

## - Supporting Information -

# Enhancement of the Mechanical Properties of Organic–Inorganic Hybrid Elastomers by Introducing Movable and Reversible Crosslinks

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## S1. Materials

Thiol-modified polydimethylsiloxane (PDMS-SH) was obtained from Shin-Etsu Chemical Co., Ltd. Triacetylated 6-arylamido methylether- $\gamma$ -cyclodextrin (TAc $\gamma$ CDAAmMe) was purchased from Kyoisha Chemical Co., Ltd. Allyl alcohol and ethyl acetate were purchased from FUJIFILM Wako Pure Chemical Corporation. 2-Hydroxy-2-methylpropiophenone (IRGACURE® 1173) was purchased from Sigma–Aldrich Co. Ethyl acrylate (EA) and 2-hydroxyethyl methacrylate were purchased from Nacalai Tesque, Inc. Dodecyl Acrylate (DA) and phenylbis(2, 4, 6-trimethylbenzoyl)phosphine oxide were purchased from Tokyo Chemical Industry Co., Ltd. Deuterated chloroform (CDCl<sub>3</sub>) was purchased from Eurisotop.

## S2. Measurements

**Nuclear magnetic resonance (NMR) spectroscopy:** <sup>1</sup>H NMR spectra were recorded at 400 MHz with a JEOL ECS-400 NMR spectrometer at 25 °C. Chemical shift values were referenced to the CHCl<sub>3</sub> value ( $\delta = 7.26$  ppm) for <sup>1</sup>H NMR.

**Gel permeation chromatography (GPC):** Number-average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and molecular weight distribution ( $M_w/M_n$ ) were measured by GPC in THF at 40 °C with two columns (Tosoh TSK gel SuperH<sub>Z</sub>M-N  $\times$ 2). The molecular weights of the samples were calculated based on calibration curve got by polystyrene standards.

**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 mm  $\times$  5 mm  $\times$  0.3 mm) were used for the tensile test. 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.

**Stress relaxation test:** Stress relaxation tests were performed using an Autograph AG-X plus (Shimadzu Co.). The test pieces were stretched until 200%. Then, the strain was held, and the stress was recorded for 1000 seconds.

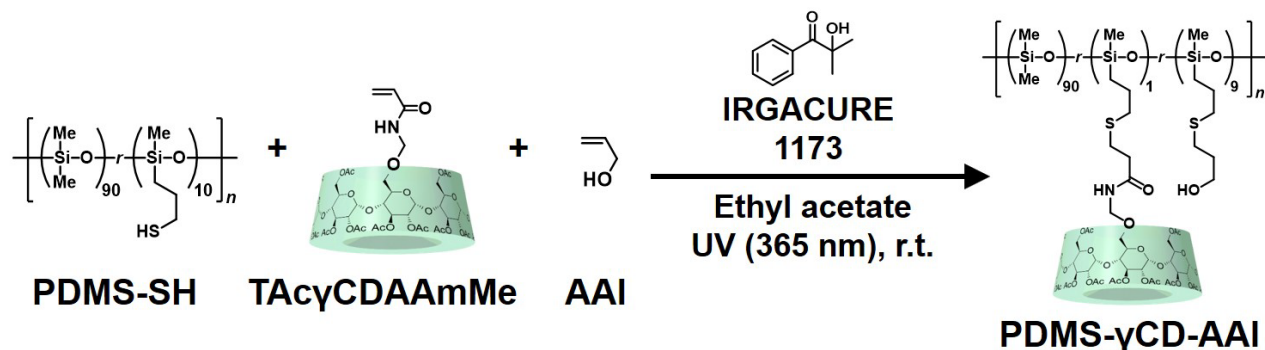
**Differential scanning calorimetry (DSC):** The glass transition temperature ( $T_g$ ) of the polymers was measured by a DSC machine under a  $N_2$  atmosphere (DSC 7020, Hitachi High-tech Corporation). Thermal transitions were measured in the temperature range of -140 to 200 °C heated 10 °C/min.

**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  $q = 4\pi\sin\theta/\lambda$  ( $2\theta$  and  $\lambda$  are the scattering angle and the wavelength, respectively).

**Cyclic tensile test:** Cyclic tensile tests were performed using an Autograph AG-X plus (Shimadzu Co.). The test pieces 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**.

**Fourier transform infrared (FT-IR) spectroscopy:** IR measurements of samples were performed at BL43IR in SPring-8, Nishiharima, Japan, with a Vertex70 FTIR spectrometer and a Hyperion 2000 infrared microscope from Bruker. The number of scans is 200, and the resolution is 4  $cm^{-1}$ .

### S3. Preparation of PDMS- $\gamma$ CD-AAI



Scheme S1. Preparation of PDMS- $\gamma$ CD-AAI.

PDMS-SH (4500 mg, SH group: 5.6 mmol, 10 eq.), TAc $\gamma$ CDAAmMe (1300 mg, 0.55 mmol, 1 eq.), allyl alcohol (290 mg, 5.0 mmol, 9 eq.), and IRGACURE 1173 (92 mg, 0.56 mmol, 1 eq.) were dissolved in ethyl acetate (20 mL). The solution was irradiated by UV light with a high-pressure Hg lamp ( $\lambda = 253$  and 365 nm) for 2 hours. Some PDMS- $\gamma$ CD-AAI would be connected to each other by the movable crosslink of CDs and did not completely dissolve in tetrahydrofuran (THF). Therefore, we evaluated by the eluted polymer chains in THF.

The number average molecular weight ( $M_n$ ) and the weight average molecular weight ( $M_w$ ) of PDMS- $\gamma$ CD-AAI were  $2.4 \times 10^4$  g/mol and  $3.0 \times 10^4$  g/mol, respectively. The  $M_w/M_n$  of PDMS- $\gamma$ CD-AAI was 1.24 (Fig. S2). Those values were smaller than the exception based on the molecular weights and polydispersity of thiol-modified poly(dimethyl siloxane) (PDMS-SH) as reported previously. In previous work<sup>42</sup>, the  $M_n$  and  $M_w$  of PDMS-SH were  $4.1 \times 10^4$  g/mol and  $1.1 \times 10^5$  g/mol, respectively. The  $M_w/M_n$  of PDMS-SH was 2.7, which were evaluated by GPC. The converted molecular weight of PDMS- $\gamma$ CD-AAI is  $5.6 \times 10^4$  g/mol, which estimated from the  $M_n$  of PDMS-SH. We considered that only the low molecular weight component in PDMS- $\gamma$ CD-AAI have eluted in THF.

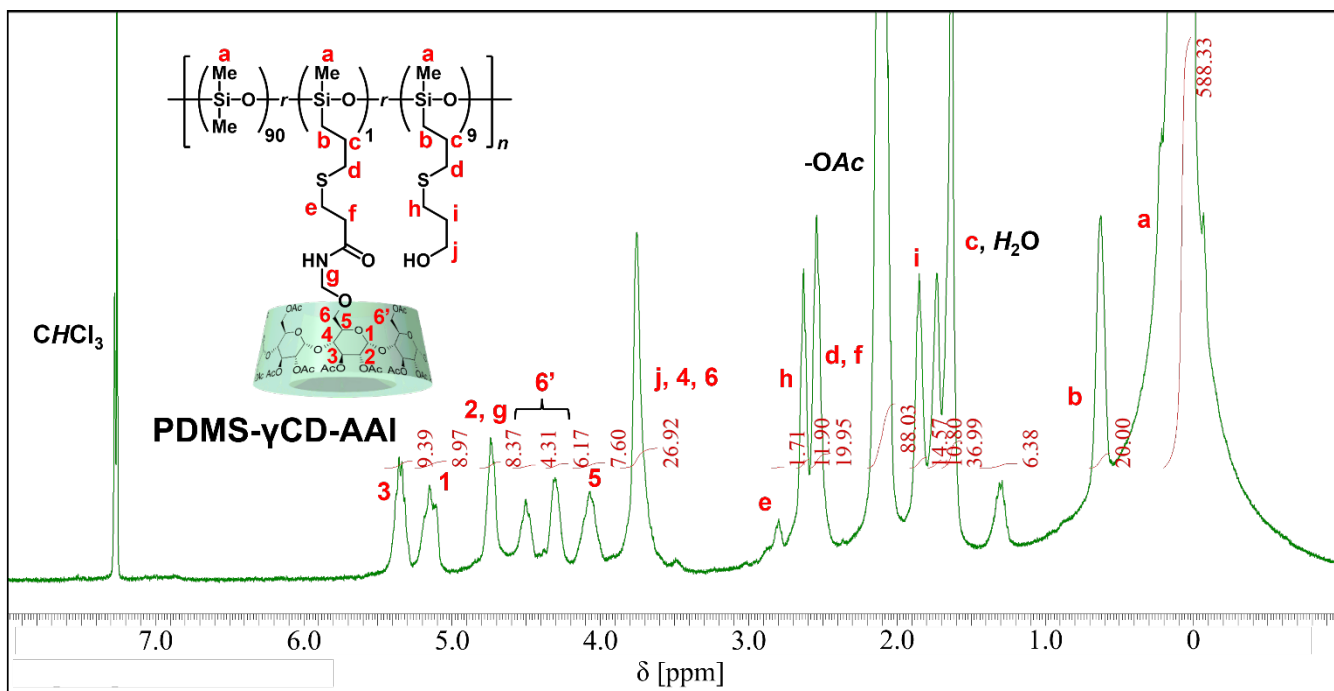
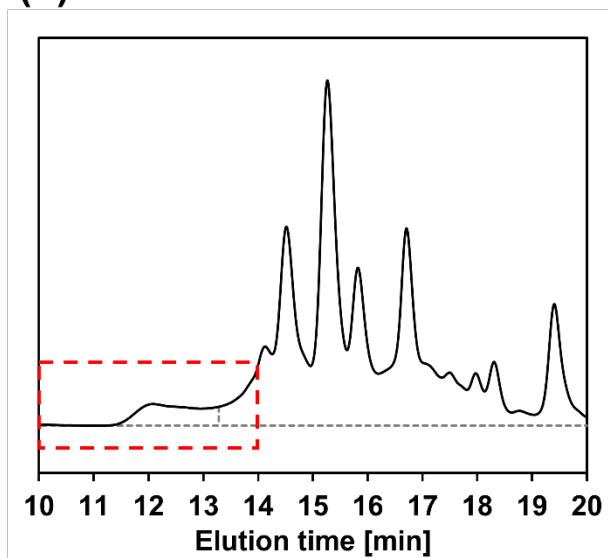


Fig. S1.  $^1\text{H}$  NMR spectrum of PDMS- $\gamma$ CD-AAI ( $\text{CDCl}_3$ , 400 MHz, 25  $^\circ\text{C}$ ).

(a)



(b)

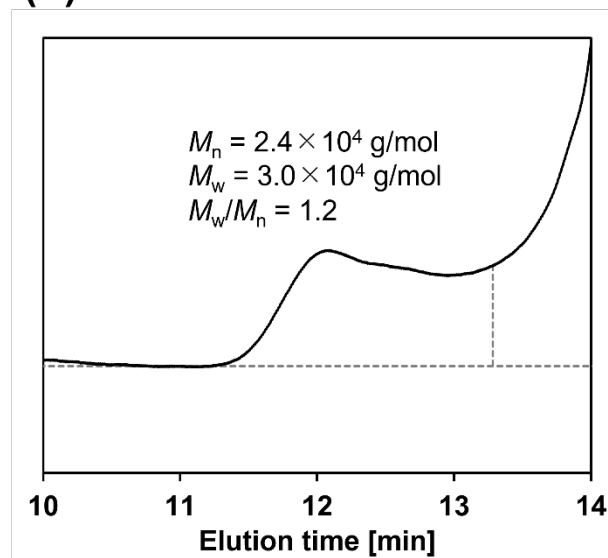
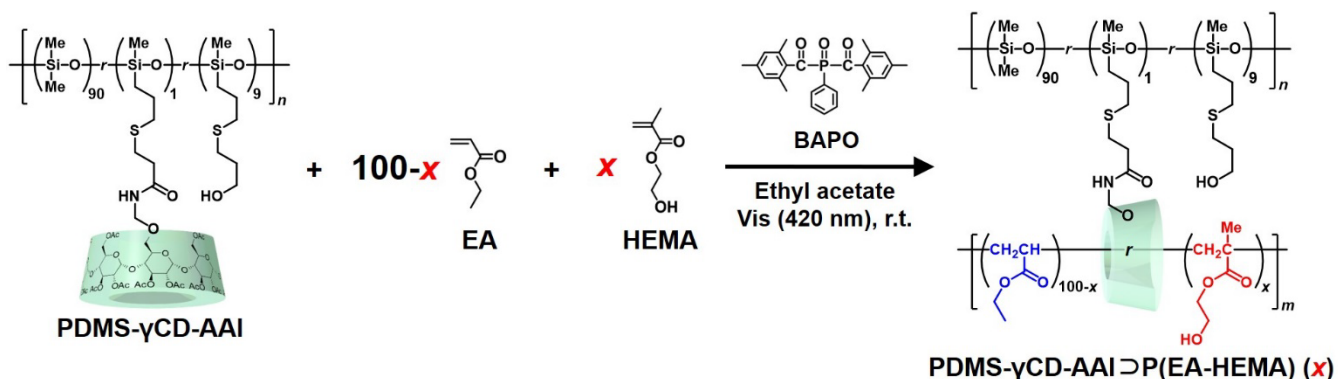


Fig. S2. (a) GPC chart of PDMS- $\gamma$ CD-AAI. (b) The enlarged chart of the red dashed line in the Fig. S2a.

