Supporting Information

Hydrophobic Cyclodextrin Dimer-Assisted Self-Healing Elastomer: Movable Crosslinks of Pseudo-Rotaxane with Recyclable and Separable Functionality

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Contents.

1. Experimental section

Materials

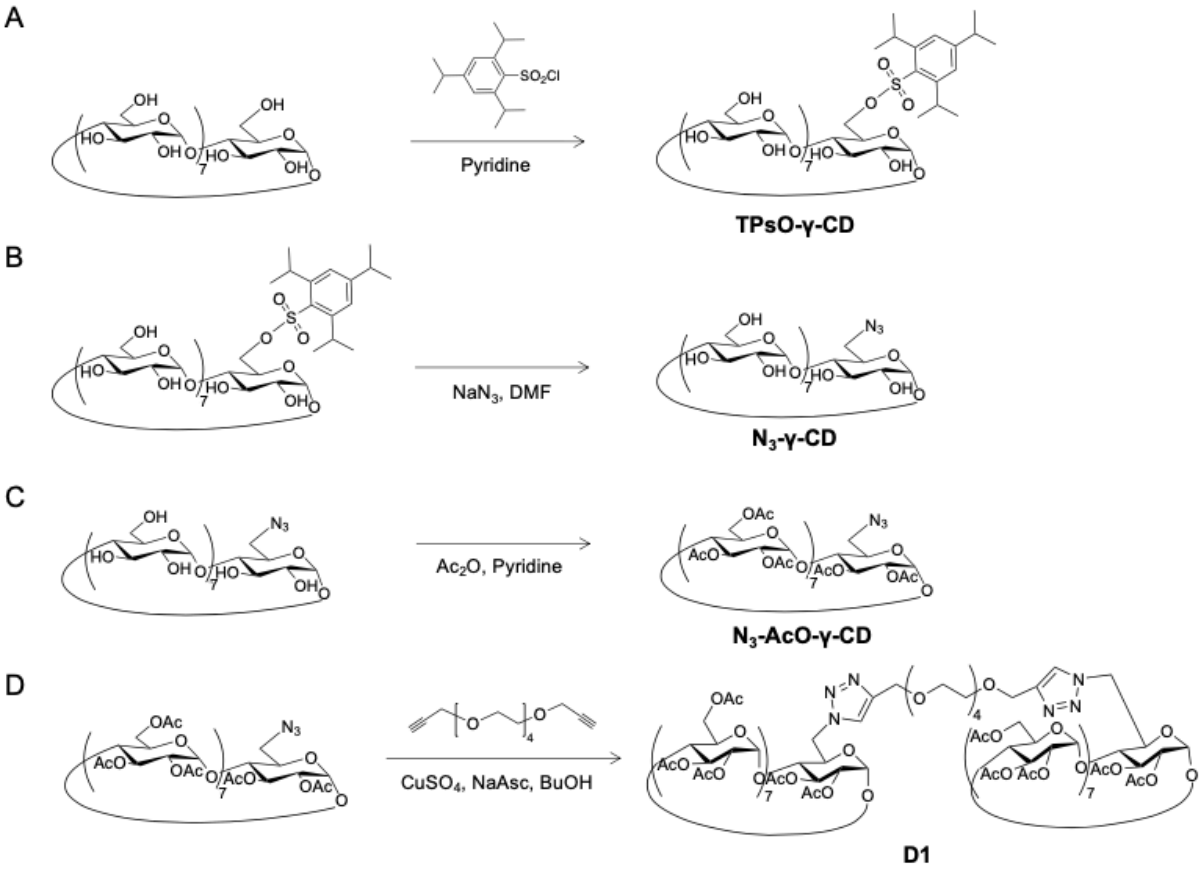
γ-Cyclodextrin (γ-CD, 97%), sodium azide (NaN_3), acetic anhydride (Ac_2O, 97%), 4-dimethylaminopyridine (DMAP, 99%), tetraethylene glycol [$(EO)_4$], propargyl bromide (95%), sodium ascorbate (NaAsc, 98%), ethyl acrylate (EA, 97%), 1,4-butanediol diacrylate (BDA, 90%), pyridine, *N,N*-dimethylformamide (DMF), *t*-butyl alcohol (*t*-BuOH), and tetrahydrofuran (THF) were purchased from Fujifilm Wako Pure Chemical (Osaka, Japan). 2,4,6-Triisopropylbenzenesulfonyl chloride (TPsCl, > 97%), sodium hydride (NaH, 60%), and 1-hydroxycyclohexyl phenyl ketone (I184, > 98%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 99.5%) was purchased from Ishizu Pharmaceutical (Osaka, Japan). All reagents were analytical grade and used without further purification.

Instruments and Measurements

NMR spectra were obtained in chloroform-d_1 at 298 K and recorded on an ECA600 system (JEOL Resonance). Tetramethyl silane (TMS; δ = 0.0 ppm) was used as the internal standard. The NMR data were processed and analyzed with Delta NMR software (v5.3). The molecular weights of the γ-CD derivatives were characterized with an AXIMA Confidence MALDI–TOF–MS spectrometer (Shimadzu) with sodium trifluoroacetate as the ionizing agent, and 2,5-dihydroxybenzoic acid or α-cyano-4-hydroxycinnamic acid as the matrix agent. Methanol for a sulfonyl derivative and chloroform for the others were used as the solvents. Preparative and recycle GPC was conducted with a GPC-908 (Japan Analytical Industry) equipped with preparative column (Shodex GPC K-2001 and GPC K-2003) and eluted by using chloroform. The

photopolymerizations of EA-based monomer with any given cross-linkers were carried out in a UV cross-linker chamber (CL-1000L; Analytik Jena) equipped with five 8-W UVA lights centered at ca. 365 nm. Analysis of molecular weights of poly(ethyl acrylate) (PEA) elastomers and separated dimer (D1) was carried out with a Waters ACQUITY Advanced Polymer Chromatography instrument equipped with a APC XT BEH column and eluted (0.6 mL/min) by using THF at 40°C with an RI detector. The relative molecular weights were estimated from the calibration curve of polystyrene standard (EasiCal PS-1, PS-2; AMR). Tensile test of elastomers was performed by using an Autograph AGS-J (Shimadzu) at a deformation rate of 1 mm/s. Young's modulus was calculated from the initial slope of the stress–strain curve. The bulk polymerizations were carried out on a polytetrafluoroethylene mold, directly adding reaction solution. After polymerization, the elastomers were cut (6.0 mm × 1.0 mm; width and thickness, respectively) and applied to the tensile tests.

Synthesis



Scheme 1 Synthetic route of AcO-γ-CD Dimer **(**D1**)**.

