- Electronic Supplementary Information -

Preparation of Mechanically Tough Poly(dimethyl siloxane) through the Incorporation of Acetylated Cyclodextrin-Based Topologically Movable Cross-links

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Content

1. Materials

(3-Mercaptopropyl)methyldimethoxysilane (MMDMS), octamethylcyclotetrasiloxane (D_4), vinyl-modified polydimethylsiloxane (PDMS-Vi), hydrosilyl-modified polydimethylsiloxane (PDMS-SiH), and $Pt_2[(Me_2SiCH{=}CH_2)_2O]_3$ (Karstedt catalyst) were kindly supplied by Shin-Etsu Chemical Co., Ltd. Chloroform was obtained from Nacalai Tesque Inc. Hexamethyldisiloxane (HMDS), 1-pentene, and trifluoromethanesulfonic acid were obtained from Tokyo Chemical Industry Co., Ltd. Deuterated chloroform ($CDCl_3$) and methanol were obtained from FUJIFILM Wako Pure Chemical Corporation. 1-Hydroxy-cyclohexyl-phenyl-ketone (IRGACURE® 184; hereinafter described as I184) was purchased from BASF Japan Ltd. 2-Hydroxy-2-methylpropiophenone (IRGACURE® 1173; hereinafter described as I1173) was purchased from Sigma–Aldrich Co. Deionized water was obtained by a Milli-Q system. Triacetylated 6-acrylamido methylether-γ-cyclodextrin (TAcγCDAAmMe) was purchased from Kyoeisha Chemical Co., Ltd.

2. Measurements

NMR measurements: ^{1}H, ^{13}C, ^{29}Si and ^{1}H-^{1}H nuclear Overhauser effect spectroscopy (NOESY) spectra were recorded with a JEOL ECA-500 NMR spectrometer at 25 °C. Chemical shift values were referenced to the $CHCl_3$ value (δ = 7.26 ppm) for ^{1}H and ^{13}C NMR and the TMS value (δ = 0 ppm) for ^{29}Si NMR. For the NMR measurements of elastomers, the elastomers were swollen by $CDCl_3$ in NMR tubes for at least twenty-four hours and measured by means of an NMR spectrometer.

Gel permeation chromatography (GPC): The number-average molecular weight (M_n), weight-average molecular weight (M_w) and molecular weight distribution (PDI, M_w/M_n) were measured by GPC in chloroform at 40 °C with two columns (Tosoh TSK gel GMHHR x2). The columns were connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive index detector. The polymer samples were dissolved in chloroform prior to loading. The molecular weights of the samples were calculated based on a calibration curve prepared using polystyrene standards. When calculating the molecular weights, the results from the RI detector were used.

Fourier transform infrared (FT-IR) spectroscopy: FT-IR spectra were acquired in ATR mode through ZnSe crystals with N_2 gas flow (JASCO FT/IR-410).

Tensile test: Tensile tests of the elastomers were performed using an Autograph AG-X plus (Shimadzu Co.) at a deformation rate of 1 mm/s. Rectangular test pieces (20 × 5 × 0.6 mm^3) were used for the tensile test ($n \geq 3$). The toughness was calculated from the integral of the stress–strain curve. The Young's modulus was calculated from the initial slope of the stress–strain curve at a range of 1-6% strain. The tensile tests were carried out at room temperature.

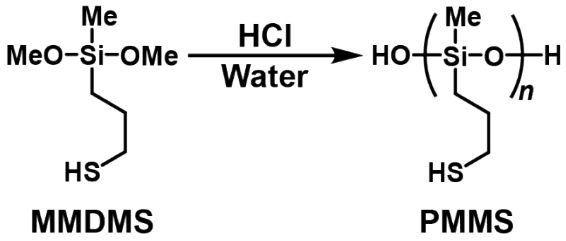
Cyclic tensile test: Cyclic tensile tests were performed using an Autograph AG-X plus (Shimadzu Co.) ($n \geq 3$). The rectangular test pieces (20 × 5 × 0.6 mm^3) were continuously stretched and retracted without intervals at a deformation rate of 1.0 mm/s, and the maximum strains are summarized in **Table S3**. The cyclic tensile tests were carried out at room temperature.

Stress relaxation test: Stress relaxation tests were performed using an Autograph AG-X plus (Shimadzu Co.). The rectangular test pieces (20 × 5 × 0.6 mm^3) stretched until certain strains were reached, as summarized in **Table S4**. Then, the strain was held, and the stress was recorded for 6000 seconds. The stress relaxation tests were carried out at room temperature.

Differential scanning calorimetry (DSC): The glass transition temperature (T_g) of the polymers was measured by a DSC machine under a N_2 atmosphere (DSC 7020, Hitachi High-tech Corporation).

X-ray scattering measurements: The internal structures of the elastomers were determined by ultrasmall-angle X-ray scattering (USAXS) and small-angle X-ray scattering (SAXS) measurements at the BL19B2 and BL40B2 beam lines in SPring-8, Nishi-harima, Japan. The powers of the incident X-ray beams for BL19B2 and BL40B2 were 18 and 12 keV, respectively. The sample-to-detector lengths for BL19B2 and BL40B2 were 41 m and 2 m, respectively. The length of the scattering vector q in the USAXS and SAXS measurements was 0.01-0.1 and 0.1-3 nm^{-1}, respectively, where $q = 4\pi\sin\theta/\lambda$ (2θ and λ are the scattering angle and the wavelength, respectively). The scattering intensities were normalized by exposure times (60 seconds for USAXS and 5 seconds for SAXS), machine coefficient (0.0118 $counts \cdot second^{-1} \cdot cm^{-1}$ for USAXS), transmittance, and thickness. The machine coefficients for SAXS measurements for each sample were appropriately adjusted to combine USAXS profiles and SAXS profiles.

3. Preparation of PMMS



Scheme S1. Preparation of PMMS

(3-Mercaptopropyl)methyldimethoxysilane (40 g, 0.18 mol) was added to 1 M HCl aq. (14 mL) at 0 ℃. The mixture was stirred at room temperature for 3 h. Volatile components were distilled off under vacuum to give PMMS (30 g, 82%).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 ℃): δ 2.49 (2H, **a**), 1.61 (1H, **b**), 1.31 (1H, **c**), 0.62 (2H, **d**), 0.08 (3H, **e**) ppm

^{29}Si NMR ($CDCl_3$, 99 MHz, 25 ℃): δ -20.1 ($\mathbf{D_{OH}}$), -22.6 (**D**) ppm

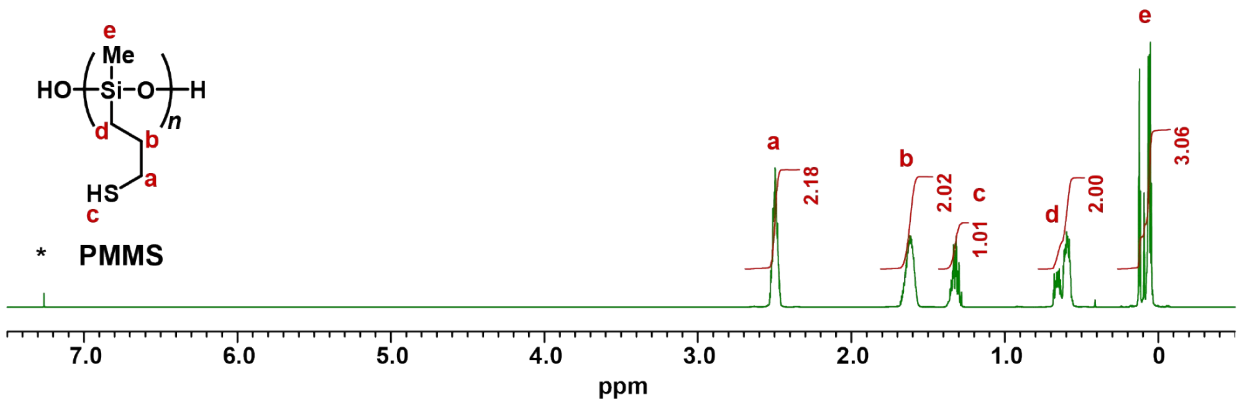


Fig. S1. ^{1}H NMR spectrum of PMMS ($CDCl_3$, 500 MHz, 25 ℃, * indicates the solvent residue peak).