#### S4. Preparation of PDMS- $\gamma$ CD-AAI $\supset$ P(EA-HEMA) ( $x$ )



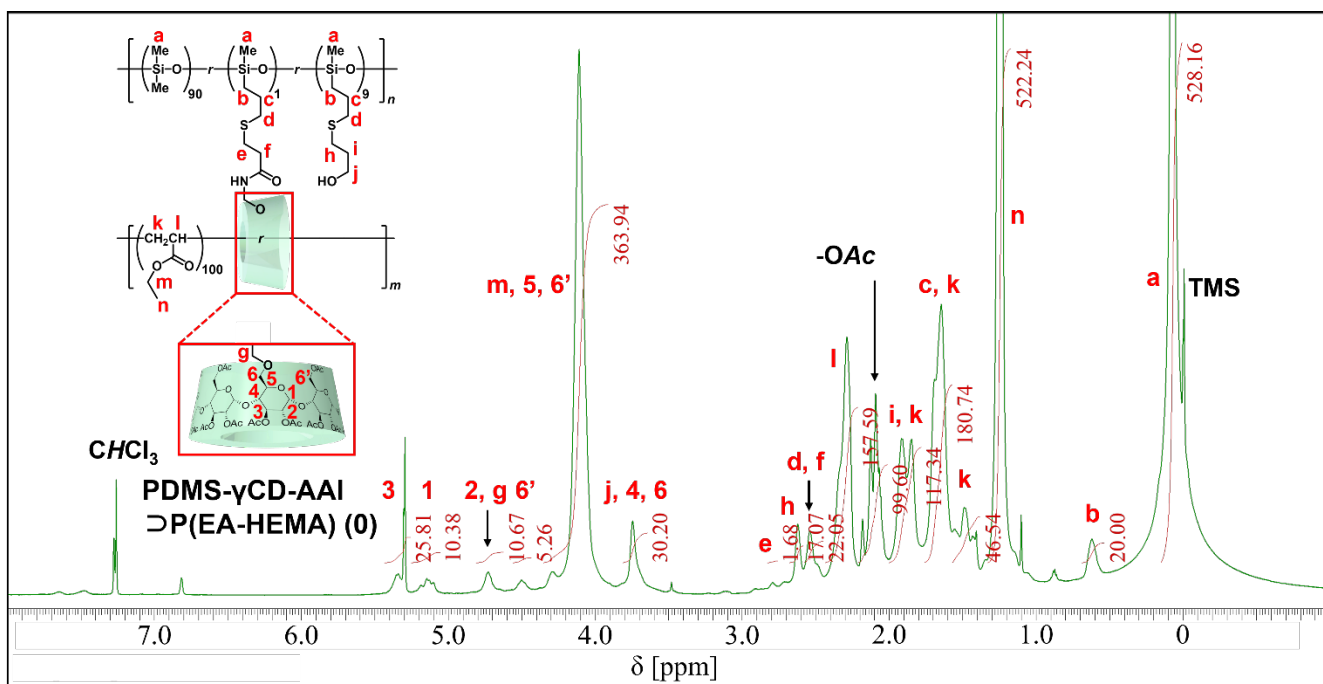
**Scheme S2.** Preparation of PDMS- $\gamma$ CD-AAI $\supset$ P(EA-HEMA) ( $x$ ).

EA, HEMA, and BAPO were added to ethyl acetate solution of PDMS- $\gamma$ CD-AAI (2400 mg, including 450 mg of PDMS- $\gamma$ CD-AAI). The solution was irradiated by visible light with a LED ( $\lambda = 420$  nm) for 1 hour. The products were dried at r.t. for 24 hours and then at 80 °C in vacuum for 24 hours. Table S1 summarize amounts of reagents in the reactions.

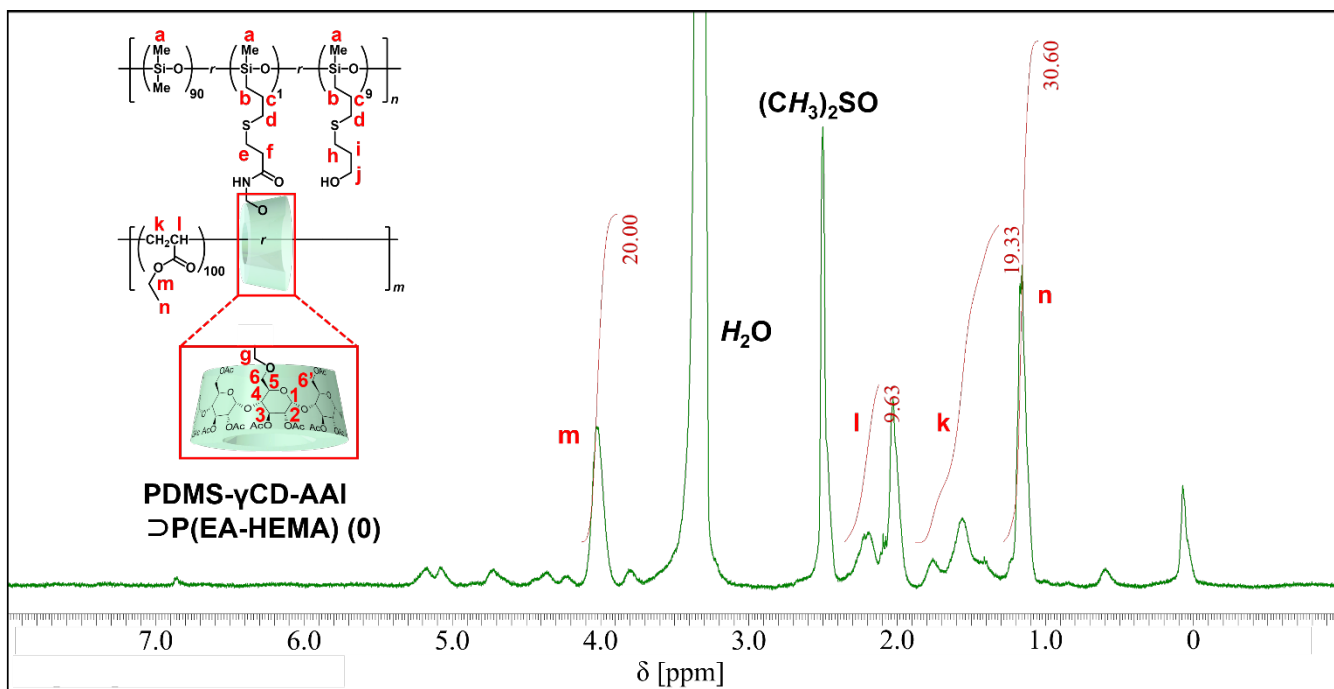
**Table S1.** Amount of each reagent for PDMS- $\gamma$ CD-AAI $\supset$ P(EA-HEMA) ( $x$ ).

$x$ [mol%]	EA		HEMA		BAPO	
	[mg]	[mmol]	[mg]	[mmol]	[mg]	[mmol]
0	450	4.5	0	0	9.4	0.022
20	340	3.4	110	0.85	8.9	0.021
43	230	2.3	230	1.8	8.3	0.020
70	110	1.1	340	2.6	7.8	0.019
100	0	0	450	3.5	7.2	0.017

(a)



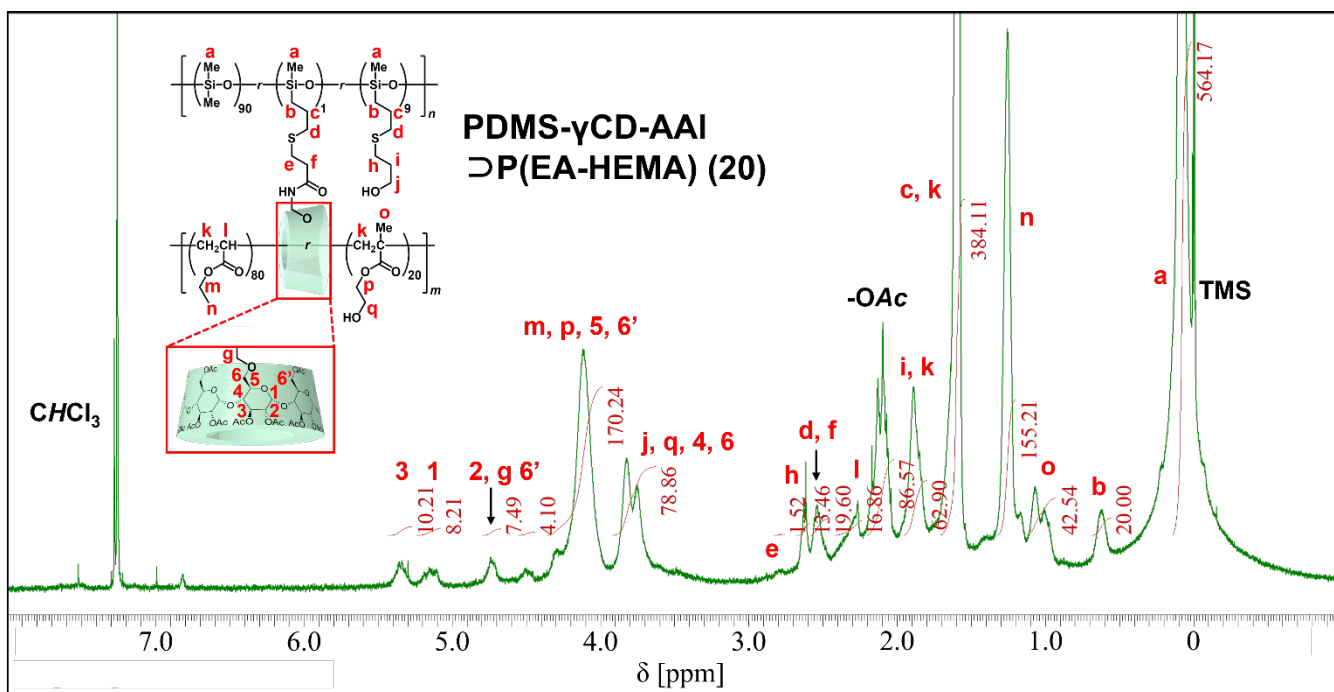
(b)



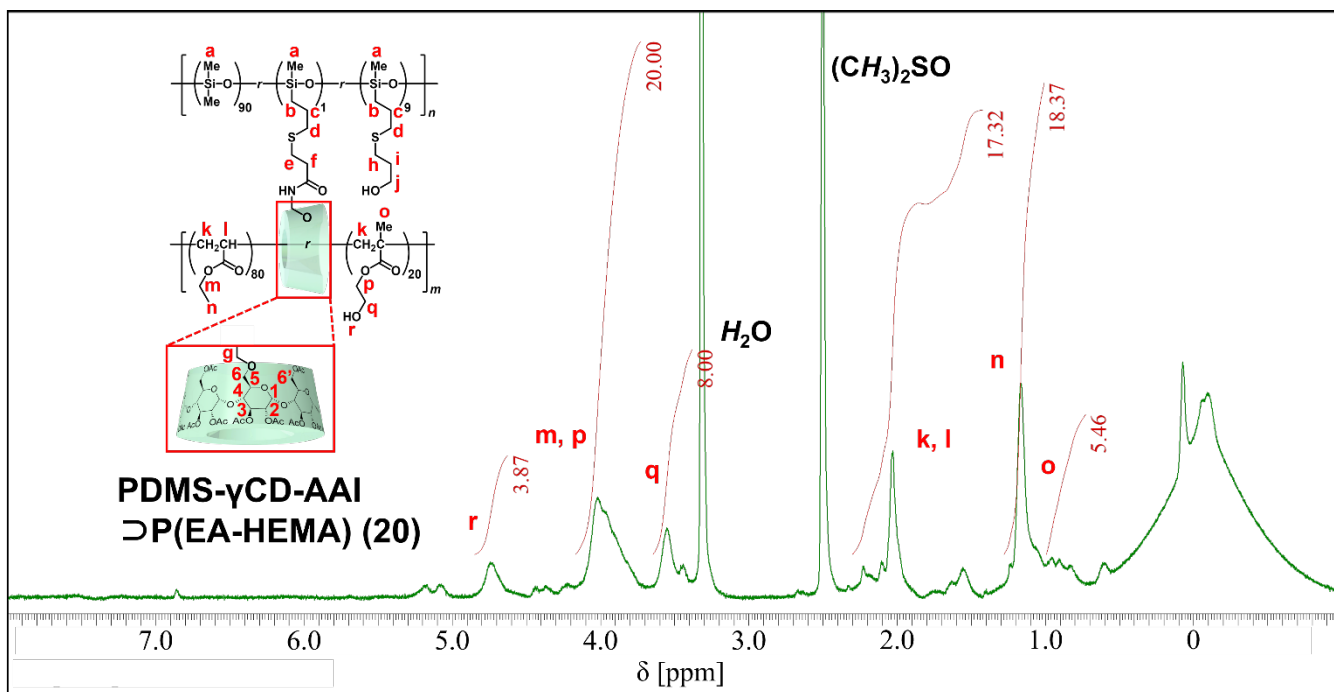
**Fig. S3.**  $^1\text{H}$  NMR spectrum of PDMS- $\gamma$ -CD-AAI  $\supset$  P(EA-HEMA) (0) in (a)  $\text{CDCl}_3$  and (b)  $\text{DMSO-}d_6$  (400 MHz, 25  $^\circ\text{C}$ ).