Mono-sulfonyl-γ-CD (TPsO-γ-CD)

First, γ-CD (5.474 g, 4.22 mmol) was vacuum-dried in a 500-mL four-necked flask at r.t. (27°C) overnight and 250 mL dry pyridine was added to the reaction vessel under argon. After the γ-CD dissolved completely, TPsCl (3.320 g, 302.86 mmol) was added to the solution under argon. The mixture was stirred at r.t. (27°C) for 23.5 h and 50 mL distilled water was added to the mixture to terminate the reaction. Concentrated solution after evaporation was poured into acetone under continuous stirring and allowed to settle overnight to obtain precipitate. Then, the solid precipitated was filtered and washed with acetone. Finally, the solid was dried overnight under vacuum. In further purification, polystyrene porous resin (Diax HP-20, Sigma–Aldrich, St. Louis, US) column chromatography was carried out by changing the proportion of aqueous methanol in the mixture to separate and collect mono-sulfonyl-γ-CD (TPsO-γ-CD). After evaporation of methanol and subsequent freeze drying, TPsO-γ-CD was obtained as the final product (2.284 g; 34.64% yield); ^{1}H NMR (600 MHz, DMSO-d_6): δ (ppm) 7.28 (s, 2H), 5.92-5.70 (m, 16H), 4.89-4.82 (m, 8H), 4.58-4.47 (m, 6H), 4.25 (s, 3H), 4.01 (sept, 2H, J = 6.5 Hz), 3.83 (m, 1H), 3.62-3.25 (m), 2.93 (sept, 1H, J = 6.5 Hz), 1.23-1.16 (m, 18H); MALDI-TOF-MS: Found *m*/*z* 1585.5, calcd. *m*/*z* 1585.5 for $[M + Na]^+$ (M: $C_{63}H_{102}O_{42}S$).

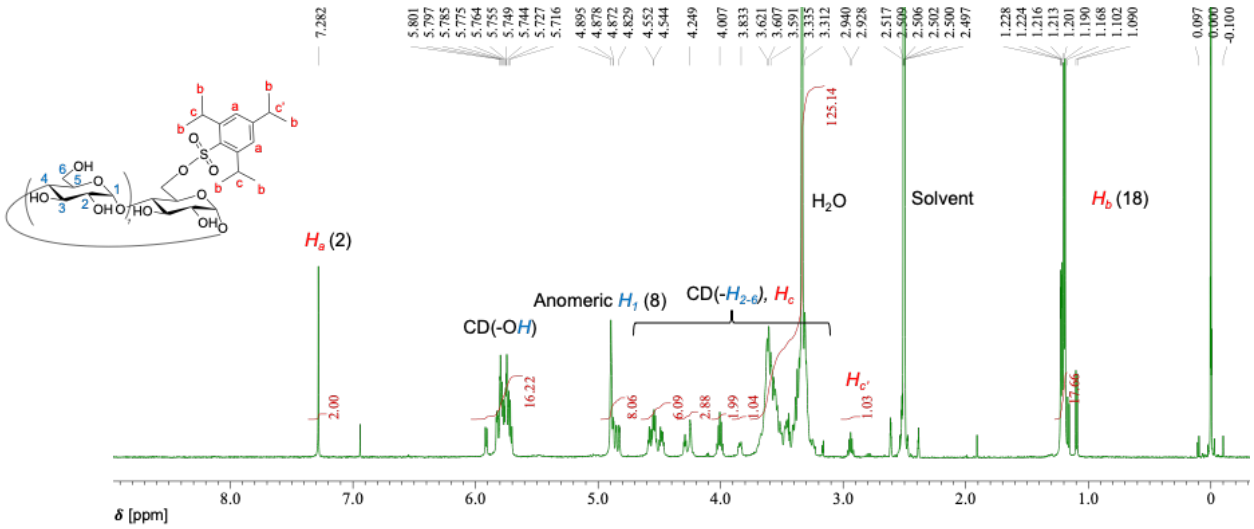


Fig. S1 ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of TPsO-γ-CD.

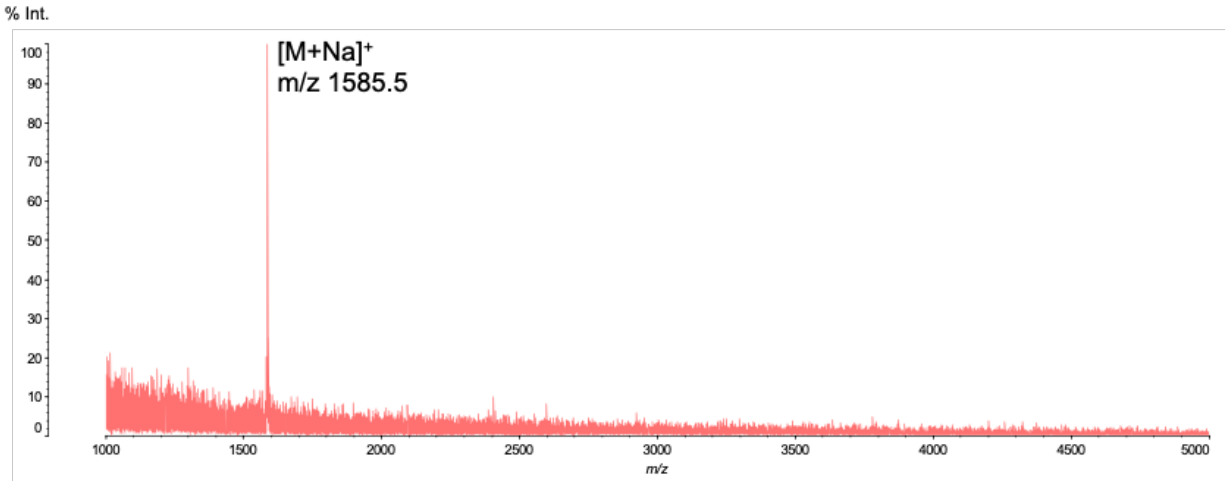


Fig. S2 MALDI-TOF-MS spectrum of TPsO-γ-CD.

Peracetylated mono-azide γ-CD (N_3-AcO-γ-CD)

TPsO-γ-CD (2.277, 1.46 mmol) was added to a reaction vessel and dissolved in 50 mL of DMF at r.t. (27°C). NaN_3 (0.984 g, 15.14 mmol) was added to the solution and stirred at 80°C for 20 h. The reaction solution was added dropwise into acetone under continuous stirring; the solid precipitate was filtered and repeatedly washed with acetone. The crude product (N_3-γ-CD) was dried overnight under vacuum (white solid; 1.504 g). The subsequent solid was dissolved in dry pyridine (8 mL); afterward, Ac_2O (4 mL) and DMAP (total 0.016 g) were added and stirred at r.t. (29°C) for 72 h to obtain hydrophobically peracetylated mono-azide γ-CD (N_3-AcO-γ-CD). After the reaction solution was dissolved in chloroform, the organic layer was washed with fresh distilled water 3× and finally washed 1× with brine. After drying over $MgSO_4$, the solution was evaporated and dried in vacuo to afford purified N_3-AcO-γ-CD (1.038 g; 39.88% yield); ^{1}H NMR (600 MHz, Chloroform-d_1): δ (ppm) 5.51-5.26 (m, 8H), 5.18-5.08 (m, 8H), 4.86-4.62 (m, 8H), 4.57-4.46 (m, 7H), 4.33-4.22 (m, 7H), 4.09-3.99 (m, 8H), 3.83-3.67 (m, 10H), 2.39-1.98 (m, 69H); MALDI-TOF-MS: Found *m*/*z* 2310, Calcd *m*/*z* 2310 for $[M + Na]^+$ (M: $C_{94}H_{125}N_3O_{62}$).