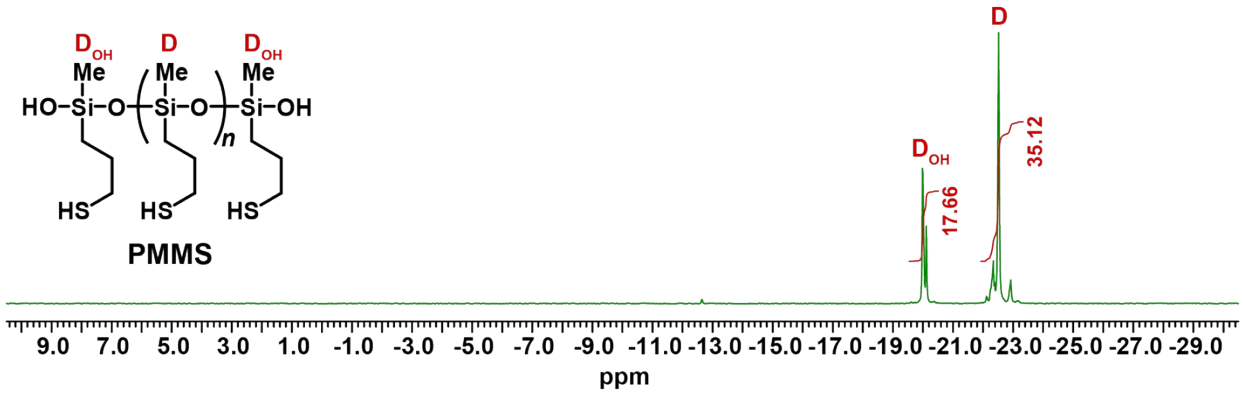
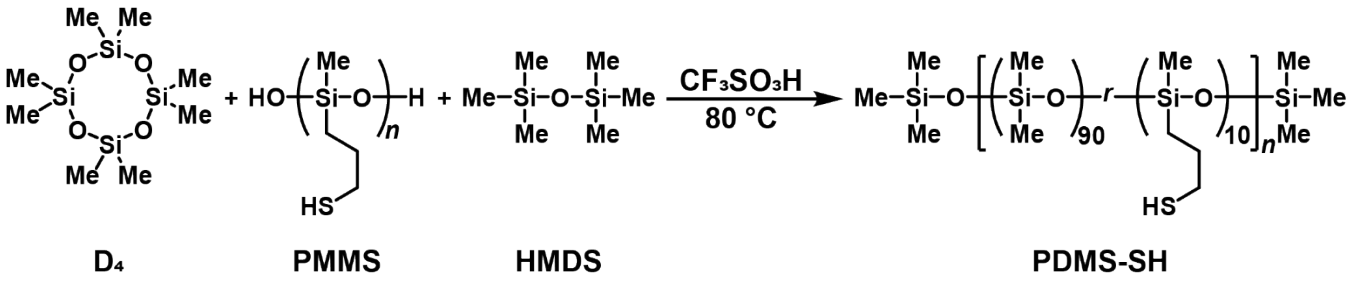


Fig. S2. ^{29}Si NMR spectrum of PMMS ($CDCl_3$, 99.4 MHz, 25 ℃).

4. Preparation of PDMS-SH



Scheme S2. Preparation of PDMS-SH.

PMMS (9.6 g, 58 mmol of SH units) was mixed with octamethylcyclotetrasiloxane (71 mL, 0.23 mol of Me_2SiO units), hexamethyldisiloxane (330 μL, 1.5 mmol) and trifluoromethanesulfonic acid (400 μL, 4.5 mmol). The mixture was stirred at 80 ℃ for 5 days. This precursor copolymer was dissolved in dichloromethane (150 mL), and the solution was washed several times with water until a neutral pH was attained. The copolymer solution was concentrated under vacuum and poured into methanol (200 mL) to remove oligomers. The precipitated oil was recovered by decantation and dried under vacuum to give PDMS-SH (36 g, 46%). The thiol group concentration calculated from the ^{1}H NMR spectrum was approximately 10 mol%. After establishing the preparation scheme, Shin-Etsu Chemical Co., Ltd., kindly provided PDMS-SH on a large scale (approximately 1 kg).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 ℃): δ 2.51 (2H, a), 1.65 (2H, b), 1.20 (1H, c), 0.60 (2H, d), 0.06 (57H, e) ppm

^{29}Si NMR ($CDCl_3$, 99 MHz, 25 ℃): δ 7.68 (M), -21.4 (D_{Me}), -22.8 (D_{SH}) ppm

Molecular weight: $M_n = 7.2 \times 10^4$ (end-group analysis by ^{29}Si NMR)

$M_n = 4.1 \times 10^4$, $M_w = 1.1 \times 10^5$, PDI = 2.7 (GPC)

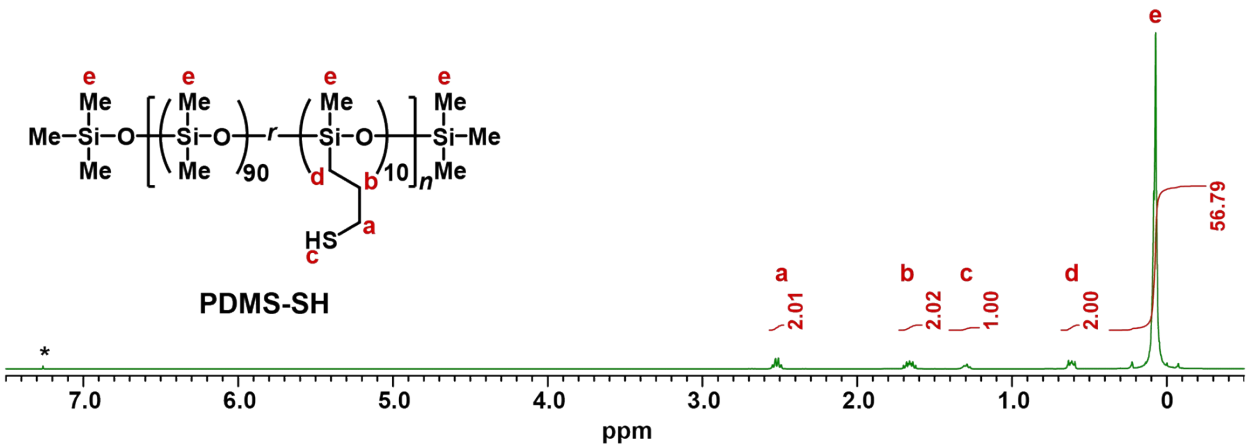


Fig. S3. ^{1}H NMR spectrum of PDMS-SH ($CDCl_3$, 500 MHz, 25 °C, * indicates the solvent residue peak).

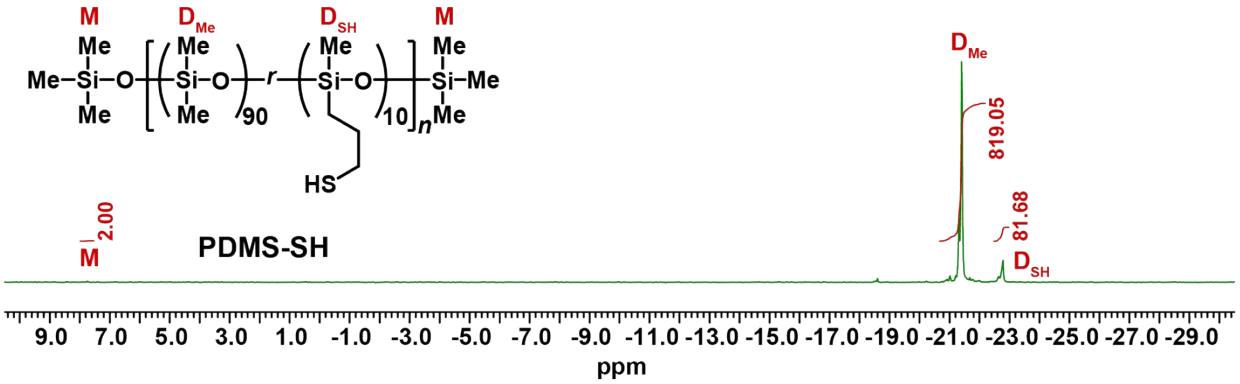
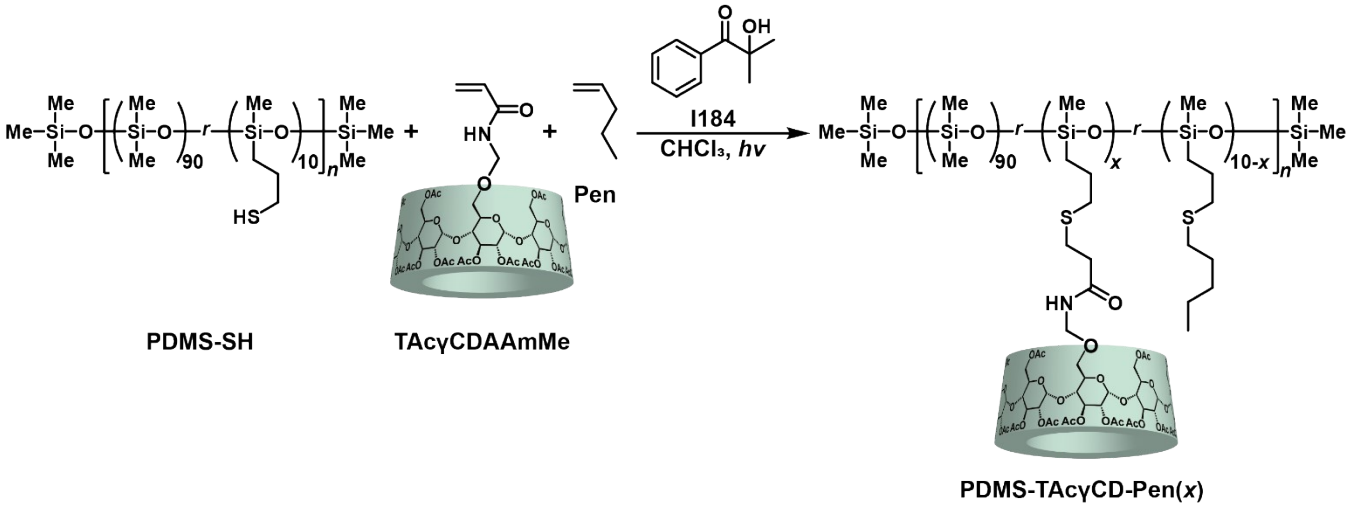