(a)

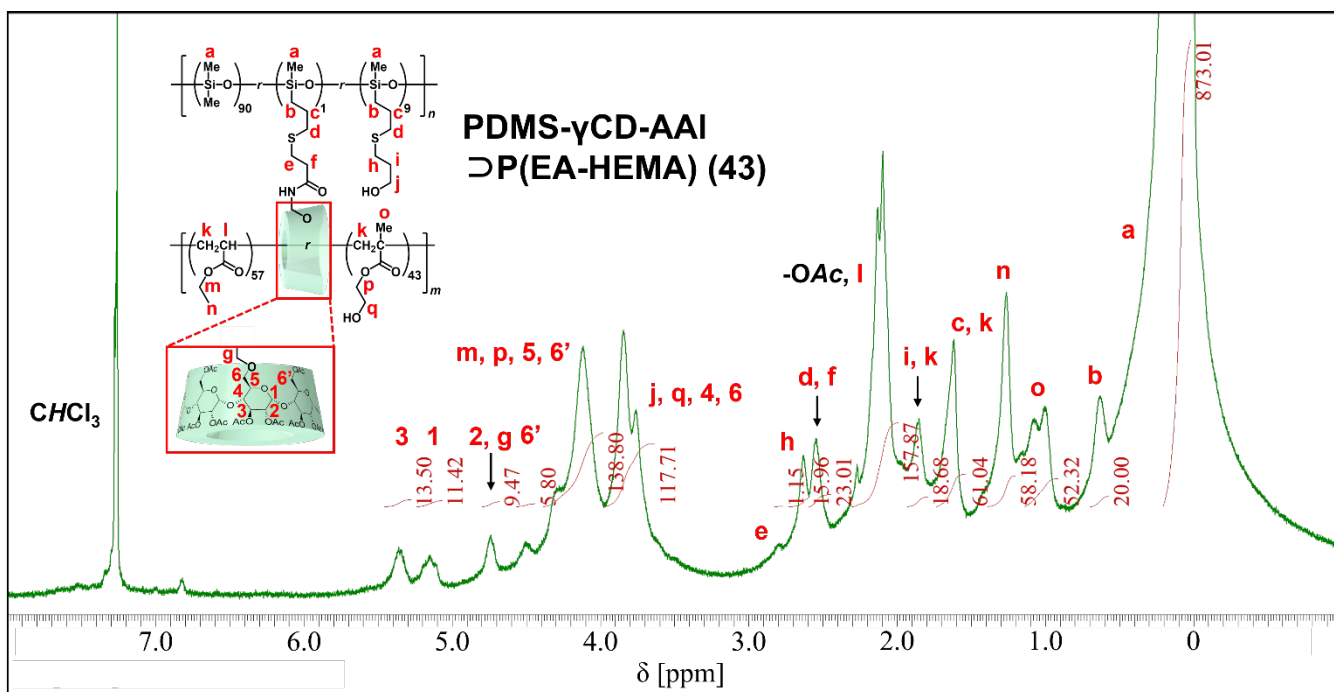


(b)

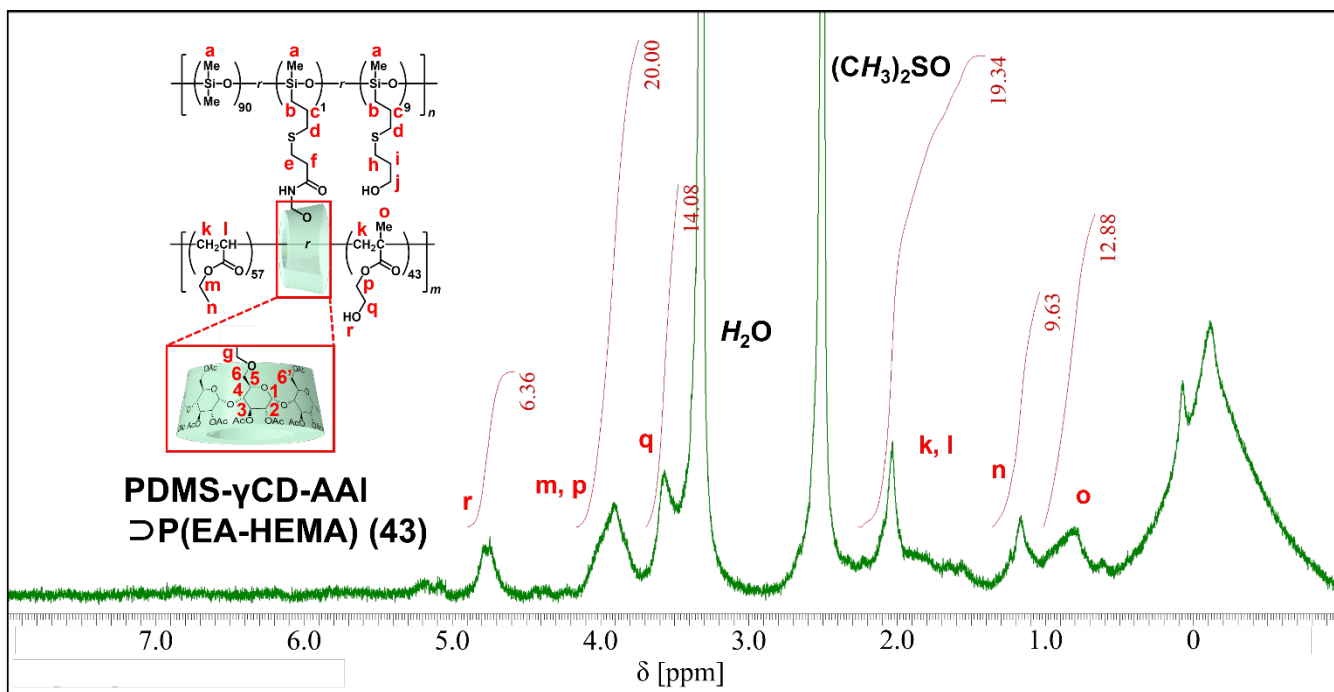


**Fig. S4.** <sup>1</sup>H NMR spectrum of PDMS- $\gamma$ CD-AAI $\supset$ P(EA-HEMA) (20) in (a) CDCl<sub>3</sub> and (b) DMSO-*d*<sub>6</sub> (400 MHz, 25 °C).

(a)



(b)



**Fig. S5.**  $^1\text{H}$  NMR spectrum of PDMS- $\gamma$ CD-AAI-gP(EA-HEMA) (43) in (a)  $\text{CDCl}_3$  and (b)  $\text{DMSO-}d_6$  (400 MHz, 25  $^\circ\text{C}$ ).

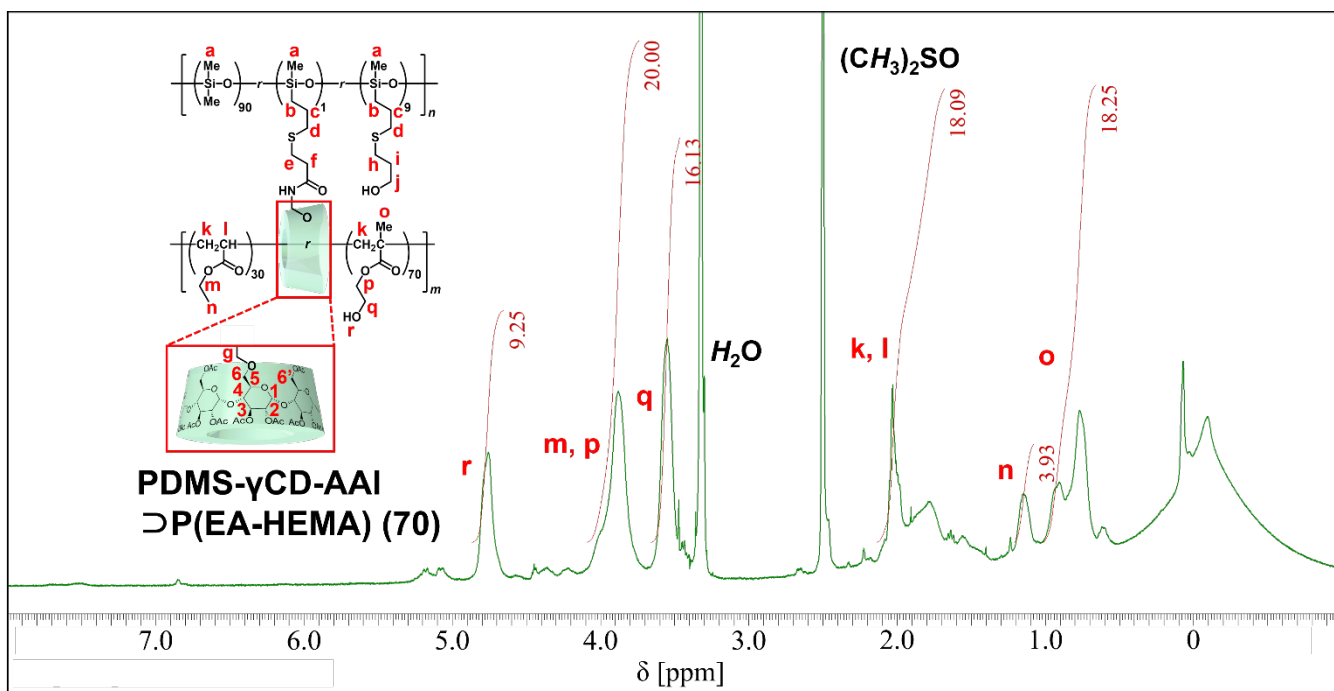


Fig. S6.  $^1\text{H}$  NMR spectrum of PDMS- $\gamma$ CD-AAI-P(EA-HEMA) (70) (DMSO- $d_6$ , 400 MHz, 25  $^\circ\text{C}$ ).