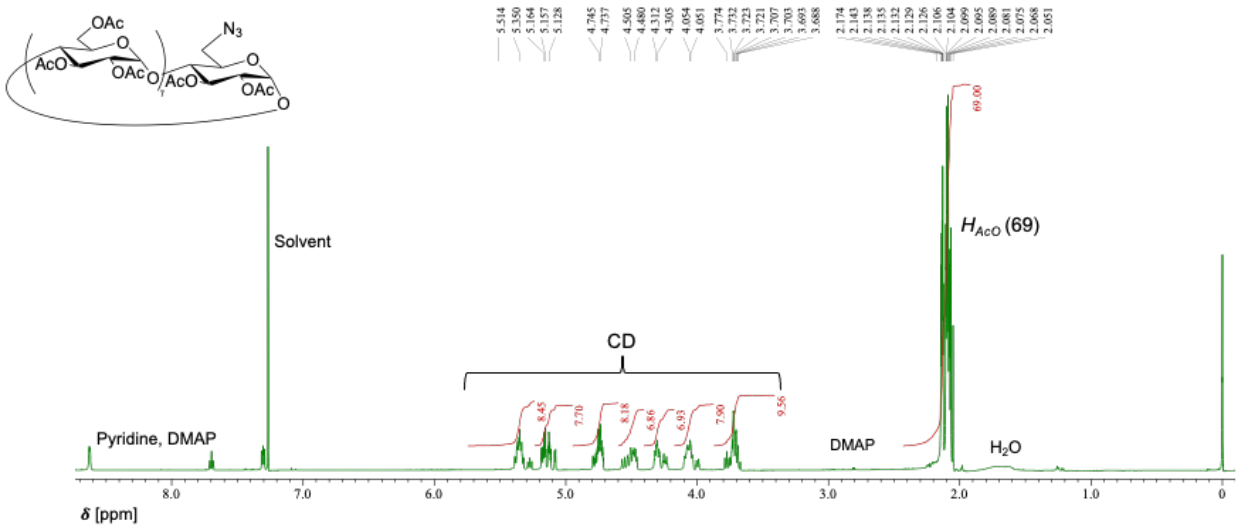


Fig. S3 ^{1}H NMR (600 MHz, Chloroform-d_1) spectrum of N_3-AcO-γ-CD.

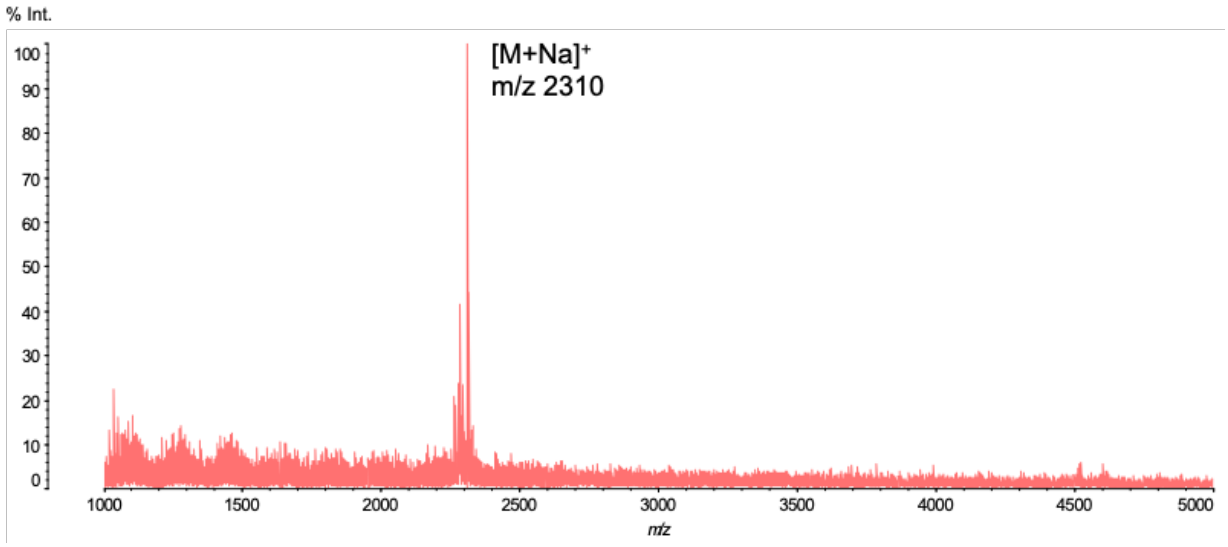


Fig. S4 MALDI-TOF-MS spectrum of N_3-AcO-γ-CD.

Di-alkynyl ethylene glycol linker, di-alkyne $(EO)_4$

Tetraethylene glycol (4.041 g, 20.81 mmol) and 100 mL THF were added into a four-necked round-bottom flask under argon. Then NaH (1.83 g) was slowly added into the solution under argon; subsequently, propargyl bromide (5.105 g, 42.91 mmol) dissolved in THF (10 mL) was added dropwise and stirred at 50°C for 20 h. After cooling to room temperature, cold water (200 mL) was added to the solution to quench the reaction. The diluted solution was extracted with chloroform 3× and washed with water and brine 3× and 1×, respectively. After drying over $MgSO_4$, the solution was filtered and the filtrate was dried under reduced pressure to remove the solvent. The residue was purified by silica column chromatography (Wakogel 60N, hexane/ethylacetate = 2: 1, v/v) to afford di-alkyne $(EO)_4$ (2.705 g, 48.10% yield); ^{1}H NMR (600 MHz, Chloroform-d_1): δ (ppm) 4.21 (q, J = 2.3 Hz, 4H), 3.71-3.66 (m, 18H), 2.44 (t, J = 2.4 Hz, 2H); DART-MS: Found *m/z* 288.3, Calcd *m/z* 288.3 for $[M + NH_4]^+$ (M: $C_{14}H_{22}O_5$).