Fig. S4. ^{29}Si NMR spectrum of PDMS-SH ($CDCl_3$, 99.4 MHz, 25 °C, * indicates the solvent residue peak).

5. Preparation of PDMS-TAcγCD-Pen(*x*)



Scheme S3. Preparation of PDMS-TAcγCD-Pen(*x*).

TAcγCDAAmMe (*x* equiv.; *x* = 0.5, 1, 1.5, 1.8, 2, 2.3, 2.5, and 3), PDMS-SH (SH group: 10 eq.), 1-pentene (10-*x* eq.), and I1173 (1 eq.) were dissolved in $CHCl_3$ (6.0 mL). The solution was irradiated by UV light with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. Then, 1-pentene (200 μL) was added to the reaction mixture. The reaction mixture was irradiated by UV light with an LED lamp (λ = 253 and 365 nm) for 30 min to consume the unreacted SH groups. After UV irradiation, the obtained material was left in a fume hood overnight to roughly evaporate $CHCl_3$. The elastomer was dried at 70 ℃ in vacuum for at least 12 h to afford PDMS-TAcγCD-Pen(*x*). The amounts of each reagent used to prepare each elastomer are summarized in Table S1.

Table S1. Amount of each reagent for PDMS-TAcγCD-Pen(*x*).

x	PDMS-SH		TAcγCDAAmMe		1-Pentene		I1173	
	/mg	/mmol [a]	/mg	/mmol	/μL	/mmol	/μL	/mmol
1	600	0.748	176	0.0748	73.8	0.674	11.4	0.0748
1.5	600	0.748	264	0.112	69.7	0.636	11.4	0.0748
1.8	600	0.748	316	0.135	67.3	0.614	11.4	0.0748
2	600	0.748	351	0.150	65.6	0.599	11.4	0.0748
2.3	600	0.748	404	0.172	63.1	0.576	11.4	0.0748
2.5	600	0.748	439	0.187	61.5	0.561	11.4	0.0748
3	600	0.748	527	0.225	57.4	0.524	11.4	0.0748

a: The molar ratio of the SH groups on PDMS-SH.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 ℃): δ 6.83 (a), 5.33 (3), 5.14 (1), 4.74 (2, b), 4.50~4.28 (6', b), 4.07~3.70 (4, 5, 6), 2.80 (c), 2.51 (d), 2.09 (AcO), 1.62 (e), 1.35 (f), 0.90 (g), 0.63 (h), 0.08 (i) ppm

^{13}C NMR ($CDCl_3$, 125 MHz, 25 ℃): δ 169.5, 96.5, 77.2, 70.9, 62.6, 43.6, 35.3, 82.2, 31.2, 29.4, 23.2, 22.5, 21.0, 17.2, 14.1, 1.2, -0.49 ppm

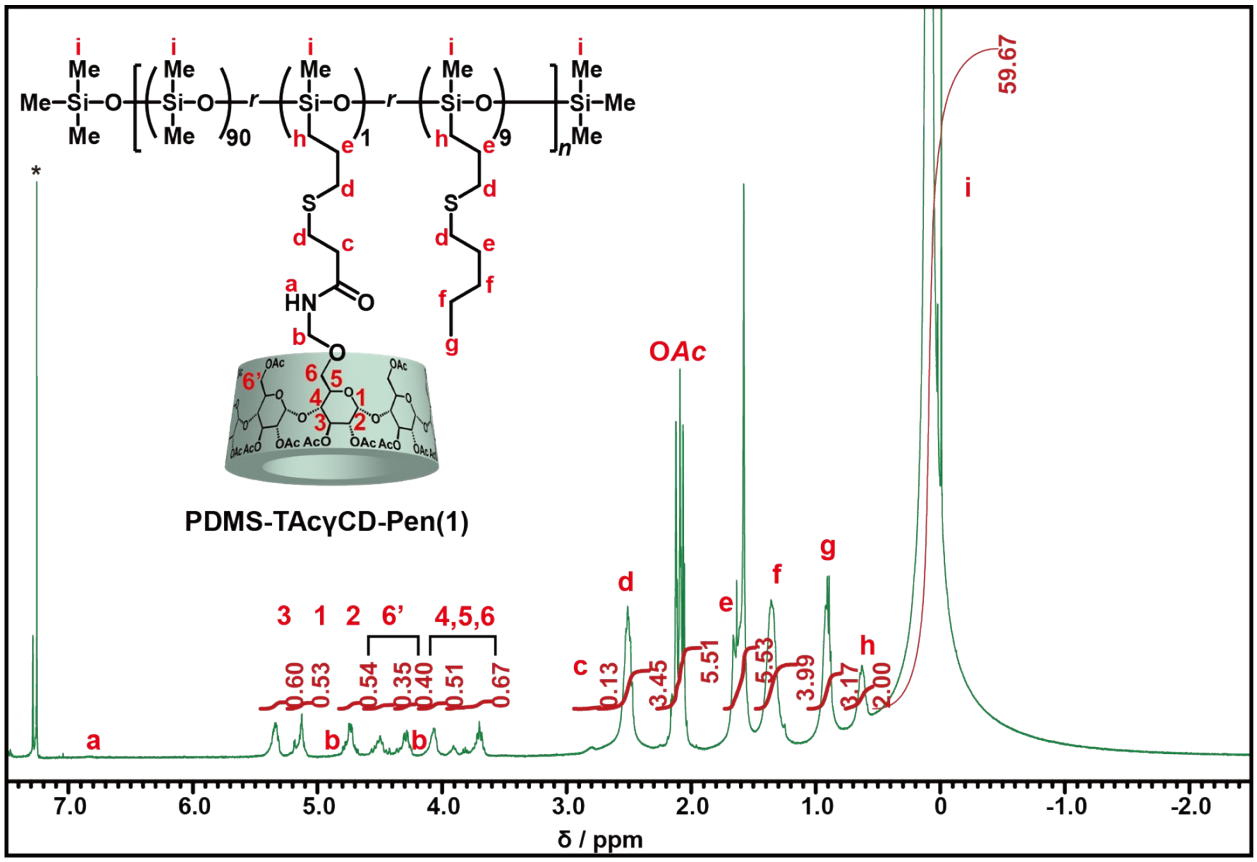


Fig. S5. ^{1}H NMR spectrum of PDMS-TAcγCD-Pen(1) ($CDCl_3$, 500 MHz, 25 ℃, * indicates the solvent residue peak).