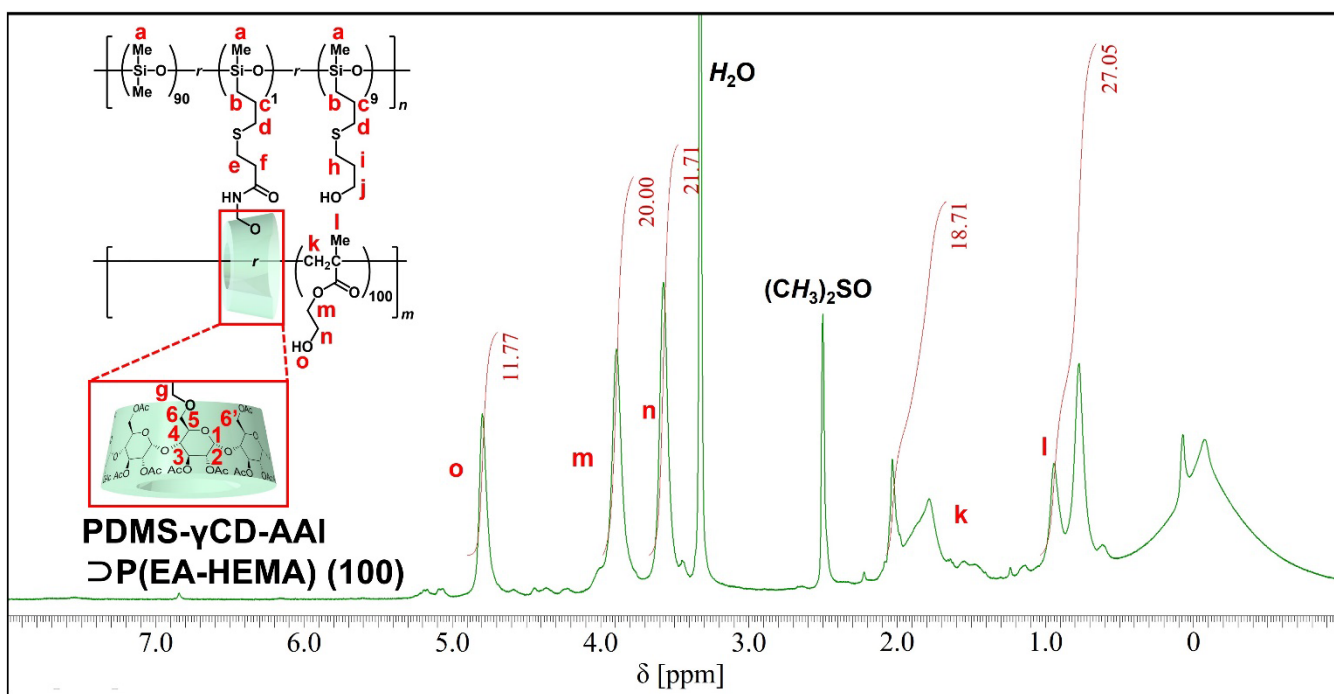
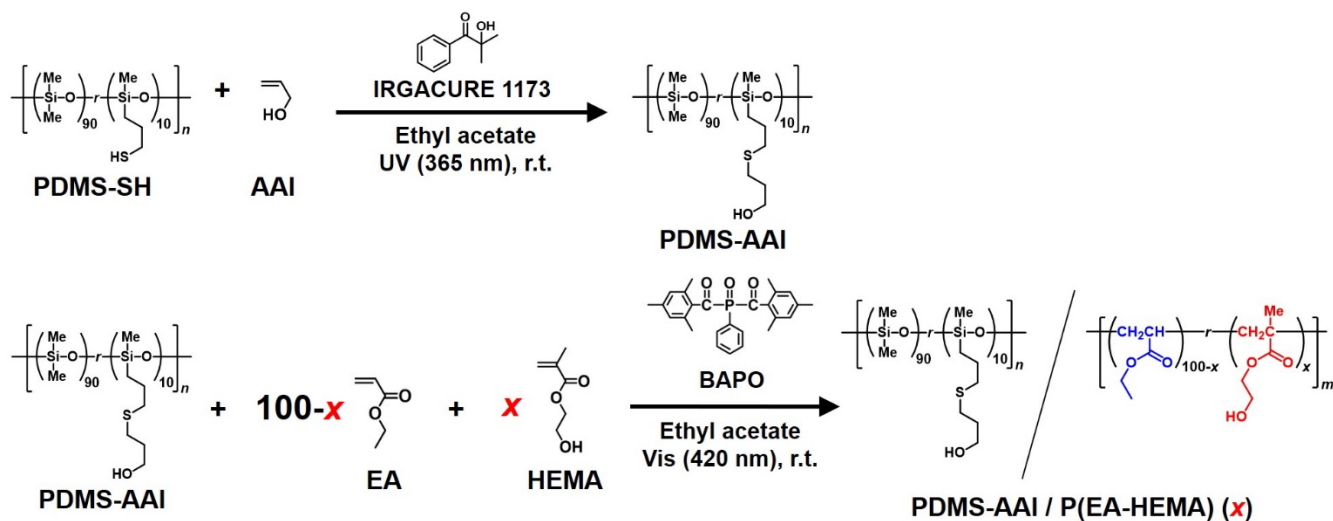


Fig. S7.  $^1\text{H}$  NMR spectrum of PDMS- $\gamma$ CD-AAI-P(EA-HEMA) (100) (DMSO- $d_6$ , 400 MHz, 25  $^\circ\text{C}$ ).

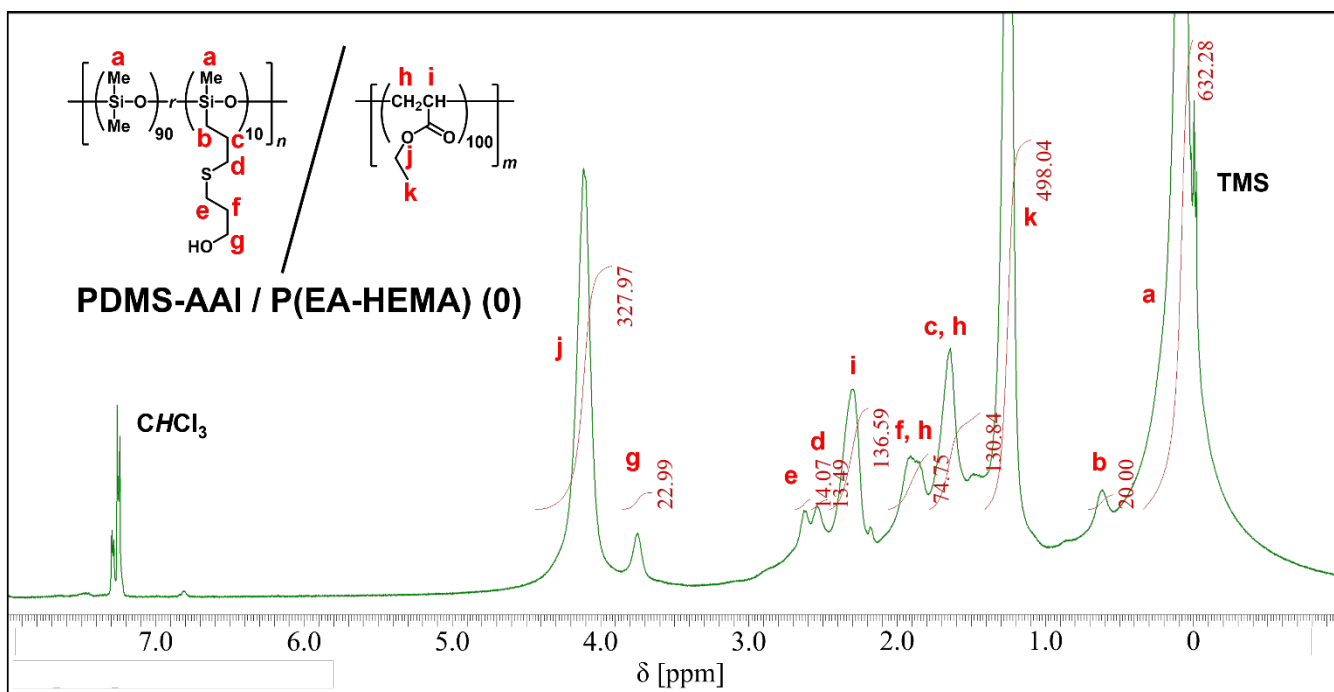
## S5. Preparation of PDMS-AAI and P(EA-HEMA) blend



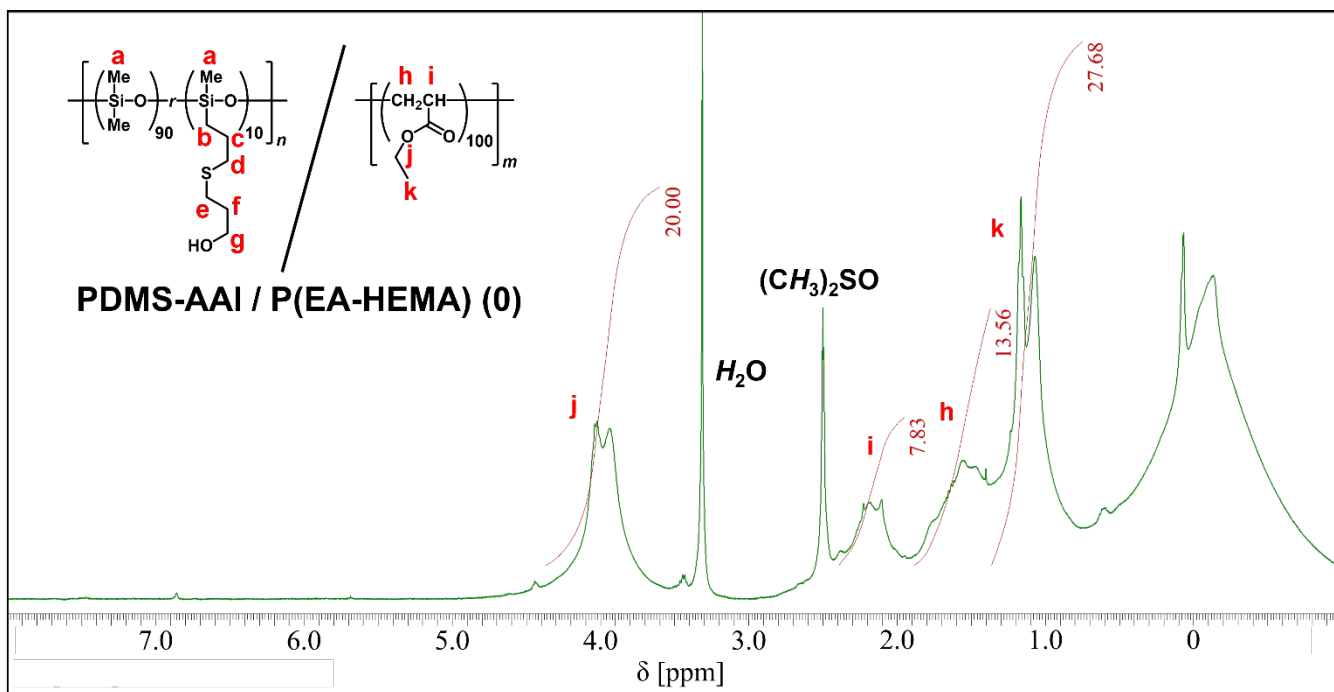
**Scheme S3.** Preparation of PDMS-AAI / P(EA-HEMA) (x).

PDMS-SH (4500 mg, SH group: 5.6 mmol, 10 eq.), allyl alcohol (330 mg, 5.7 mmol, 10 eq.), and IRGACURE 1173 (92 mg, 0.56 mmol, 1 eq.) were dissolved in ethyl acetate (20 mL). The solution was irradiated by UV light with a high-pressure Hg lamp (the dominant wavelength,  $\lambda = 253$  and 365 nm) for 2 hours. The exposure energy is 2.05 mW/cm<sup>2</sup> at  $\lambda = 365$  nm. EA, HEMA, and BAPO were added to obtained ethyl acetate solution of PDMS-AAI (2400 mg, including 450 mg of PDMS-AAI). The solution was irradiated by visible light with a LED ( $\lambda = 420$  nm) for 1 hour. The products were dried at r.t. for 24 hours and then at 80 °C in vacuum for 24 hours. Table S1 summarize amounts of reagents in the reactions.

(a)

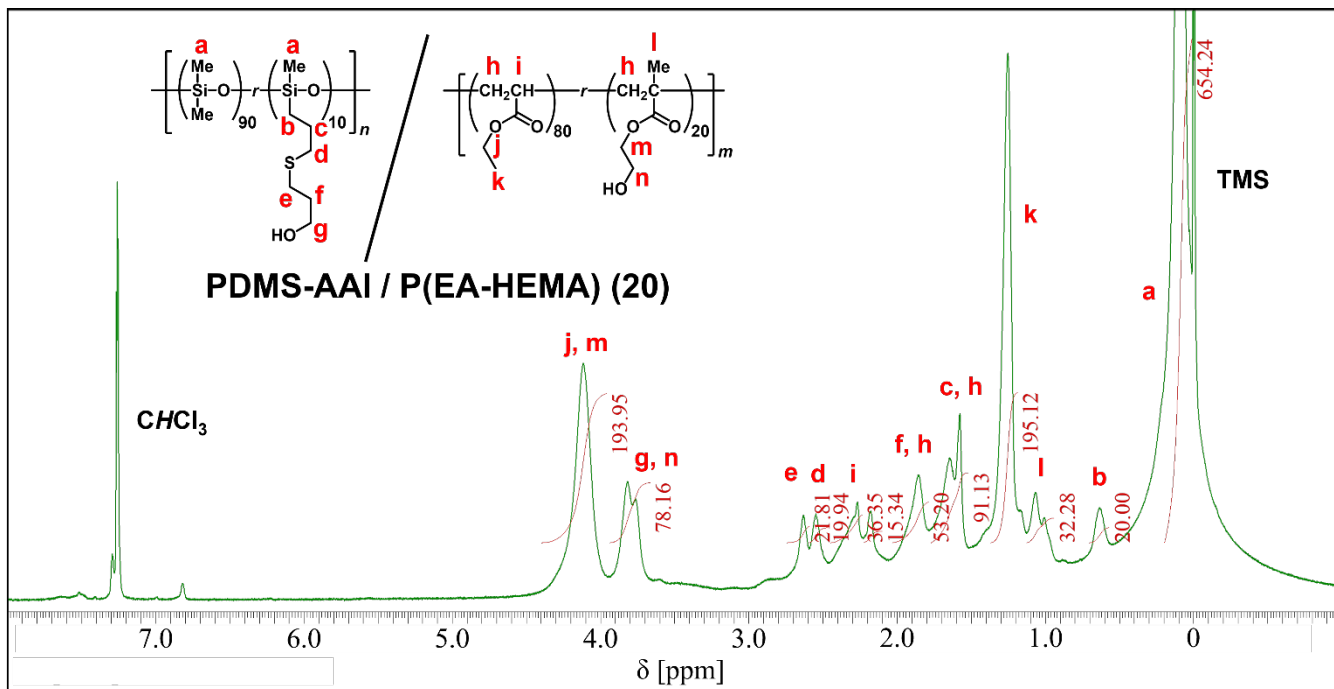


(b)