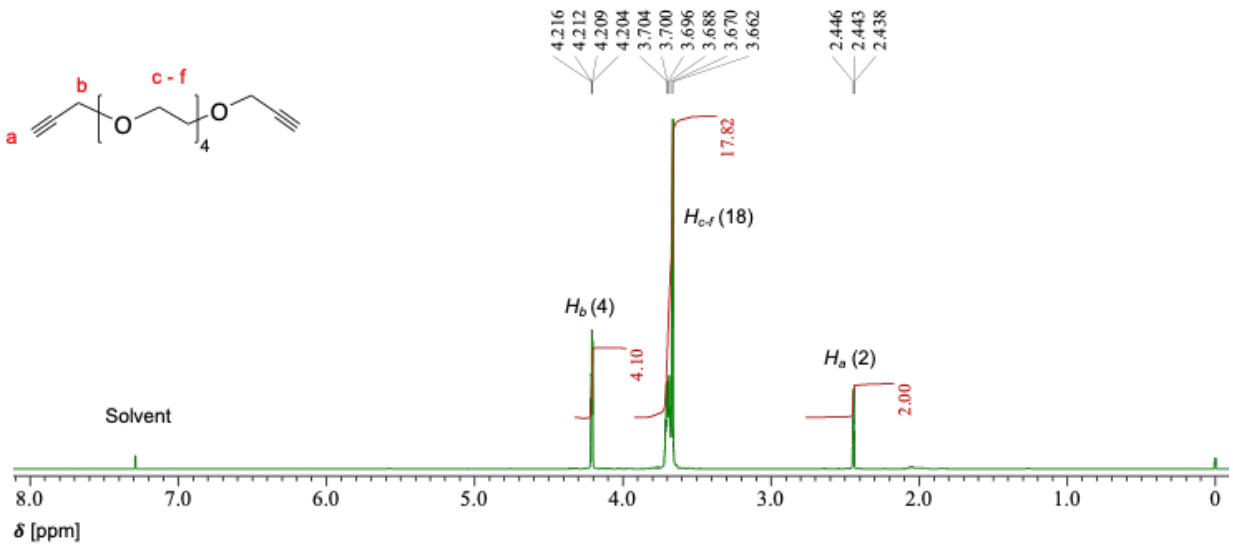


Fig. S5 ^{1}H NMR (600 MHz, Chloroform-d_1) spectrum of di-alkyne $(EO)_4$.

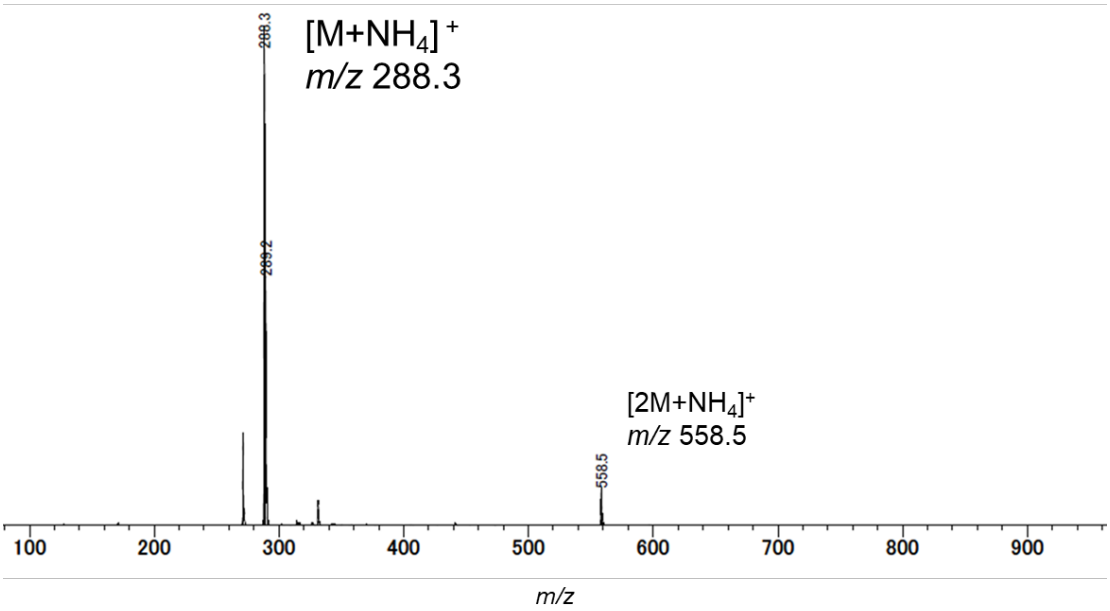


Fig. S6 DART-MS spectrum of di-alkyne $(EO)_4$.

AcO-γ-CD-dimer (D1).

To a solution of N_3-AcO-γ-CD (1.83 g, 0.787 mmol) in *t*-BuOH (15 mL), 5 mL of di-alkyne $(EO)_4$ (0.0982 g, 0.393 mmol) in *t*-BuOH, and 15 mL of 0.05 mol/L $CuSO_4 \cdot 5H_2O$ were added under argon. After subsequent dropwise addition of 15 mL freshly prepared 0.05 mol/L aqueous NaAsc, the solution was stirred for 72 h at r.t. After evaporation of the solvent, the residue was extracted with chloroform and washed with EDTA•4Na aq., water, and brine, respectively; 1× each. After drying over $MgSO_4$, the solution was filtered, and the filtrate was dried under reduced pressure to remove the solvent. The crude was purified by preparative gel permeation chromatography (GPC; GPC-908, Japan Analytical Technology; column: GPC K-2001, GPC K-2003, Showa Denko; eluent: chloroform) to afford the final product D1 (1.15 g, 30.1% yield); ^{1}H NMR (600 MHz, Chloroform-d_1): δ (ppm) 7.66 (s, 2H, triazole H_a), 5.73 (d, 2H, J = 3.4 Hz,), 5.41-5.27 (m, 16H, H_3), 5.26 (d, 2H, J = 3.8 Hz, H_1), 5.24 (d, 2H, J = 3.8 Hz, H_1), 5.12 (m, 8H, H_1), 5.05 (d, 2H, J = 3.4 Hz, H_1), 4.92 (dd, 2H, J = 3.8 Hz, J = 9.2 Hz, H_2), 4.78-4.66 (m, 16H, H_2 and *methylene*), 4.60-4.43 (m, 18H, H_2 and H_6), 4.35-4.25 (m, 16H, H_5 and $H_{6'}$), 4.19 (m, 2H, H_5), 4.14-4.01 (m, 12H, H_5), 3.81-3.63 (m, 32H, H_4 and *oxyethylene*), 3.58 (t, J = 9.2 Hz, H_4), 2.17-2.00 (m, 138H); MALDI-TOF-MS: Found *m*/*z* 4868, Calcd *m*/*z* 4868 for $[M + Na]^+$ (M: $C_{202}H_{272}N_6O_{129}$).