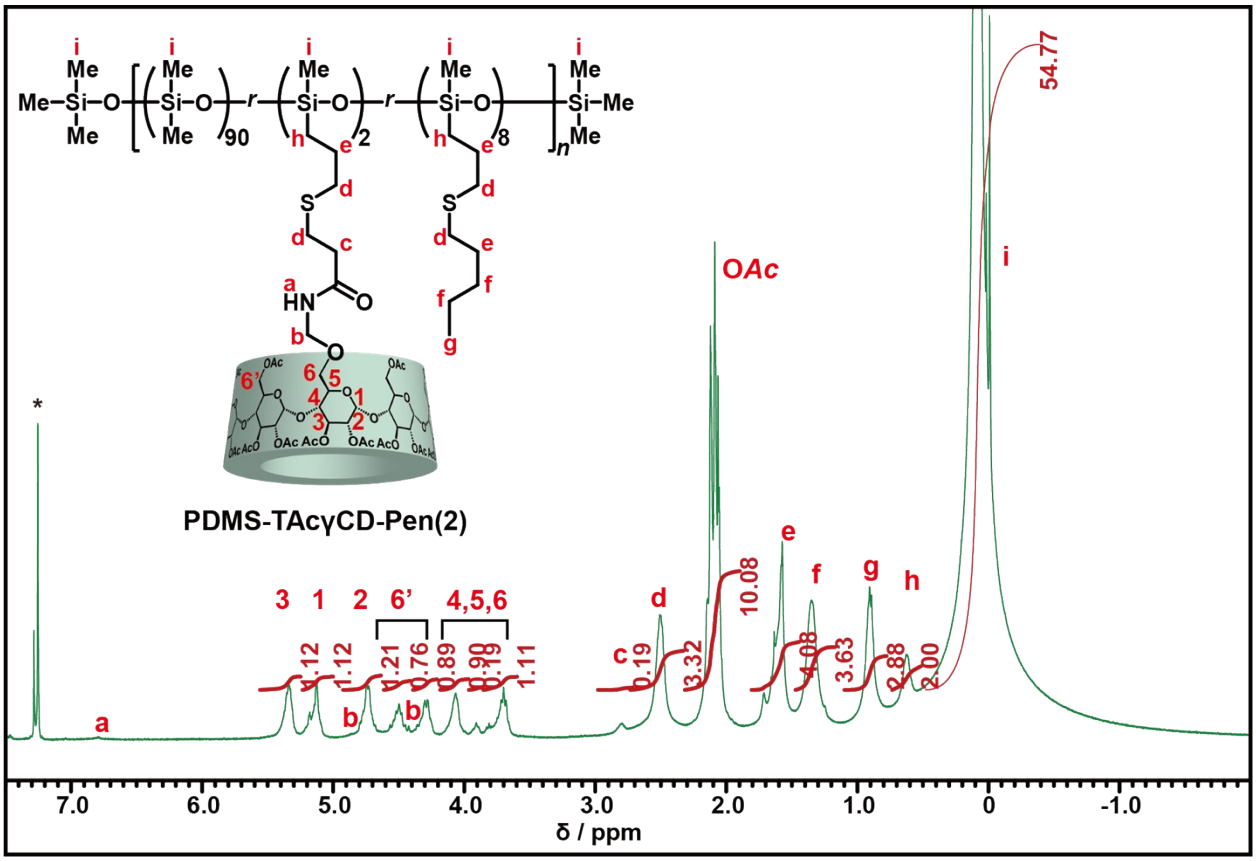


Fig. S6. ^{1}H NMR spectrum of PDMS-TAcγCD-Pen(2) ($CDCl_3$, 500 MHz, 25 °C, * indicates the solvent residue peak).

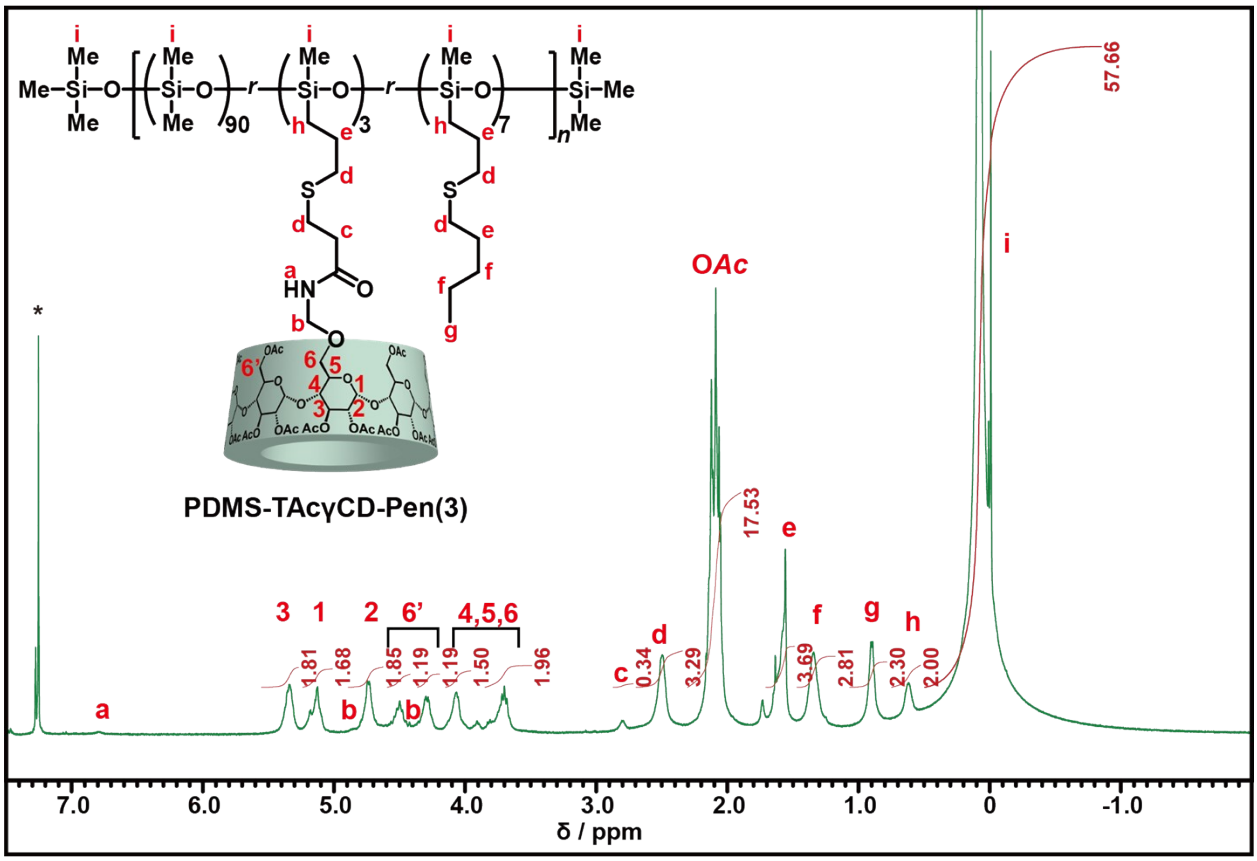


Fig. S7. ^{1}H NMR spectrum of PDMS-TAcγCD-Pen(3) ($CDCl_3$, 500 MHz, 25 °C, * indicates the solvent residue peak).

Table S2. CD modification ratio in PDMS-TAcγCD-Pen(*x*) calculated from ^{1}H NMR spectra.

x	CD modification ratio[a]
1	0.80
2	1.46
3	2.54

a: The CD modification ratio was calculated from the integral ratio of the ^{1}H NMR spectrum between peak OAc in CD and peak h.