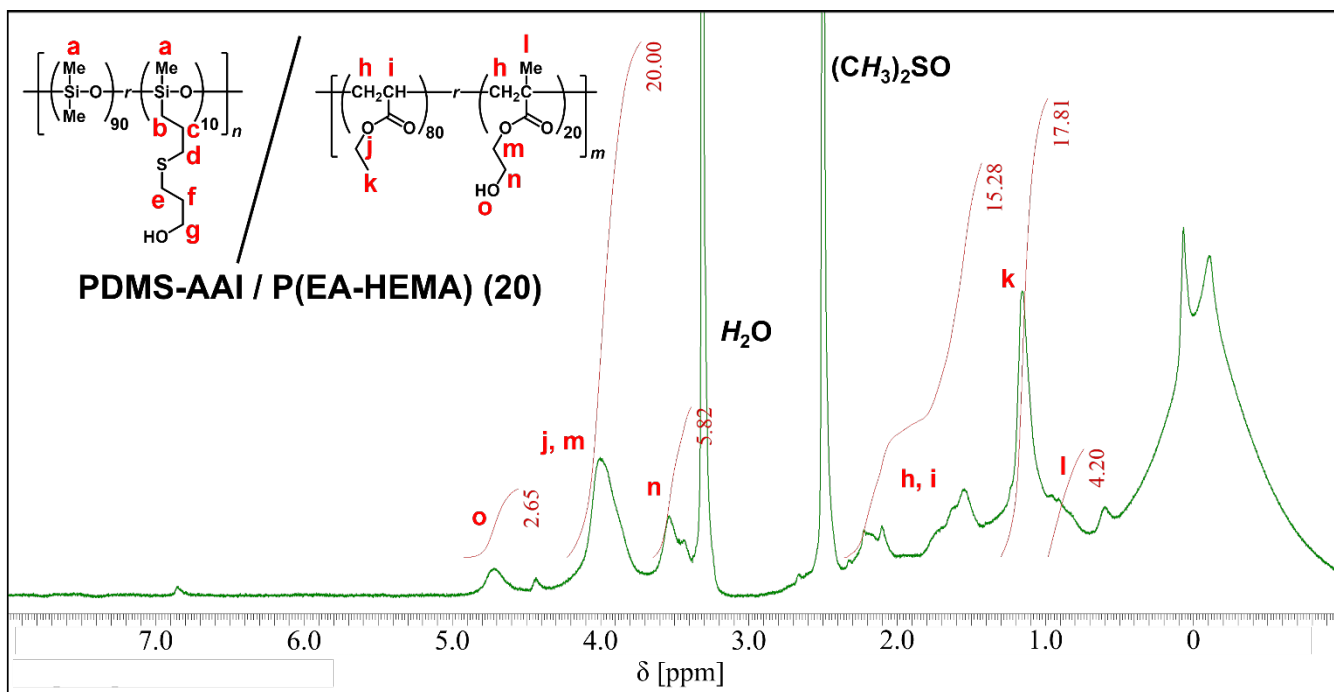


**Fig. S8.**  $^1\text{H}$  NMR spectrum of PDMS-AAI / P(EA-HEMA) (0) in (a)  $\text{CDCl}_3$  and (b)  $\text{DMSO-}d_6$  (400 MHz,  $25^\circ\text{C}$ ).

(a)

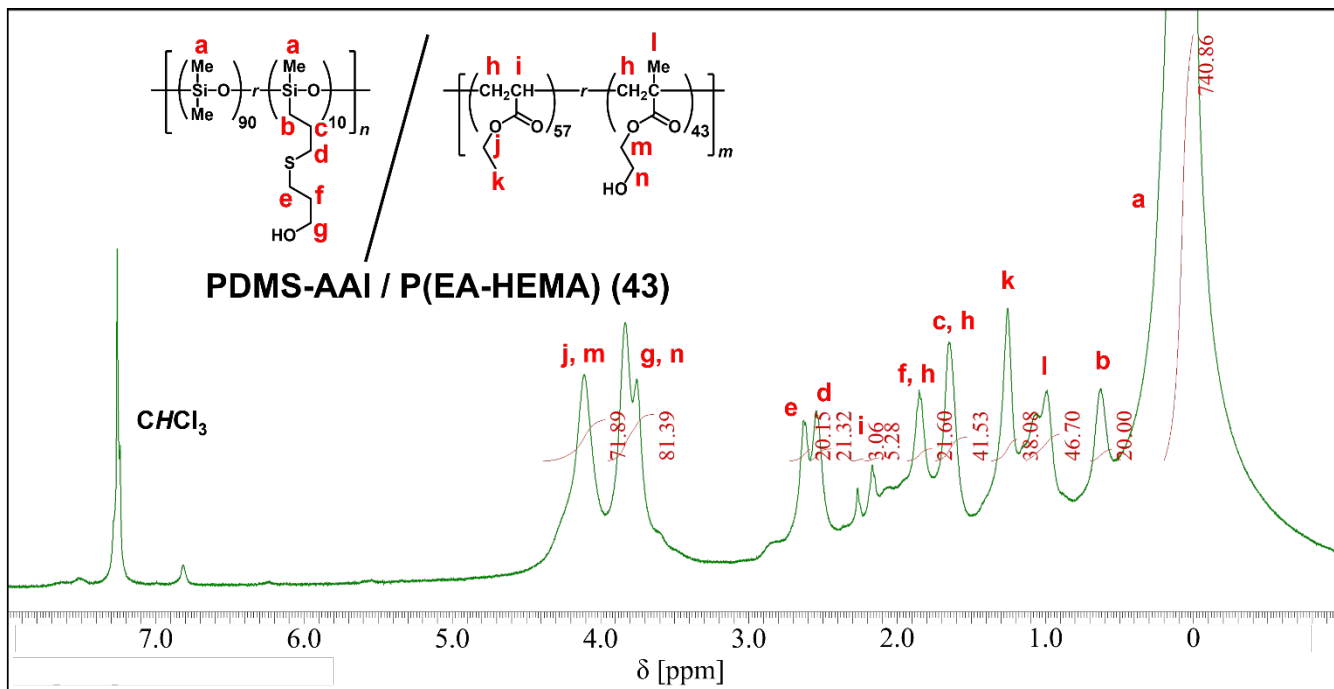


(b)

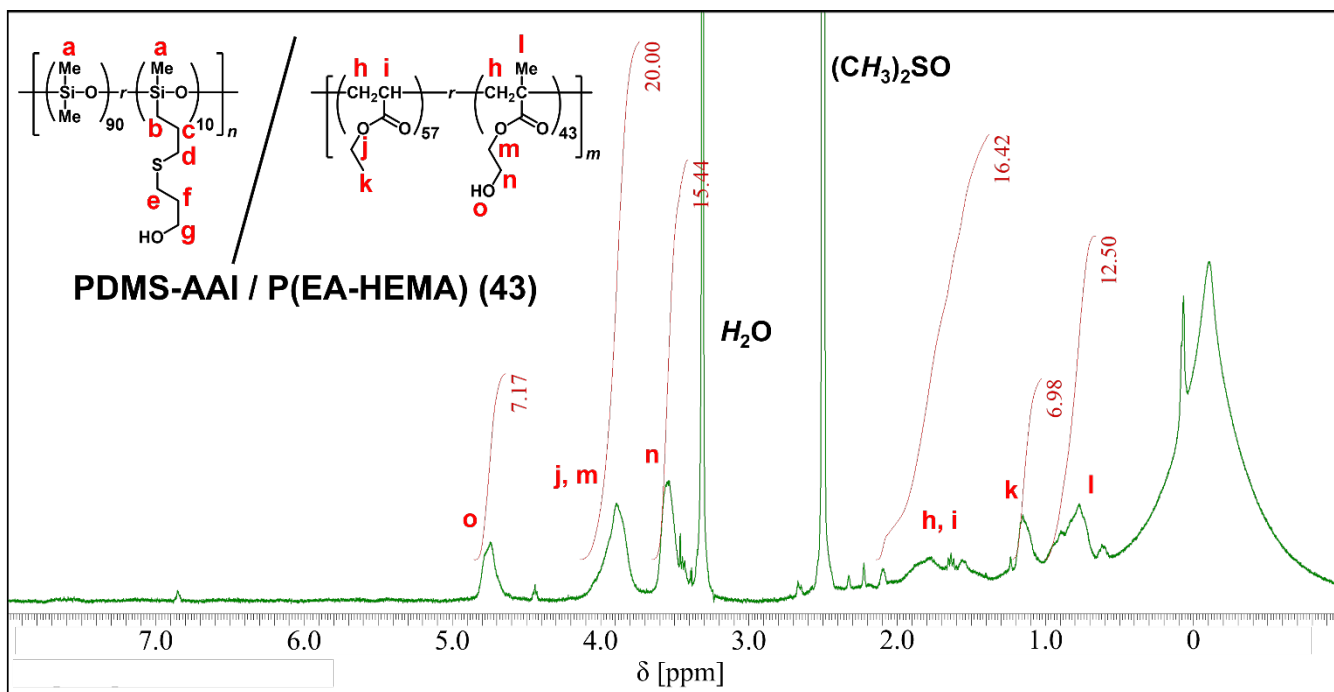


**Fig. S9.**  $^1\text{H}$  NMR spectrum of PDMS-AAI / P(EA-HEMA) (20) in (a)  $\text{CDCl}_3$  and (b)  $\text{DMSO-}d_6$  (400 MHz, 25 °C).

(a)



(b)



**Fig. S10.**  $^1\text{H}$  NMR spectrum of PDMS-AAI / P(EA-HEMA) (43) in (a)  $\text{CDCl}_3$  and (b)  $\text{DMSO-}d_6$  (400 MHz, 25 °C).

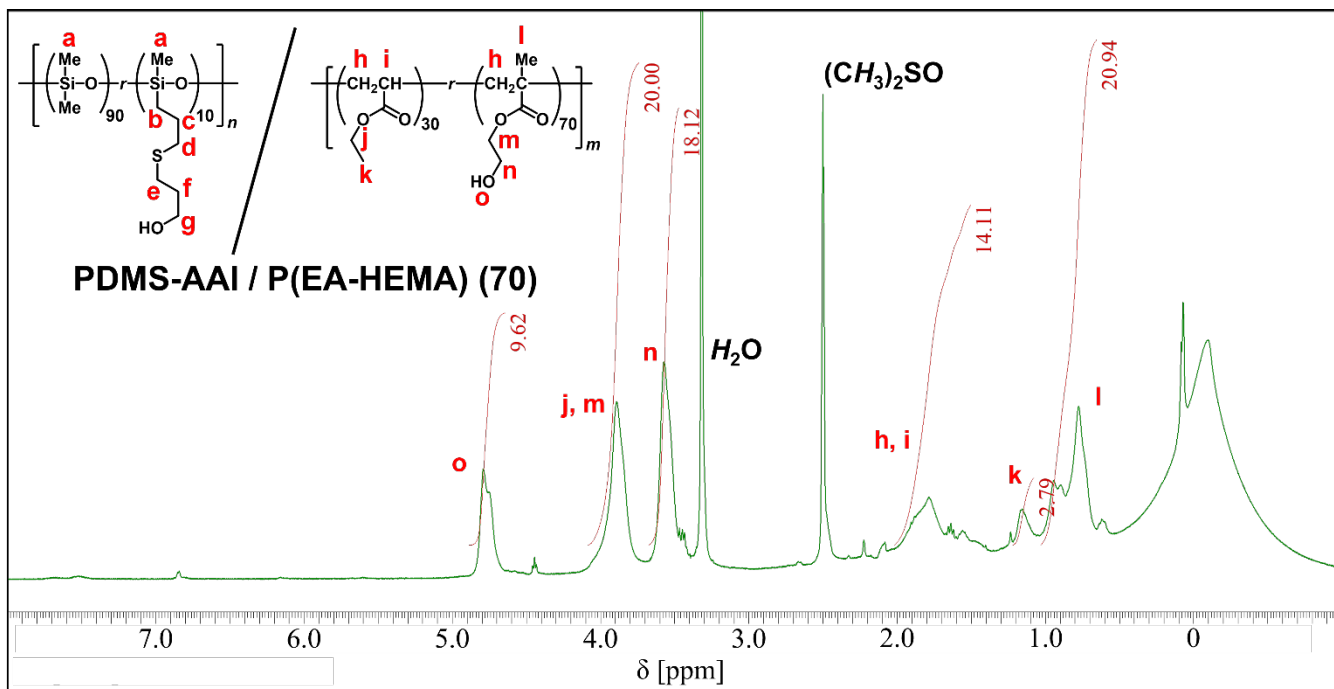


Fig. S11.  $^1\text{H}$  NMR spectrum of PDMS-AAI / P(EA-HEMA) (70) (DMSO- $d_6$ , 400 MHz, 25 °C).