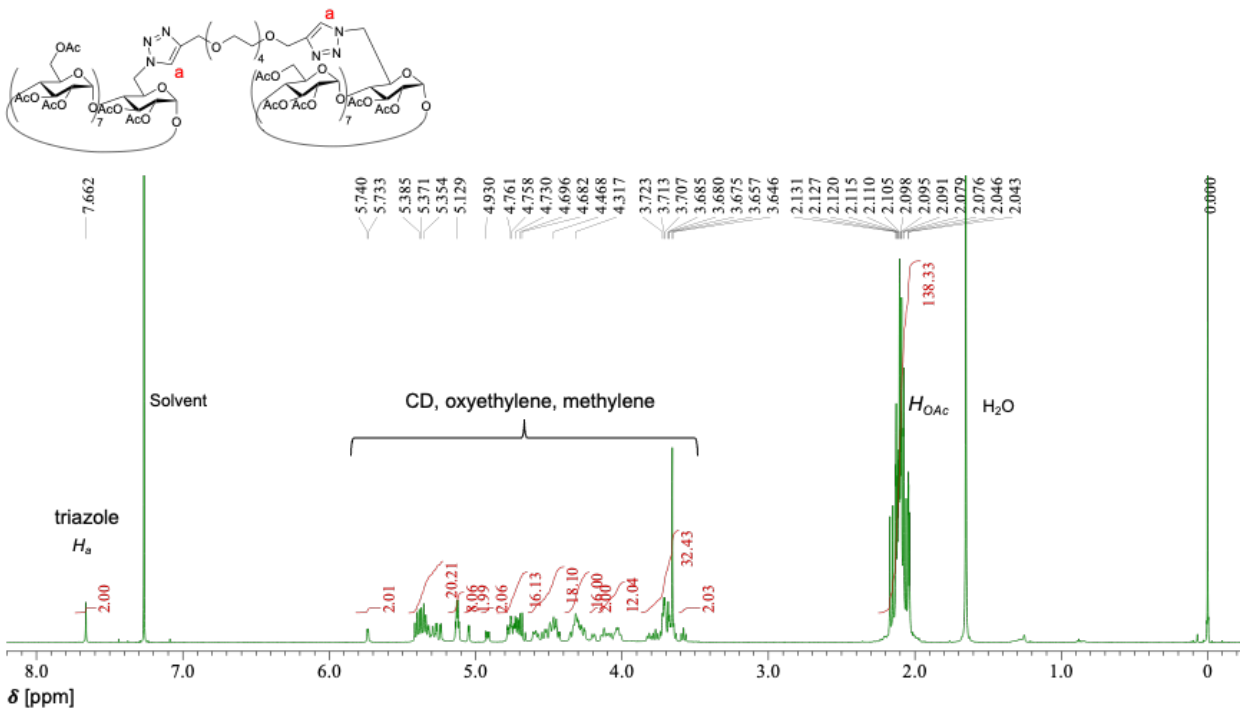


Fig. S7 ^{1}H NMR (600 MHz, Chloroform-d_1) spectrum of AcO-γ-CD-Dimer (D1).

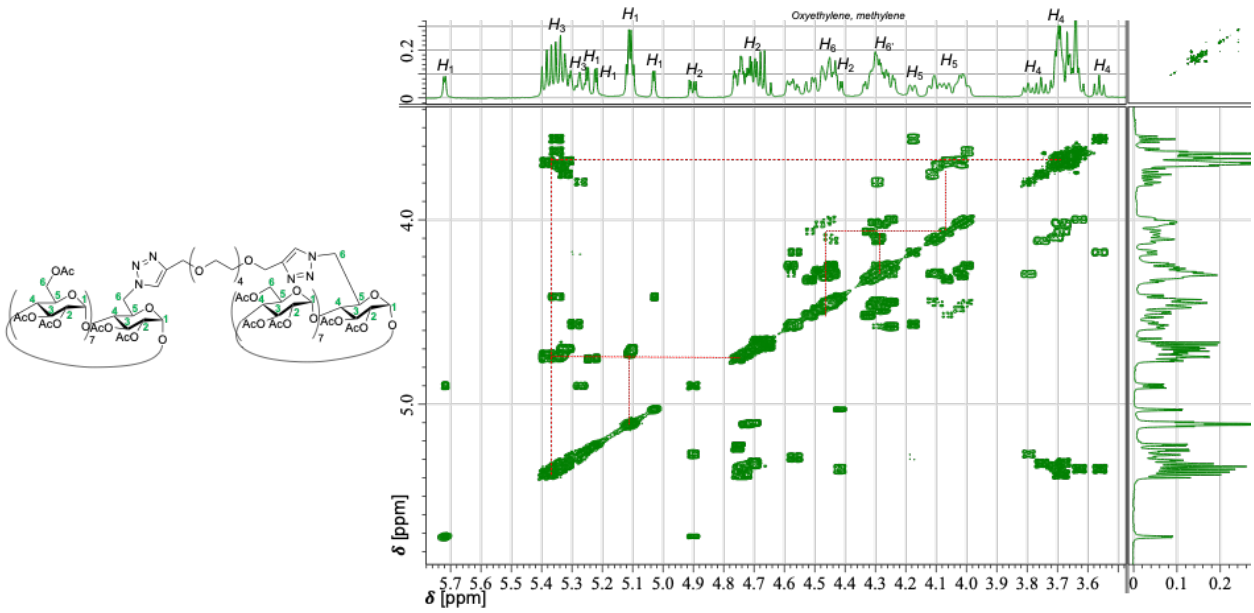


Fig. S8 COSY (600 MHz, Chloroform-d_1) spectra (partial) of AcO-γ-CD-Dimer (D1).