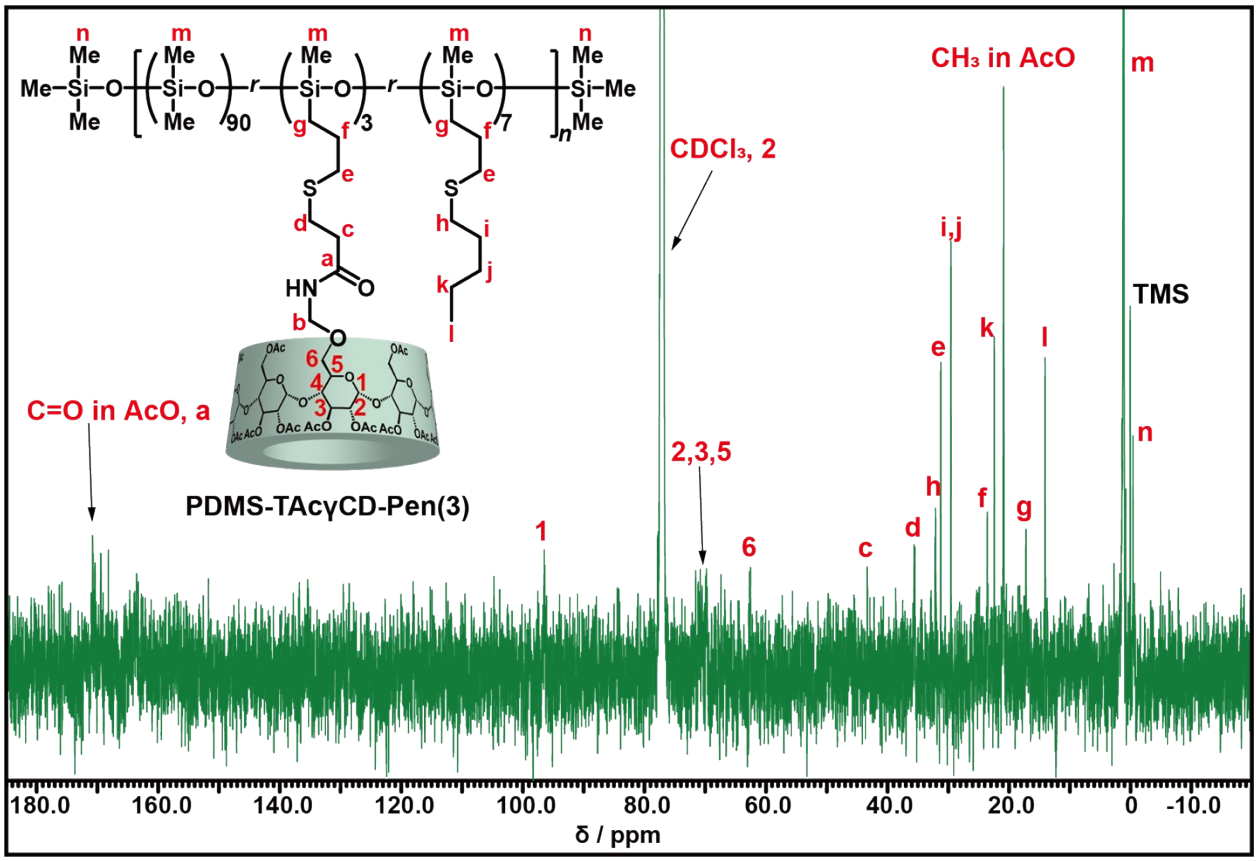
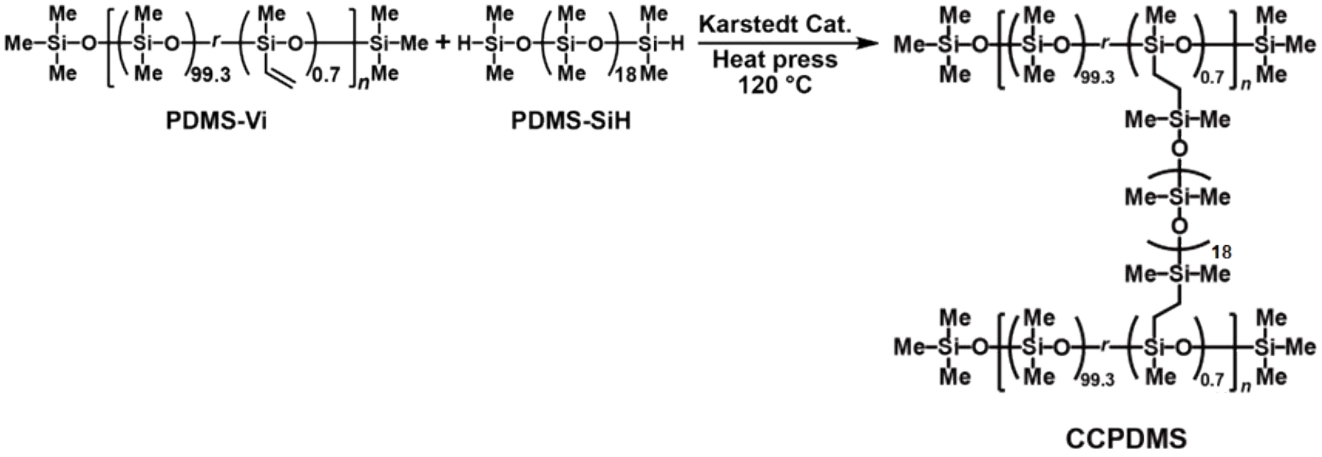


Fig. S8. ^{13}C NMR spectrum of PDMS-TAcγCD-Pen(3) ($CDCl_3$, 125 MHz, 25 ℃, * indicates the solvent residue peak).

6. Preparation of chemically cross-linked PDMS (CCPDMS)



Scheme S4. Preparation of CCPDMS.

CCPDMS was prepared from a two-part addition of cured silicone elastomer kindly supplied by Shin-Etsu Chemical Co. Ltd. PDMS-Vi, PDMS-SiH, and Karstedt catalyst were mixed by a kneading machine (Thinky ARE-300). The mixture was heat-pressed and dried *in vacuo* at room temperature for an hour to be degassed. The mixture was pressed to obtain the elastomer. The elastomer was dried at 70 °C *in vacuo* for at least 12 h to give CCPDMS.

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 0.07 (a) ppm

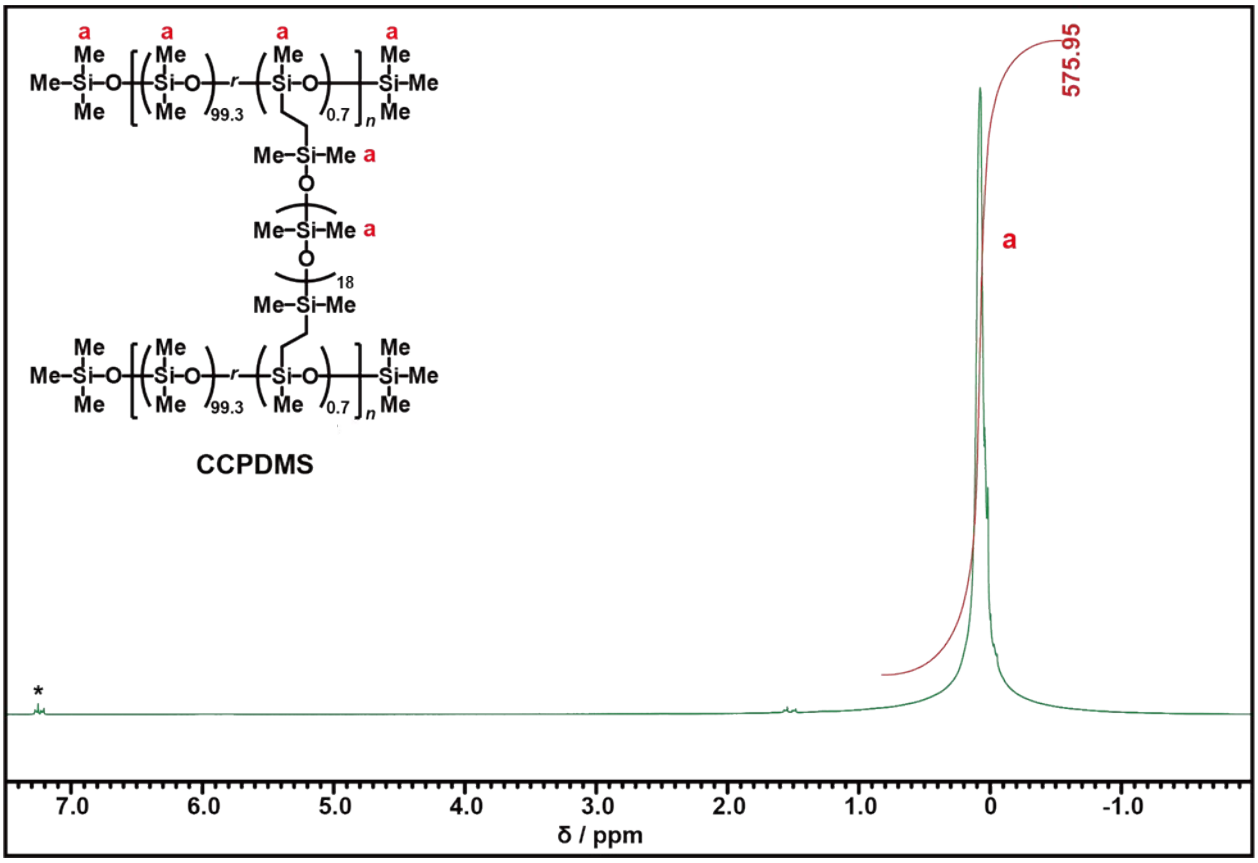


Fig. S9. ^{1}H NMR spectrum of CCPDMS ($CDCl_3$, 500 MHz, 25 ℃, * indicates the solvent residue peak).