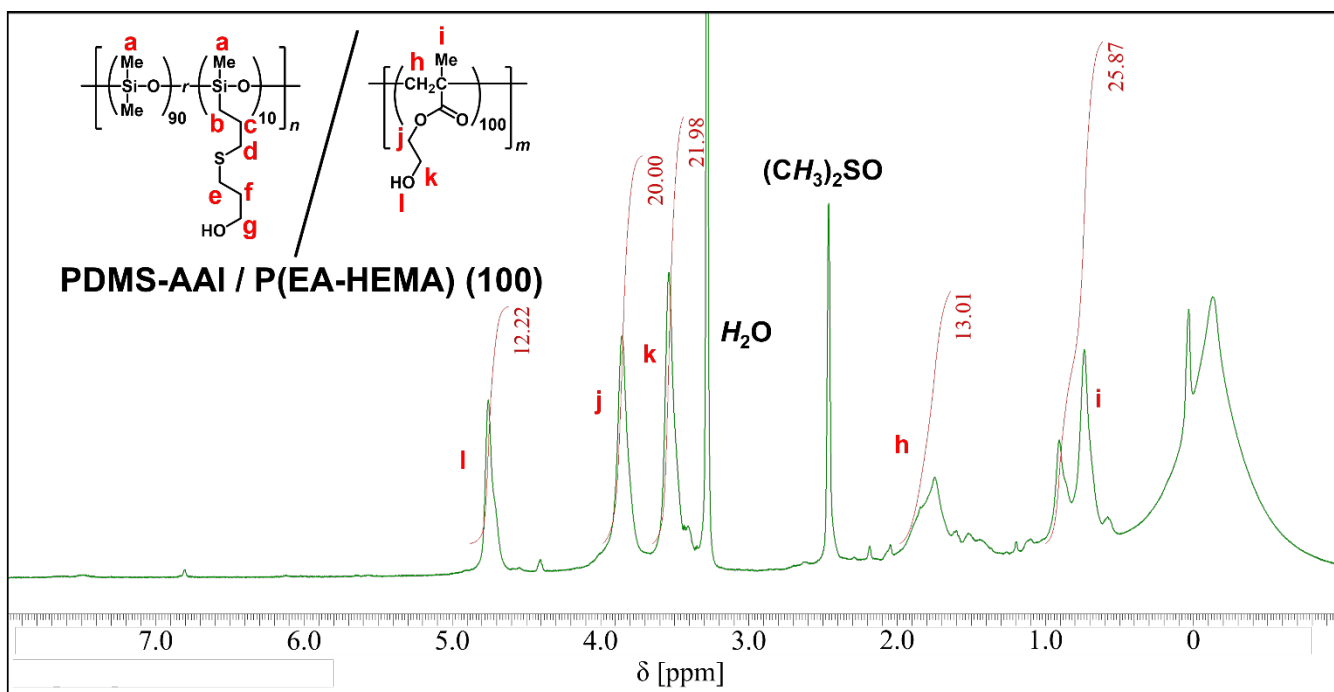
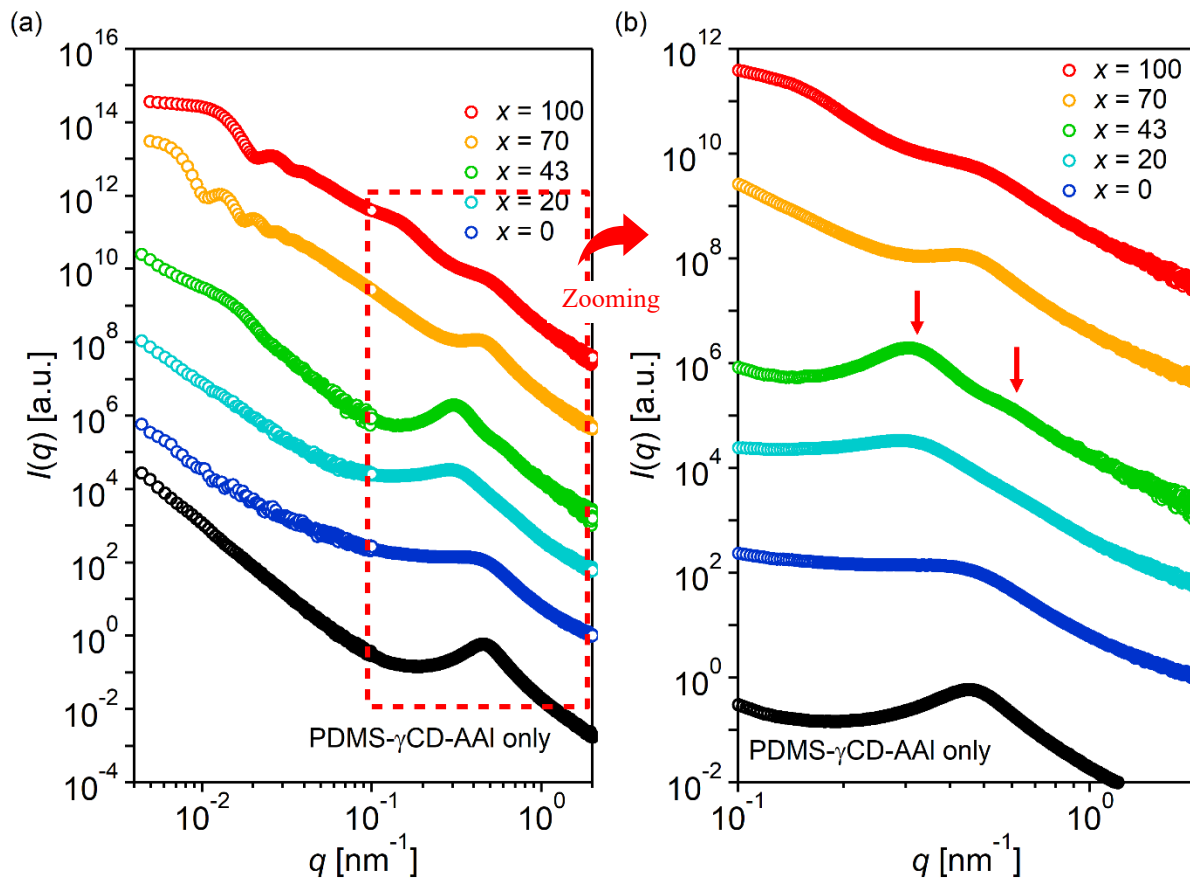


Fig. S12.  $^1\text{H}$  NMR spectrum of PDMS-AAI / P(EA-HEMA) (100) (DMSO- $d_6$ , 400 MHz, 25 °C).



## S6. USAXS and SAXS

**Fig. S13a** shows USAXS and SAXS profiles of PDMS- $\gamma$ CD-AAI added to **Fig. 3a**. The peaks at  $q = 0.45 \text{ nm}^{-1}$  is attributed to the correlation distance of aggregated  $\gamma$ CD in PDMS as reported in our previous study. We considered that the scattering from the phase-separated structure of PDMS and acrylate polymers was observed at the same  $q$  value as the scattering from the  $\gamma$ CD aggregation. Considering the volume of scatters, the scattering from phase-separated structures concealed the scattering from the aggregation of  $\gamma$ CD. This hypothesis is supported by the two peaks in the SAXS profile at  $x = 43$  as shown in **Fig. S13b** (red arrows) and the scattering from the phase-separated structure of PDMS and acrylate copolymer at  $q = 0.4 \text{ nm}^{-1}$ , observed in PDMS-AAI/P(EA-HEMA) without movable crosslinks too as shown in **Fig. 3b**.



**Fig. S13. (a)** USAXS and SAXS profiles of PDMS- $\gamma$ CD-AAI added to **Fig. 3a**. **(b)** Enlarged profiles of the red dashed line in the **Fig. S12a**.

The domain size of the phase-separated structure of PDMS- $\gamma$ CD-AAI $\supset$ P(EA-HEMA) ( $x$ ) and PDMS- $\gamma$ CD-AAI/P(EA-HEMA) ( $x$ ) was estimated as the following equation.

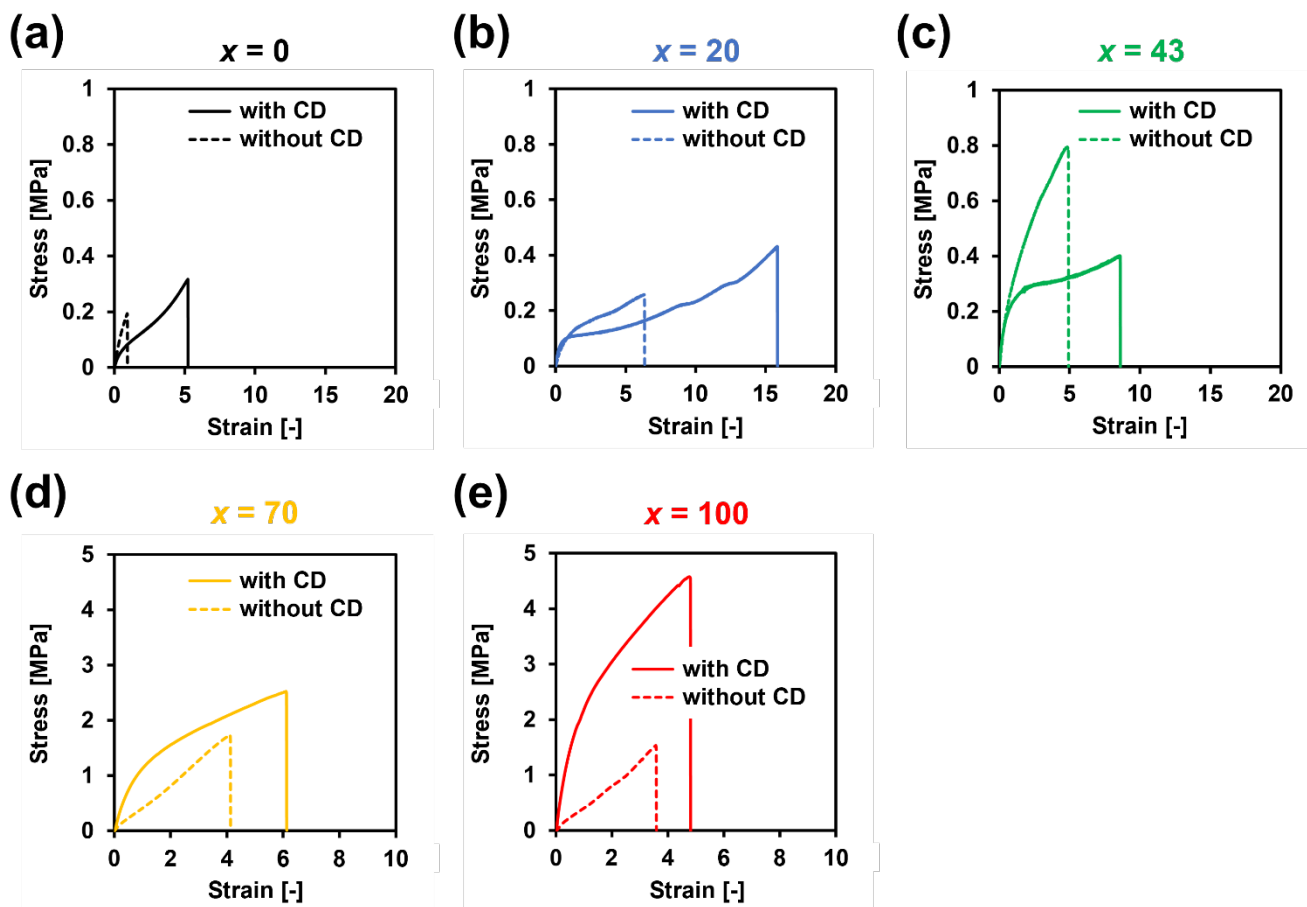
$$d = \frac{2\pi}{q^*} \quad (\text{S1})$$