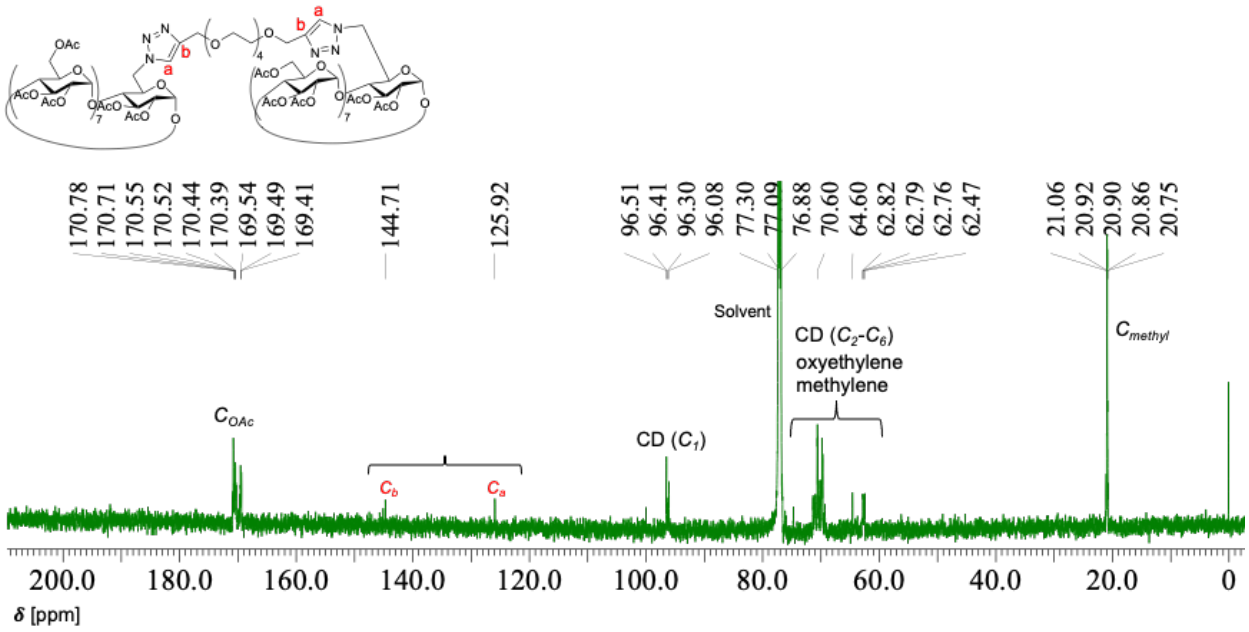


Fig. S9 ^{13}C NMR (150 MHz, Chloroform-d_1) spectrum of AcO-γ-CD-Dimer (D1).

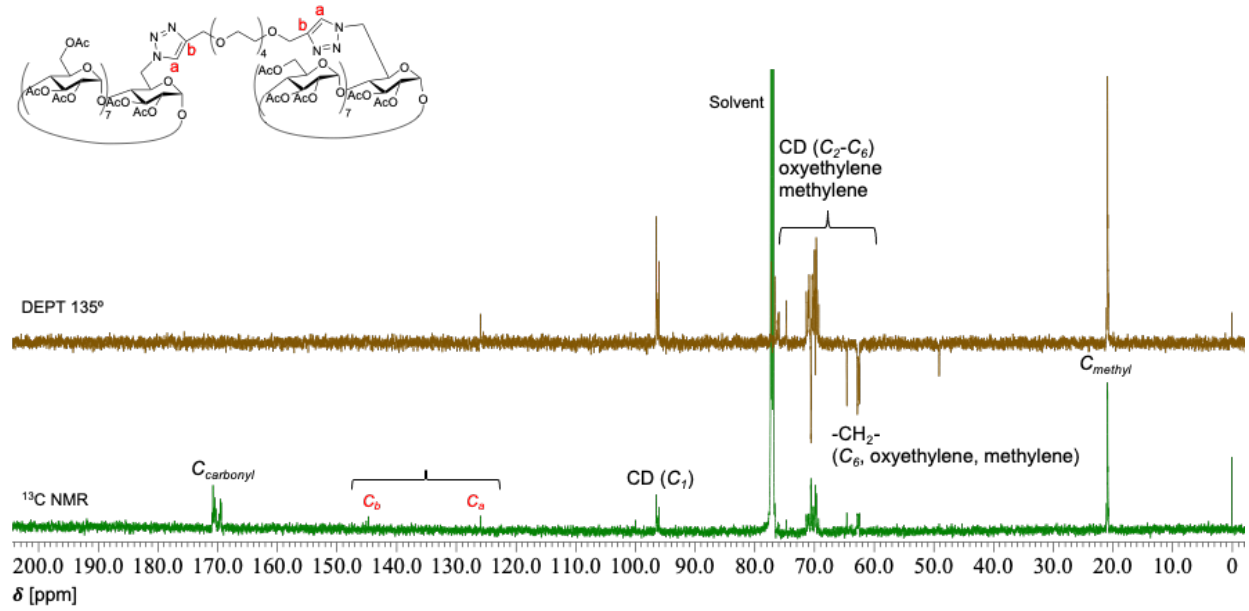


Fig. S10 ^{13}C and DEPT 135° NMR (150 MHz, Chloroform-d_1) spectra of AcO-γ-CD-Dimer (D1).

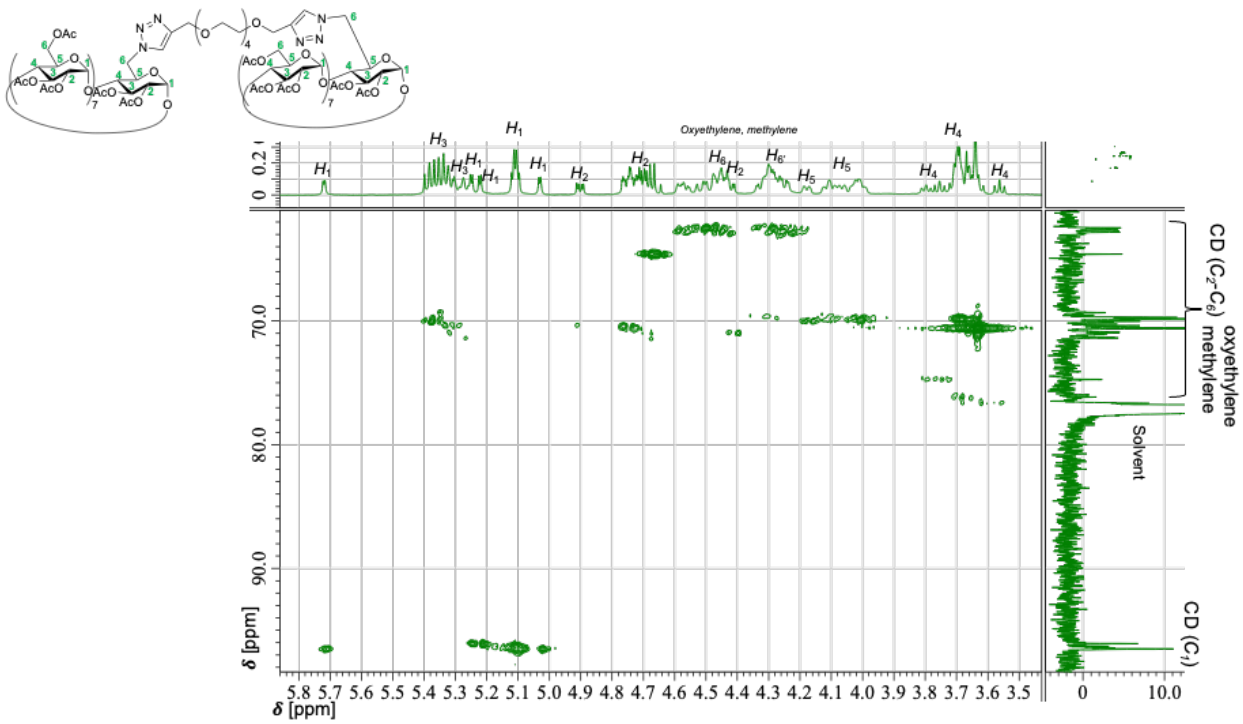


Fig. S11 HMQC (600 MHz, Chloroform-d_1) spectra (partial) of AcO-γ-CD-Dimer (D1).