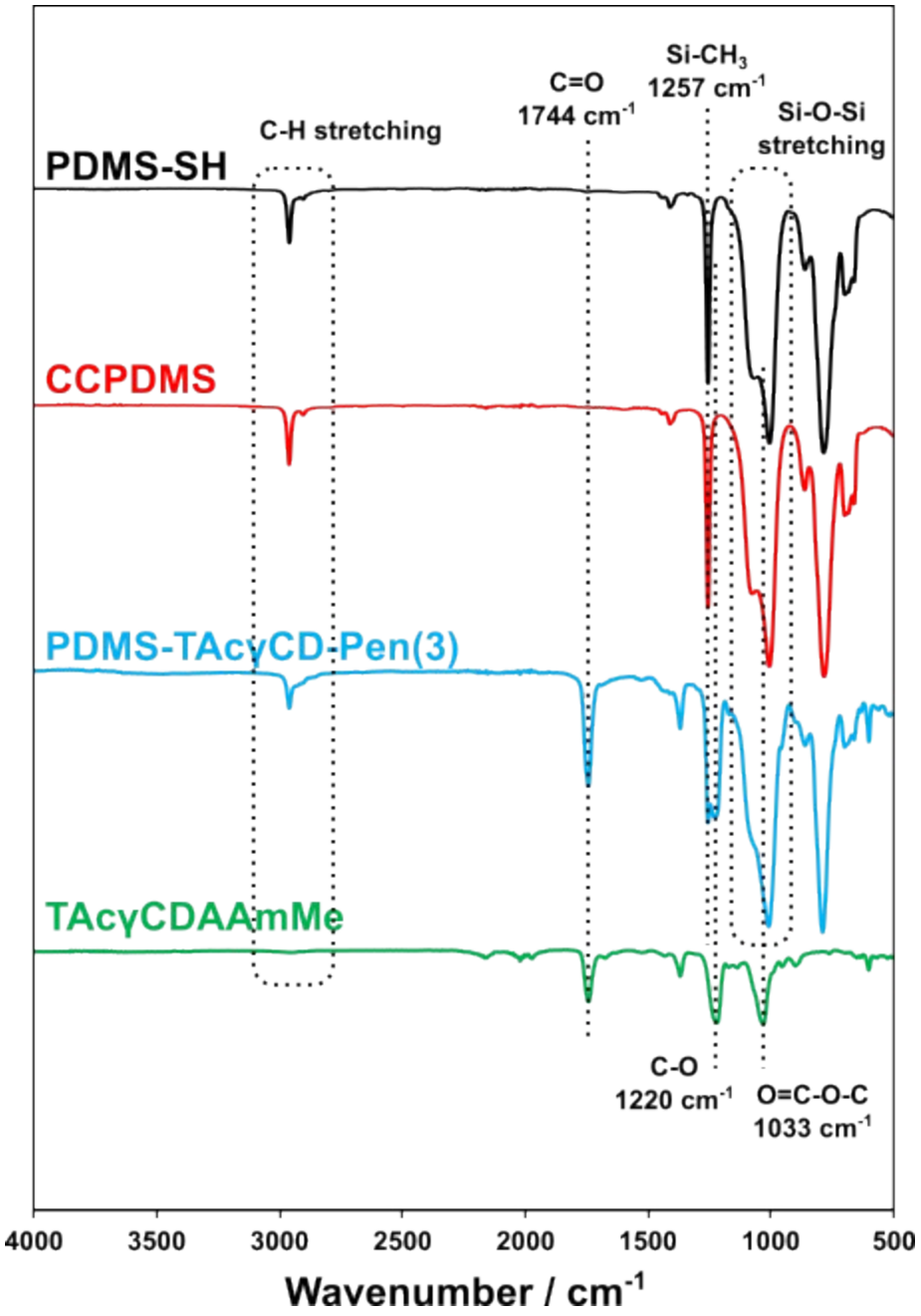


Fig. S10. FT-IR spectra of PDMS-SH, CCPDMS, PDMS-TAcγCD-Pen(3), and TAcγCDAAmMe.

7. Cyclic tensile tests.

Table S3. Maximum strains for the cyclic tensile test.

Elastomer	Maximum strain at the nth cycle/%										
	1st	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**	**8th**	**9th**	**10th**	**11th**
PDMS-TAcγCD-Pen(1)	5	10	25	50	75	-	-	-	-	-	-
PDMS-TAcγCD-Pen(1.5)	5	10	50	100	150	200	250	300	-	-	-
PDMS-TAcγCD-Pen(2)	10	50	100	200	300	400	500	-	-	-	-
PDMS-TAcγCD-Pen(2.5)	5	10	50	100	150	200	250	300	-	-	-
PDMS-TAcγCD-Pen(3)	5	10	20	30	40	50	60	70	80	90	100
CCPDMS	5	10	25	50	75	100	150	-	-	-	-

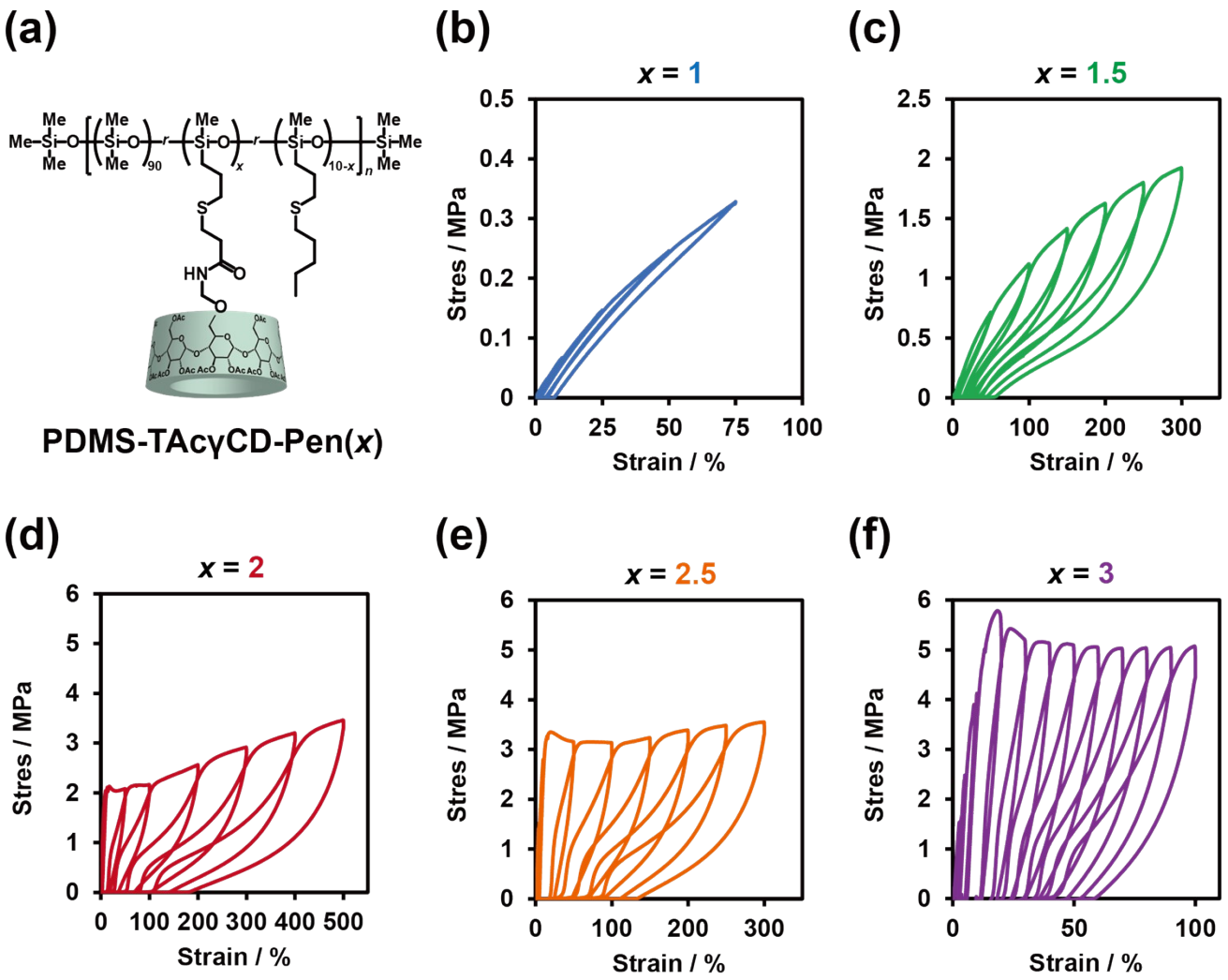


Fig. S11. **(a)** Chemical structure of PDMS-TAcγCD-Pen(*x*) and cyclic stress–strain curves of PDMS-TAcγCD-Pen(*x*) when *x* = **(b)** 1, **(c)** 1.5, **(d)** 2, **(e)** 2.5, and **(f)** 3.

8. Stress relaxation tests

Table S4. Holding strains for stress relaxation tests.