Here,  $d$  characterizes the distance between neighbouring PDMS and acrylate copolymer domains.  $q^*$  is the  $q$  value at the peak top in SAXS region. The  $q^*$  values listed in **Table S2**

**Table S2.** The  $q^*$  value used to estimate the domain size as shown in **Table 1**.

HEMA ratio, $x$ [mol%]	$q^*$ [nm <sup>-1</sup> ]	
	with CD	without CD
0	0.393	0.351
20	0.291	0.252
43	0.304	0.255
70	0.406	N/A
100	0.448	N/A

## S7. Stress strain curve

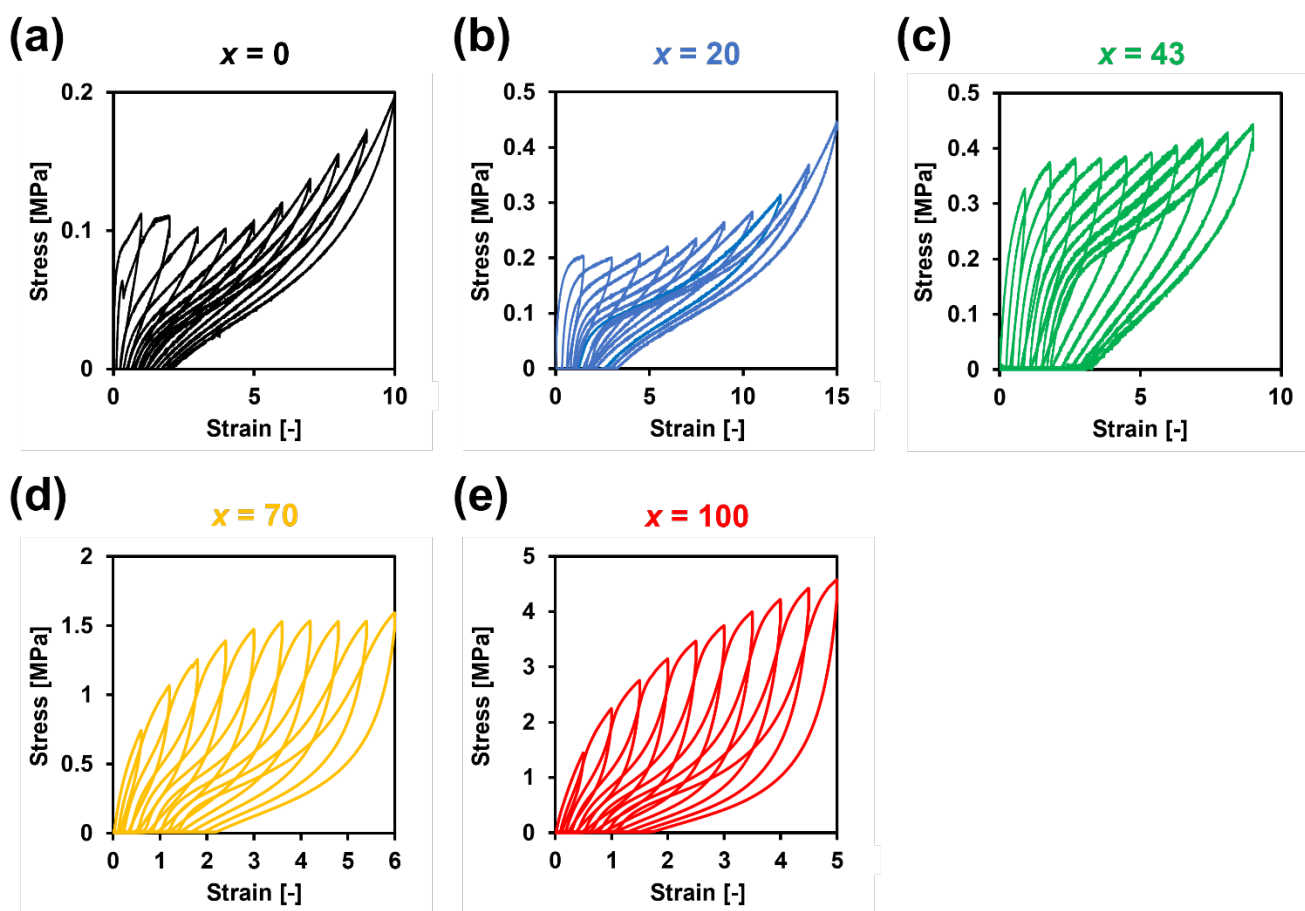


**Fig. S14.** Stress-strain curves for PDMS- $\gamma$ CD-AA1/P(EA-HEMA) ( $x$ ) (with CD, solid line) and PDMS-AA1/P(EA-HEMA) ( $x$ ) (without CD, dashed line) when  $x =$  (a) 0, (b) 20, (c) 43, (d) 70, and (e) 100.

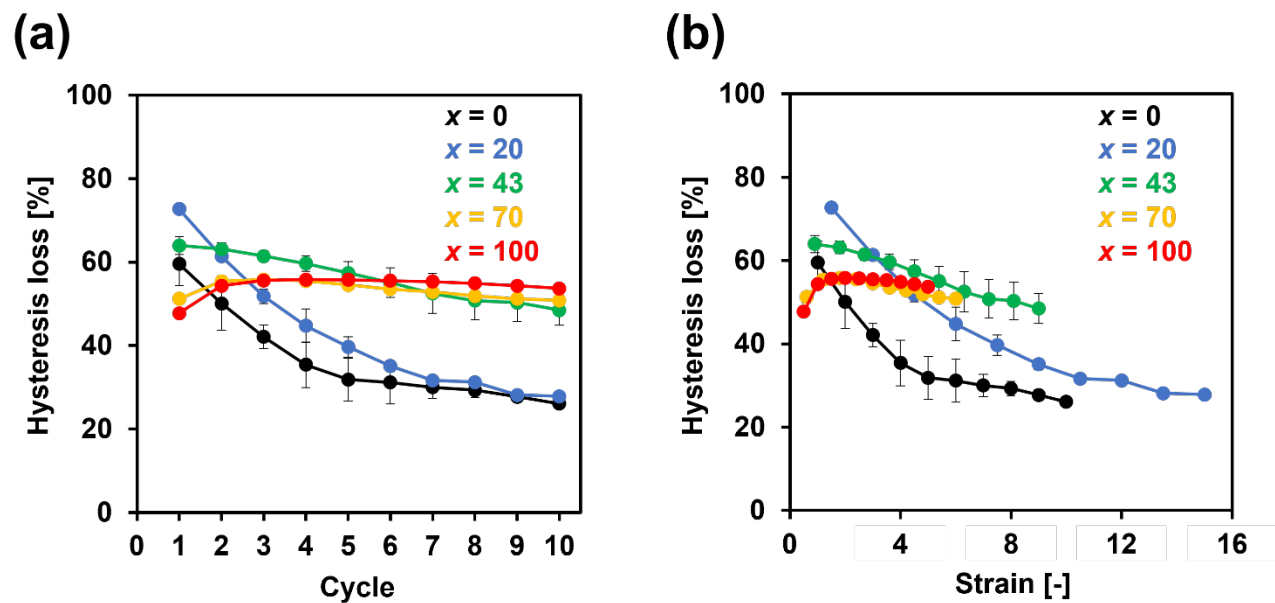
## S8. Cyclic tensile tests

**Table S3.** Maximum strains for the cyclic tensile test.

x [mol%]	Maximum strain at the nth cycle [-]									
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
0	1	2	3	4	5	6	7	8	9	10
20	1.5	3	4.5	6	7.5	9	10.5	12	13.5	15
43	0.9	1.8	2.7	3.6	4.5	5.4	6.3	7.2	8.1	9
70	0.6	1.2	1.8	2.4	3	3.6	4.2	4.8	5.4	6
100	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5

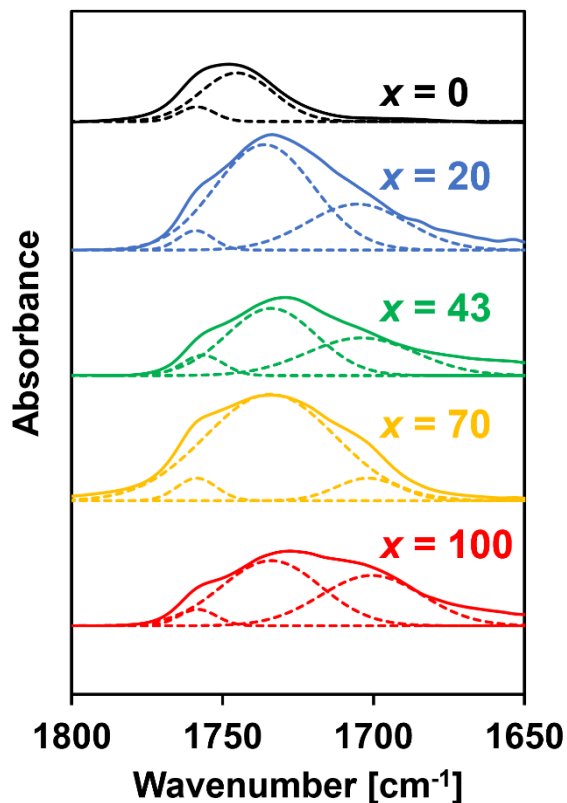


**Fig. S15.** Cyclic stress–strain curves of PDMS- $\gamma$ CD-AA1 $\supset$ P(EA-HEMA) ( $x$ ) when  $x =$  (a) 0, (b) 20, (c) 43, (d) 70, and (e) 100.



**Fig. S16.** Hysteresis loss ratios at each cycle of PDMS- $\gamma$ CD-AAI- $\Delta$ -P(EA-HEMA) ( $x$ ). Horizontal axis is (a) cycle and (b) strain.

## S9. FT-IR

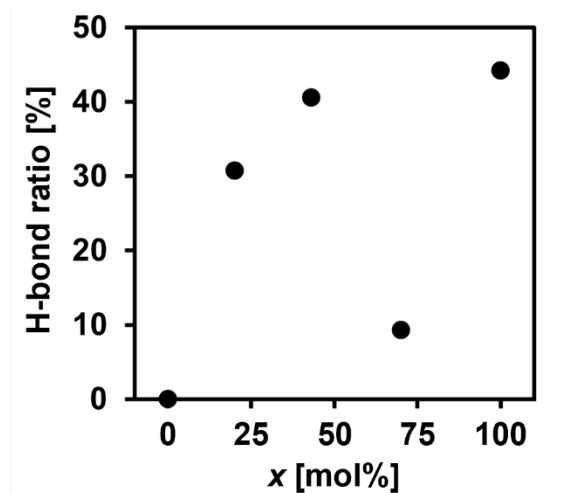


**Fig. S17.** FT-IR spectra of PDMS- $\gamma$ CD-AAI $\supset$ P(EA-HEMA) ( $x$ ).

**Fig. S17** shows the H-bonded C=O band ( $A_{C=O}^{\text{H-bond}}$ ) at about  $1700 \text{ cm}^{-1}$  and the free C=O band ( $A_{C=O}^{\text{free}}$ ) at about  $1735 \text{ cm}^{-1}$ . The bands at  $1755 \text{ cm}^{-1}$  were assigned to the C=O groups in  $\gamma$ CD. We calculated H-bond ratio using the following equation.