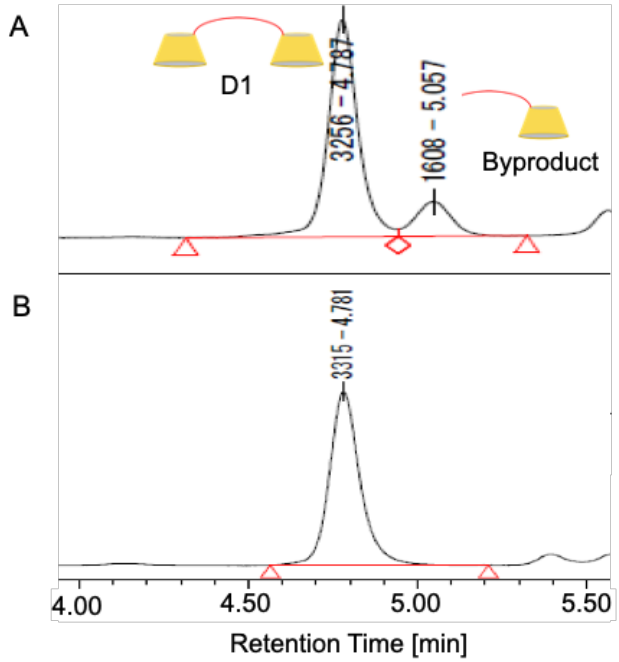


Fig. S12 GPC analysis of D1 compound before and after purification by preparative GPC. Inset images are corresponding compounds.

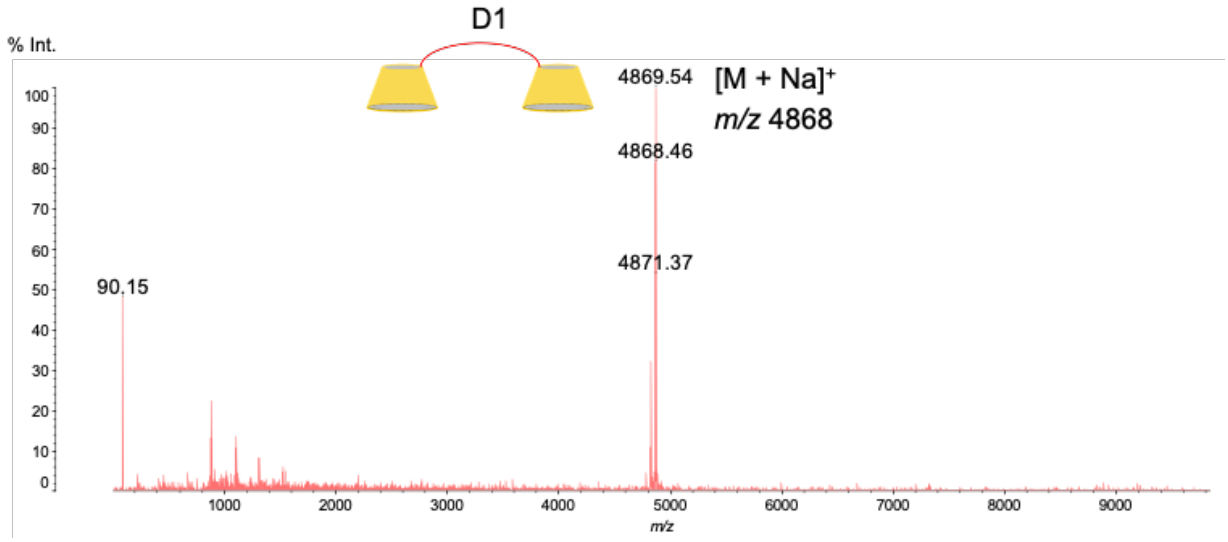


Fig. S13 MALDI-TOF-MS spectrum of AcO-γ-CD-Dimer (D1). Inset image is corresponding compound.

PAcO-γ-CD (M1).

After γ-CD (0.302 g, 0.233 mmol) was dissolved in dry pyridine (2 mL), Ac_2O (1 mL) was added and stirred at r.t. (27°C) for 48 h. The reaction solution was diluted in chloroform and the organic layer was washed with 1 N aqueous HCl, aqueous $NaHCO_3$ (100 g/L), and pH-neutral water; all under cold conditions. After drying over $MgSO_4$, the solution was filtered and the filtrate was dried under reduced pressure to remove the solvent, affording PAcO-γ-CD (M1) (0.477 g, 88.8% yield). MALDI-TOF-MS: Found *m/z* 2330, Calcd *m/z* 2329 for $[M + Na]^+$ (M: $C_{96}H_{128}O_{64}$).

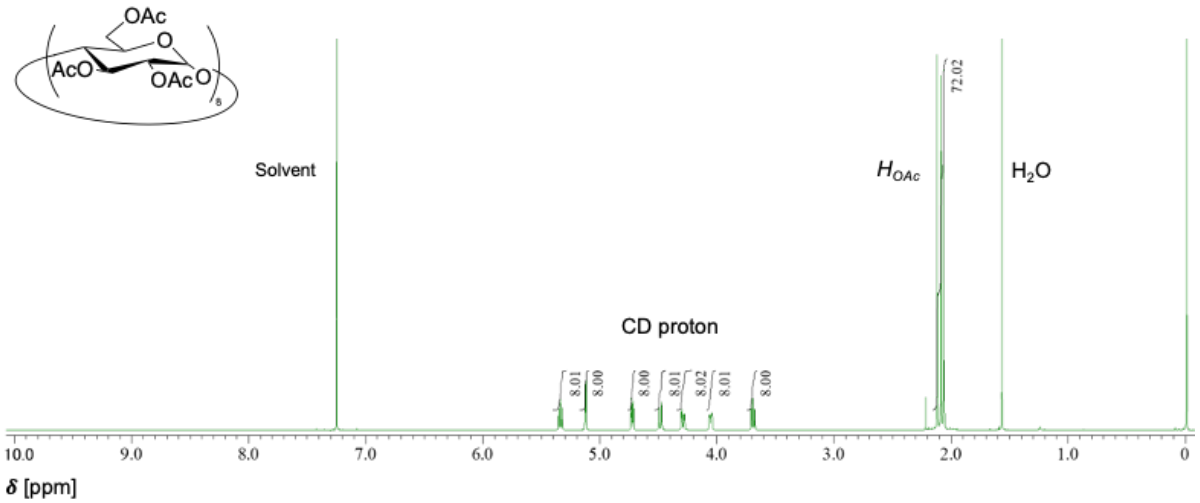


Fig. S14 1H NMR (600 MHz, Chloroform-*d1*) spectrum of PAcO-γ-CD (M1).