Elastomer	Holding strain/%
PDMS-TAcγCD-Pen(1)	200
PDMS-TAcγCD-Pen(2)	400
PDMS-TAcγCD-Pen(3)	50
CCPDMS	100

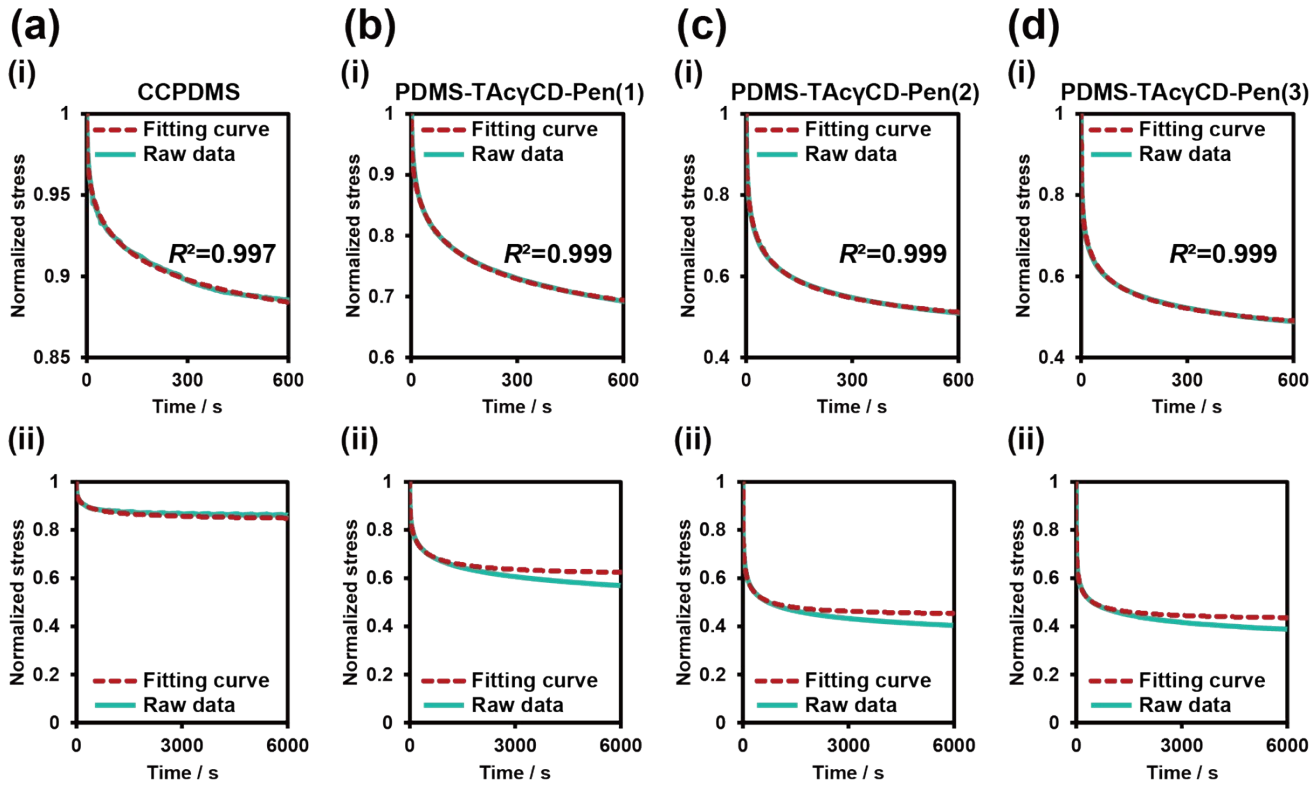


Fig. S12. Stress relaxation curves of **(a)** CCPDMS and **(f)** PDMS-TAcγCD-Pen(*x*) when *x* = **(b)** 1, **(b)** 2, and **(b)** 3 with fitting curves focusing on the initial 600 second regime. The parameters for fitting curves were determined from the 600 second regime and fixed when expanded the range by 6000 seconds. **(i)** Plots by 600 seconds and **(ii)** plots by 6000 seconds (raw data: cyan solid line, fitting curves: red dashed line).

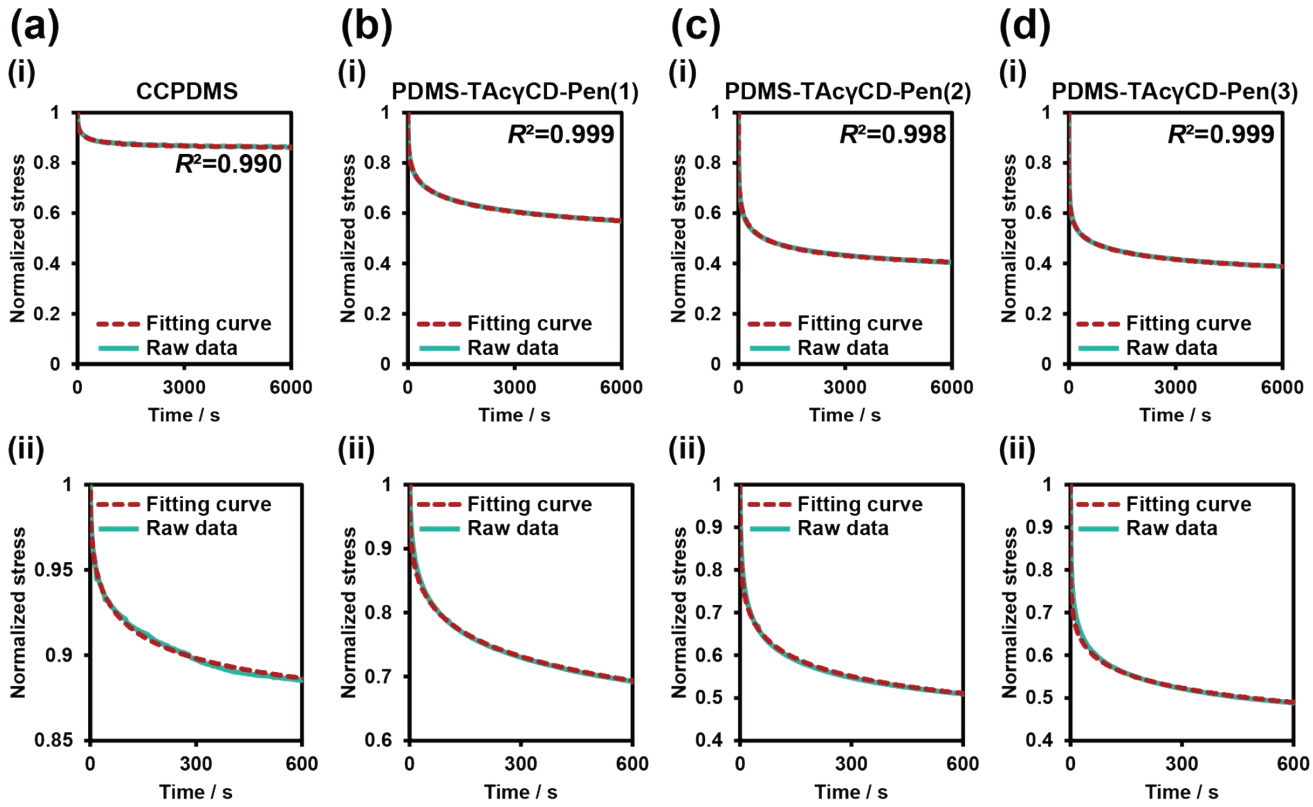


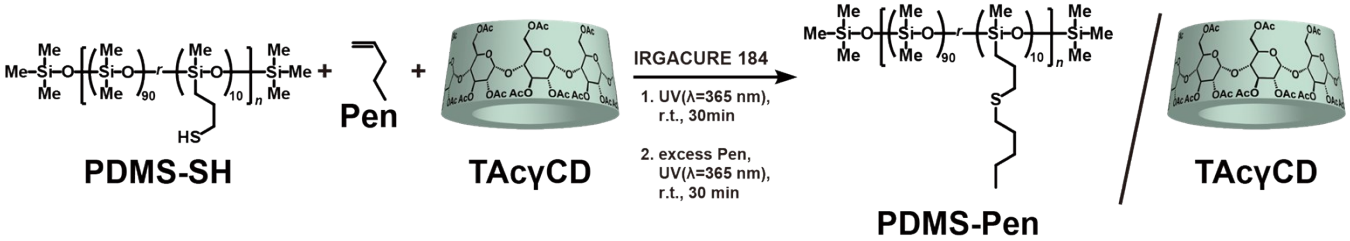
Fig. S13. Stress relaxation curves of **(a)** CCPDMS and **(f)** PDMS-TAcγCD-Pen(*x*) when *x* = **(b)** 1, **(b)** 2, and **(b)** 3 with fitting curves over the entire range (6000 seconds). The parameters for fitting curves were determined from the entire range and fixed when focused on the range by 600 seconds **(i)** Plots by 6000 seconds and **(ii)** plots by 600 seconds (raw data: cyan solid line, fitting curves: red dashed line).

Table S5. Fitting parameters of PDMS-TAcγCD-Pen(*x*) and CCPDMS for the KWW models over the entire range (6000 seconds).