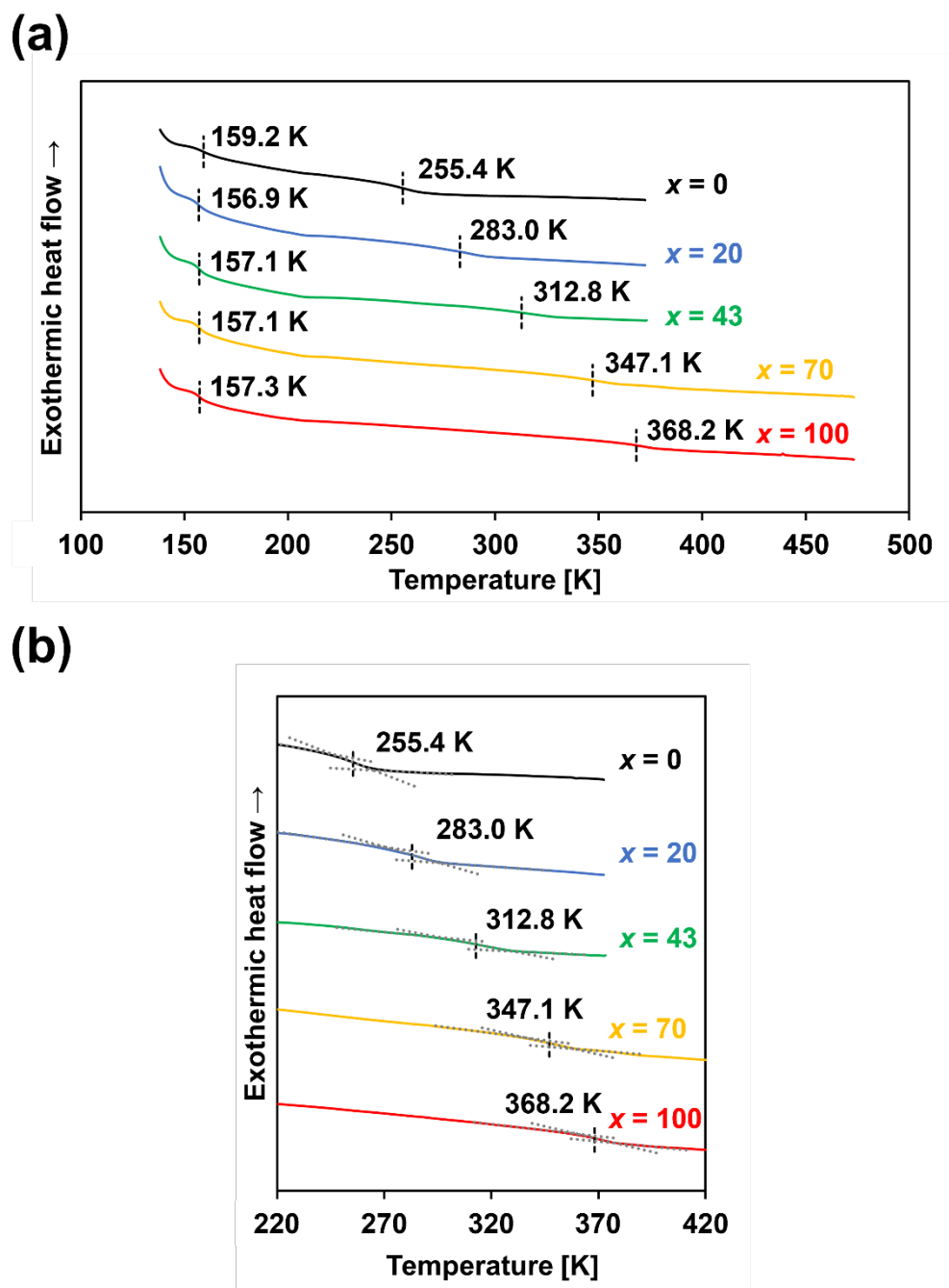
$$\text{H-bond ratio} = \frac{A_{C=O}^{\text{H-bond}}}{A_{C=O}^{\text{H-bond}} + A_{C=O}^{\text{free}}} \times 100\% \quad (\text{S3})$$

Here,  $A_{C=O}^{\text{H-bond}}$  and  $A_{C=O}^{\text{free}}$  are the band area of the H-bonded C=O band and the free C=O band.



**Fig. S18.** H-bond ratios of PDMS- $\gamma$ CD-AA1 $\supset$ P(EA-HEMA) ( $x$ ).

## S10. DSC measurements



**Fig. S19.** (a) DSC curves of PDMS- $\gamma$ CD-AAI-P(EA-HEMA) ( $x$ ). (b) Enlarged DSC curves at the glass transition of acrylate copolymers.



The Fox equation is a widely used formula for predicting glass transition temperature ( $T_g$ ) of polymeric mixtures, including random copolymers, polymer blends, and plasticized polymer, because of its simplicity and ease of use. We used the following equation to estimate  $T_g$  of acrylate copolymers containing with ethyl acrylate (EA) and hydroxy ethyl methacrylate (HEMA).

$$\frac{1}{T_g} = \frac{W_{EA}}{T_{g EA}} + \frac{W_{HEMA}}{T_{g HEMA}} \quad (S3)$$

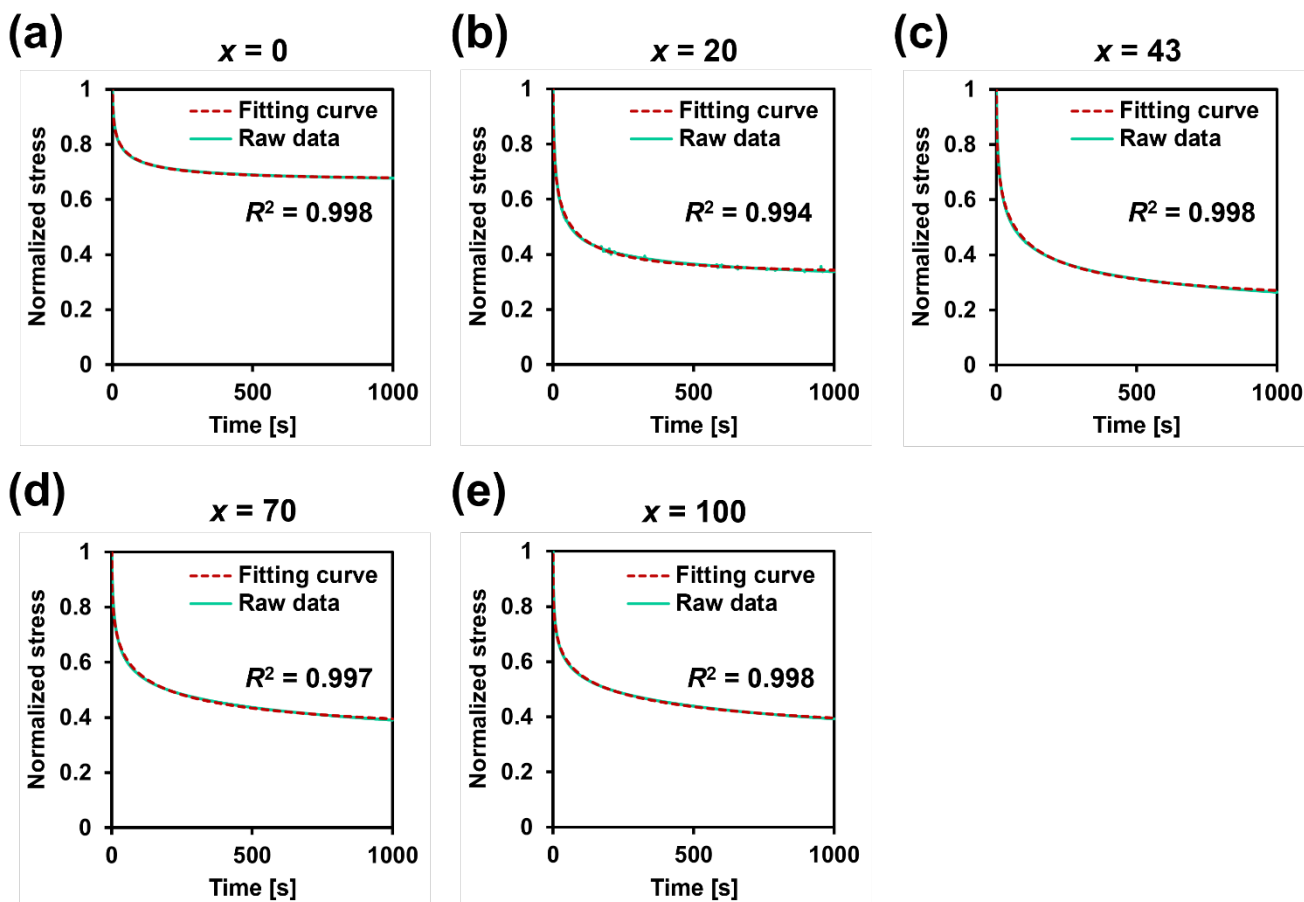
Here,  $W_{EA}$  and  $W_{HEMA}$  are weight fraction of EA and HEMA.  $T_{g EA}$  and  $T_{g HEMA}$  are the  $T_g$  of PEA and PHEMA ( $T_{g EA} = 249$  K,  $T_{g HEMA} = 328$  K).

## S11. Stress relaxation tests

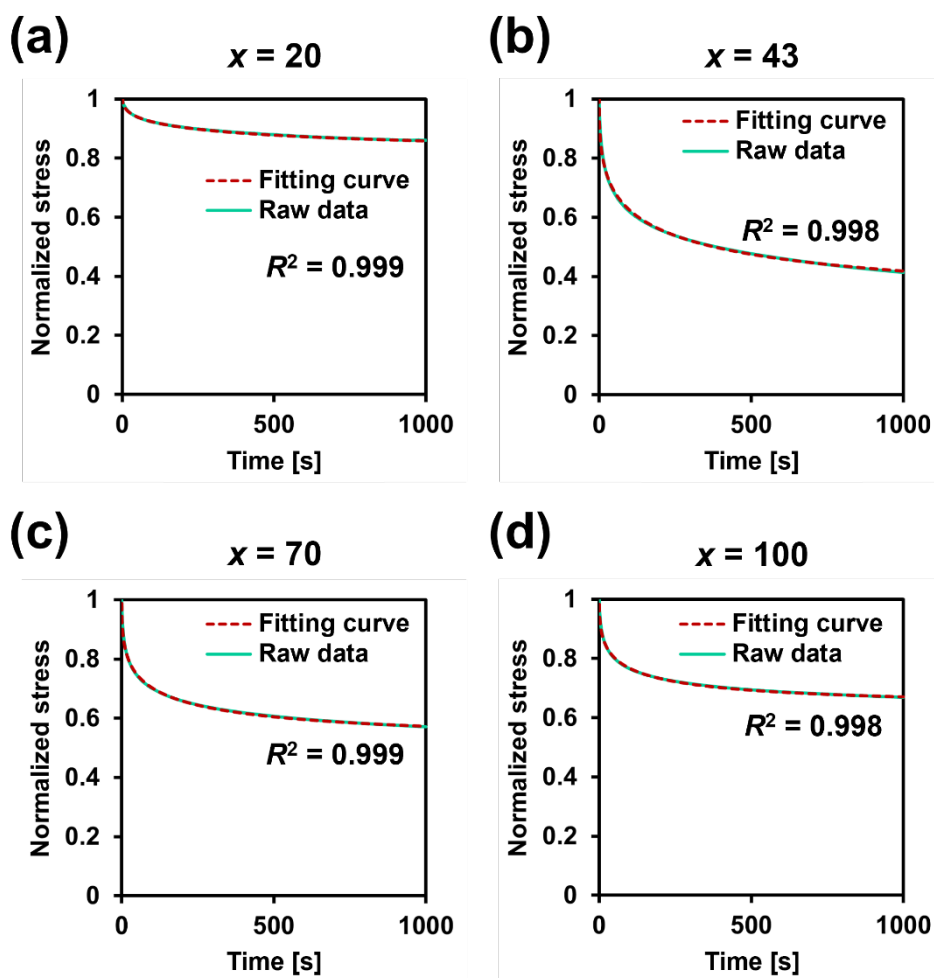
Curve fitting was carried out on the obtained stress  $\sigma$  versus relaxation time  $t$  curves using the Kohlrausch–Williams–Watts models, as described by the following equation.

$$\sigma = \sigma_r \exp\left\{-\left(\frac{t}{\tau}\right)^\beta\right\} + \sigma_\infty \quad (\text{S4})$$

In the above equation,  $\sigma_r$  is the relaxable stress,  $\sigma_\infty$  is the residual stress,  $\tau$  is the time constant, and  $\beta$  is the stretching exponent.



**Fig. S20.** Stress relaxation curves of PDMS- $\gamma$ CD-AAI $\supset$ P(EA-HEMA) ( $x$ ) when  $x =$  (a) 0, (b) 20, (c) 43, (d) 70, and (e) 100 with fitting curves (raw data: cyan solid line, fitting curves: brown dashed line).



**Fig. S21.** Stress relaxation curves of PDMS-AA1 / P(EA-HEMA) ( $x$ ) when  $x =$  (a) 20, (b) 43, (c) 70, and (d) 100 with fitting curves (raw data: cyan solid line, fitting curves: brown dashed line).

**Table S4.** Fitting parameters obtained for PDMS- $\gamma$ CD-AAI  $\supset$  P(EA-HEMA) ( $x$ ) by using the KWW models.

$x$ [mol%]	Relaxable component			Residual component
	$\sigma_r / \sigma_0$	$\tau$ [s]	$\beta$	$\sigma_\infty / \sigma_0$
0	0.34	27	0.39	0.66
20	0.69	24	0.38	0.31
43	0.79	50	0.35	0.21
70	0.68	61	0.33	0.32
100	0.71	78	0.28	0.29

**Table S5.** Fitting parameters obtained for PDMS-AAI / P(EA-HEMA) ( $x$ ) by using the KWW models.

$x$ [mol%]	Relaxable component			Residual component
	$\sigma_r / \sigma_0$	$\tau$ [s]	$\beta$	$\sigma_\infty / \sigma_0$
0	N/A	N/A	N/A	N/A
20	0.20	417	0.40	0.80
43	0.72	168	0.34	0.28
70	0.49	88	0.35	0.51
100	0.37	73	0.37	0.63