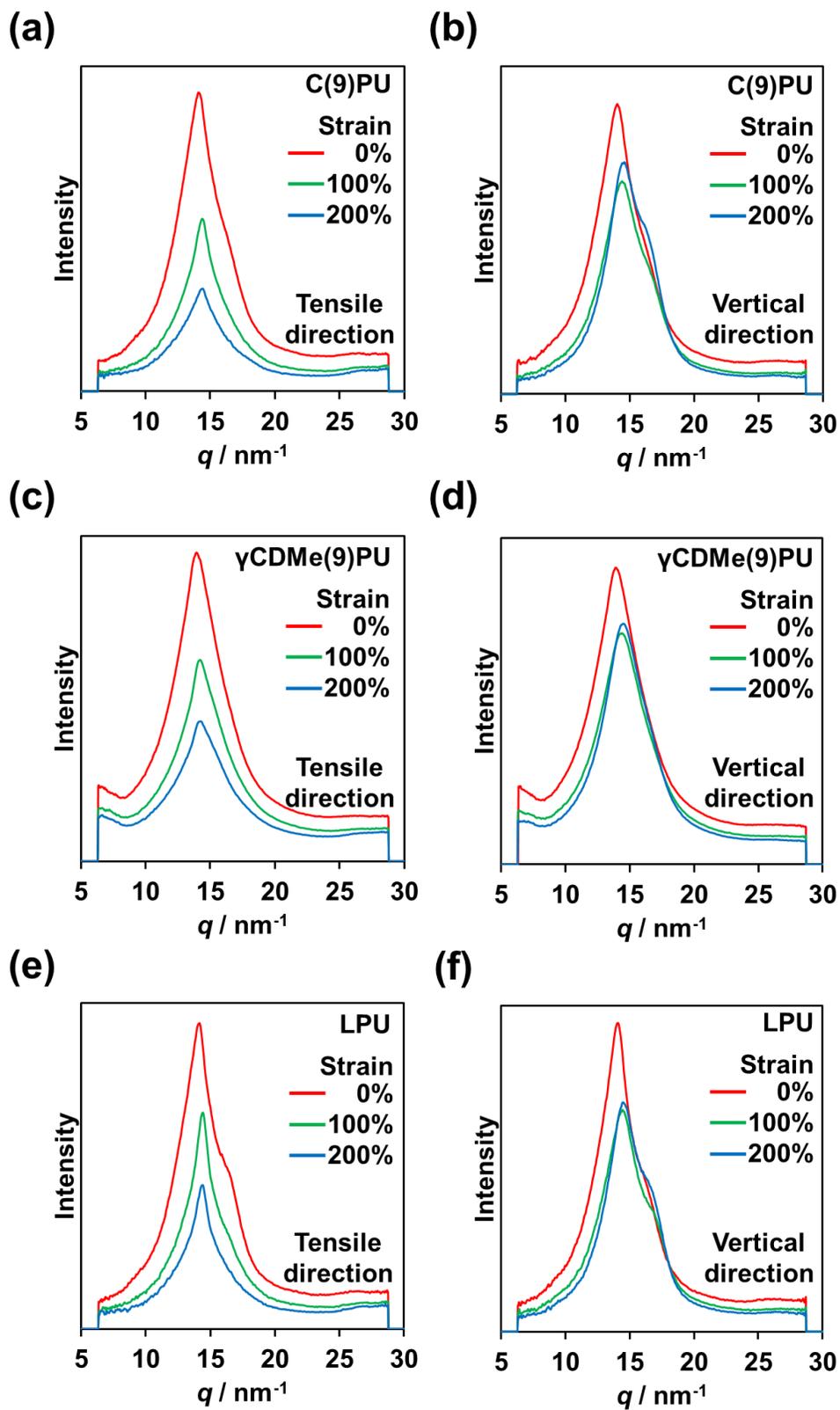


**Fig. S13.** 2D SAXS patterns of (a-c) LPU with 0%, 100% and 200% strains. The direction of tensile is shown by the arrow. SAXS profiles of LPU with 0%, 100% and 200% strains in (d) tensile and (e) vertical directions.

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)  $\gamma\text{CDMe(9)PU}$  and (e-f) LPU with 0%,100% and 200% strains in tensile and vertical directions.

## References

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- 2 S. Nomimura, M. Osaki, J. Park, R. Ikura, Y. Takashima, H. Yamaguchi and A. Harada, *Macromolecules*, 2019, **52**, 2659–2668.