PDMS materials	Relaxable components			Residual components
	σ_r^a/σ_o^e	τ^b (second)	β^c	$\sigma_\infty^d/\sigma_o^e$
CCPDMS	0.15	111	0.33	0.86
PDMS-TAcγCD-Pen(1)	0.61	895	0.25	0.45
PDMS-TAcγCD-Pen(2)	0.72	102	0.23	0.35
PDMS-TAcγCD-Pen(3)	0.73	205	0.18	0.27

[a] Relaxable stress, [b] Relaxation time, [c] Stretching exponent, [d] Residual stress, [e] Initial stress

9. Two-dimensional NOESY NMR measurements



Scheme S5. Preparation of the model mixture for PDMS-Pen/TAcγCD.

Triacetylated-γCD (TAcγCD; 144 mg, 0.0624 mmol), PDMS-SH (100 mg, SH group: 0.125 mmol), 1-pentene (13.7 μL, 0.125 mmol), and I184 (2.55 mg, 0.0125 mmol) were dissolved in $CHCl_3$ (1 mL). The solution was irradiated by UV light with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. Then, 1-pentene (30 μL) was added to the reaction mixture. The reaction mixture was irradiated by UV light with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min to consume the unreacted SH groups. After UV irradiation, the obtained material was left in a fume hood overnight to roughly evaporate $CHCl_3$. The residue was dried at 70 ℃ under vacuum for at least 12 hours to afford the model compound. The obtained polymers (20 mg) were dissolved in $CDCl_3$ (600 μL), and the 500 MHz 2D ^{1}H-^{1}H NOESY-NMR spectrum of the solution was measured (mixing time = 200 ms).

10. DSC measurements

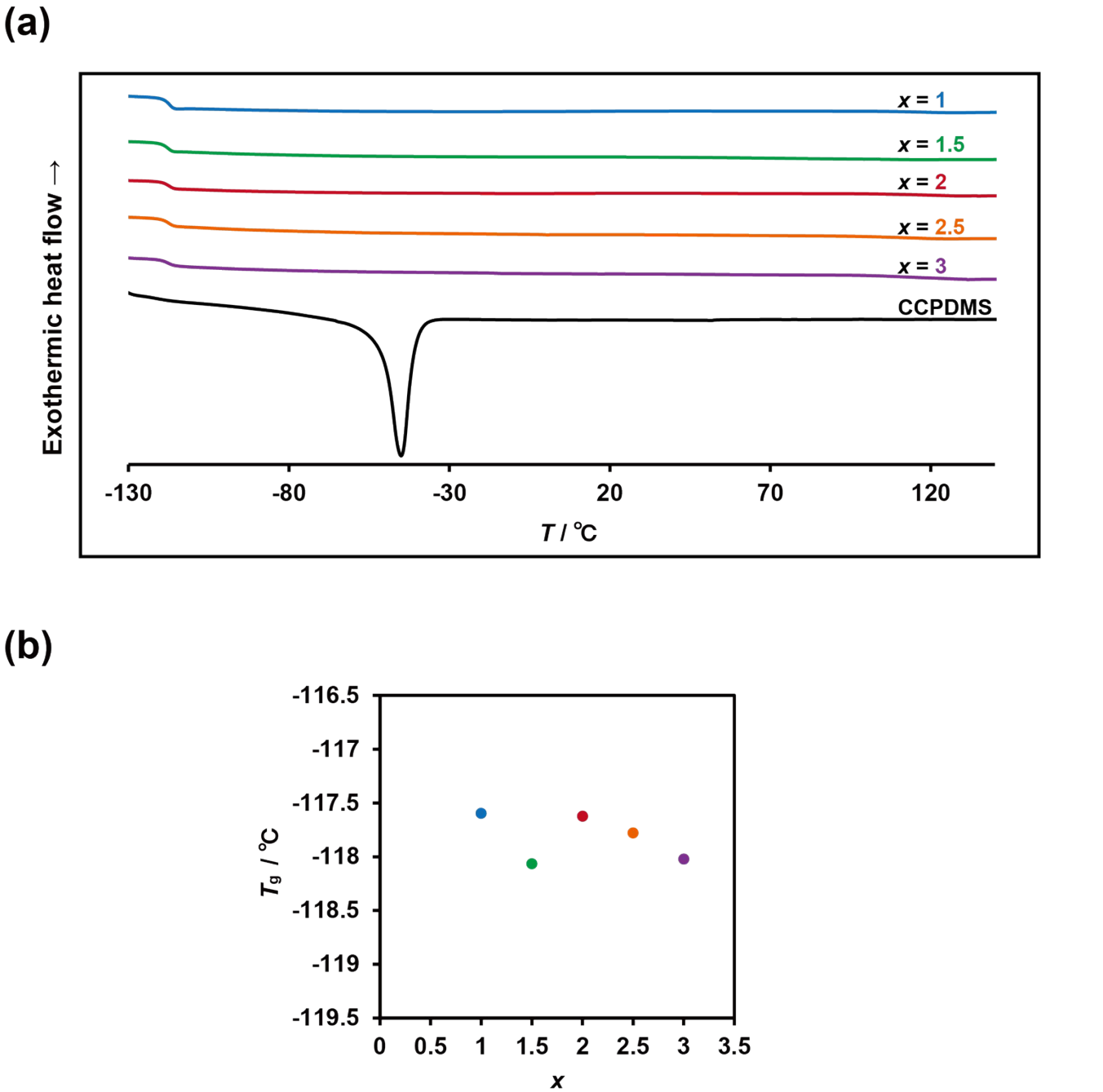


Fig. S14. **(a)** DSC thermograms of CCPDMS and PDMS-TAcγCD-Pen(x) on the second scan and **(b)** T_g versus the amount of TAcγCD (x = 1, 1.5, 2, 2.5, and 3).

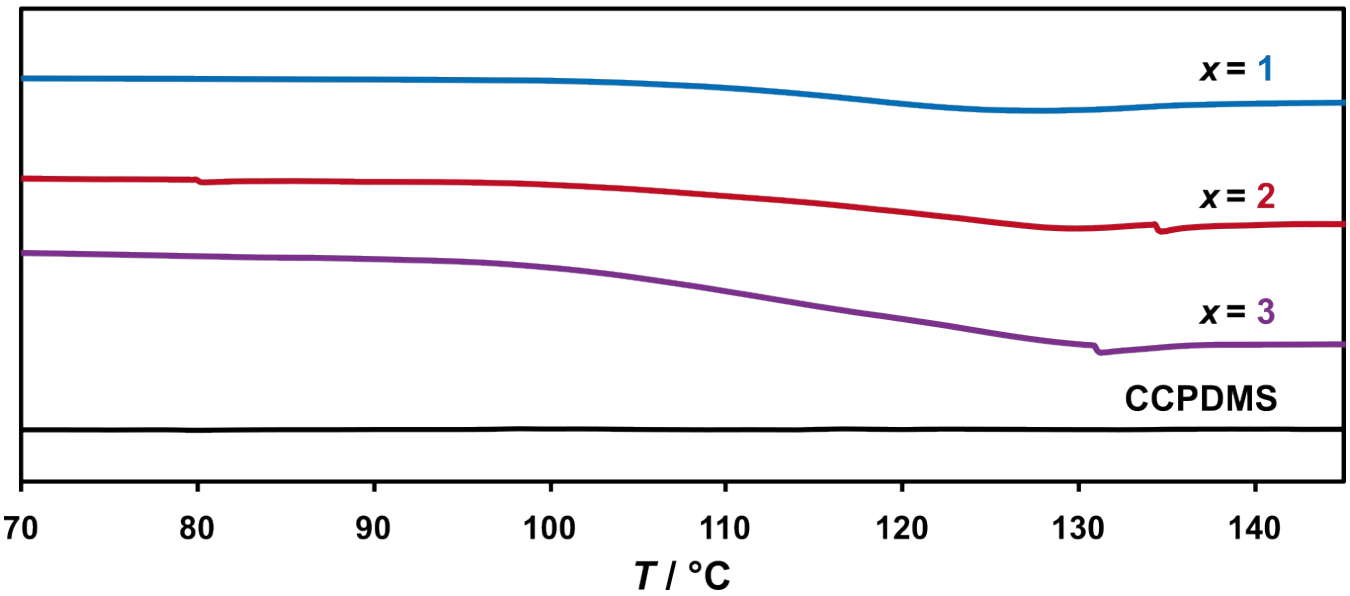


Fig. S15. Zoomed DSC thermograms of CCPDMS, PDMS-TAcγCD-Pen(1), PDMS-TAcγCD-Pen(2), and PDMS-TAcγCD-Pen(3) on the second scan.