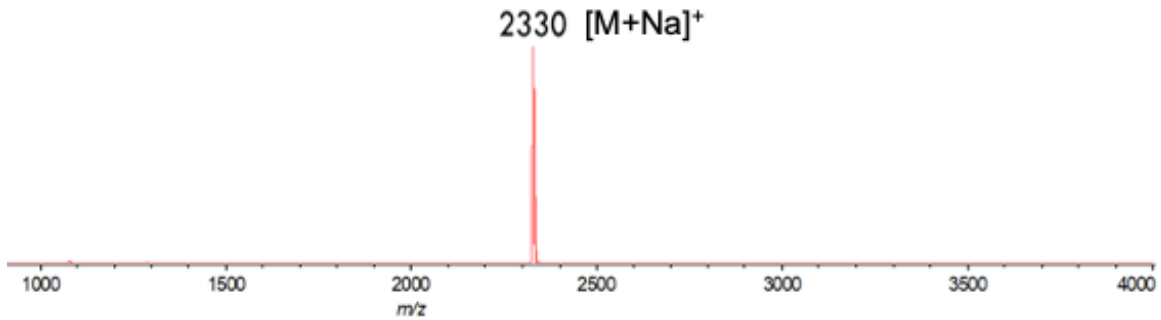


Fig. S15 MALDI-TOF-MS spectrum of PAcO-γ-CD (M1).

Polymerization: PEA–D1 elastomer

After D1 (0.1, 0.2, or 0.5 mol% for EA) was dissolved in EA (0.368 g, 3.68 mmol) to homogeneity, a photo-initiator I184 (0.2 mol% for EA) was added to the mixture in the dark. Bulk photo-polymerization was carried out by UV irradiation, at 365 nm for 2.0 h with a UV lamp (1.1 J/cm) in a UV chamber. The product was dried at 80°C under reduced pressure for 24 h to evaporate the residual monomer.

In comparing with PEA-D1 elastomer, PEA-M1 and PEA-BDA elastomers [respectively containing M1 (0.2 mol% for EA) and BDA (chemical cross-linker; 0.1 mol% for EA)] were synthesized by essentially the same procedures described for the PEA-D1 system; ^{1}H NMR (600 MHz, Chloroform-d_1): δ (ppm) 7.66 (s, 2H), 5.74 (s, 2H), 5.42-5.24 (m, 30H), 5.13 (d, J = 4.8 Hz, 10H), 5.05 (s, 3H), 4.92 (d, J = 9.6 Hz, 3H), 4.78-4.66 (m, 21H), 4.59-4.43 (m, 22H), 4.35-4.26 (m, 20H), 4.21-4.11 (m, 362H), 3.83-3.57 (m, 44H), 2.34-2.29 (m, 158H), 2.21-2.01 (m, 189H), 1.91 (t, J = 6.9 Hz, 75H), 1.56-1.42 (m, 80H), 1.35 (s, 5H), 1.19 (d, J = 63.9 Hz, 504H).

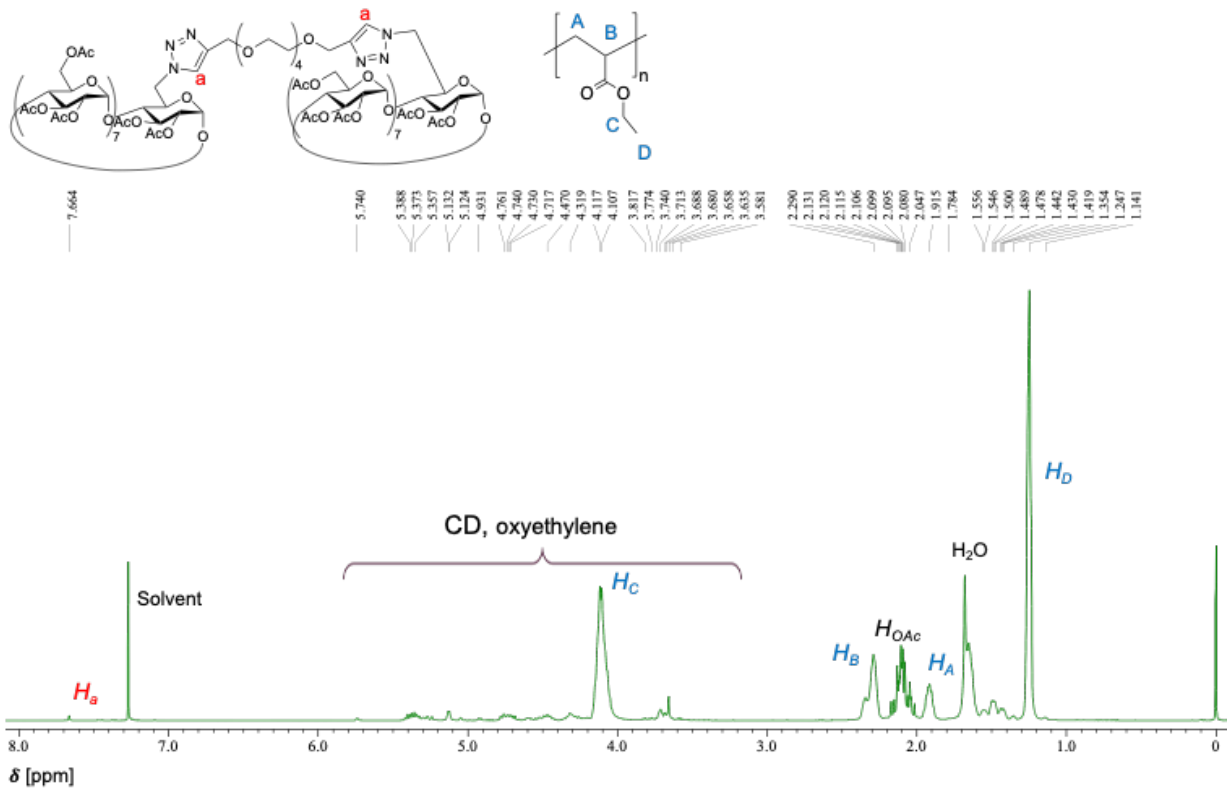


Fig. S16 ^{1}H NMR (600 MHz, Chloroform-d_1) spectrum of PEA-D1-0.5.

2. Characterization of synthesized compounds

Characterization of threaded inclusion complex structures of PEA-D1, stoppered with bulky DA chains (1D NMR, NOE differential spectra)

After bulky dodecyl acrylate (DA; molar ratio of EA: DA=99.9:0.1) and D1 (1.25 mol% total monomer) were dissolved in EA (0.368 g, 3.68 mmol), I184 (0.2 mol% total monomer) was added to the mixture in the dark. PEA-D1 copolymer with bulky DA chains was synthesized by UV irradiation, performed at 365 nm for 2.0 h by using UV lamps (1.1 J/cm) in a UV chamber. The obtained piece of elastomer was dissolved in chloroform-d_1 and ^{1}H NMR was performed to confirm the threaded intermolecular correlation between the PEA main chain (guest) and γ-CD (host), measuring by the nuclear Overhauser effect (NOE) signals of 1D NMR spectroscopy (**Fig. S17**).

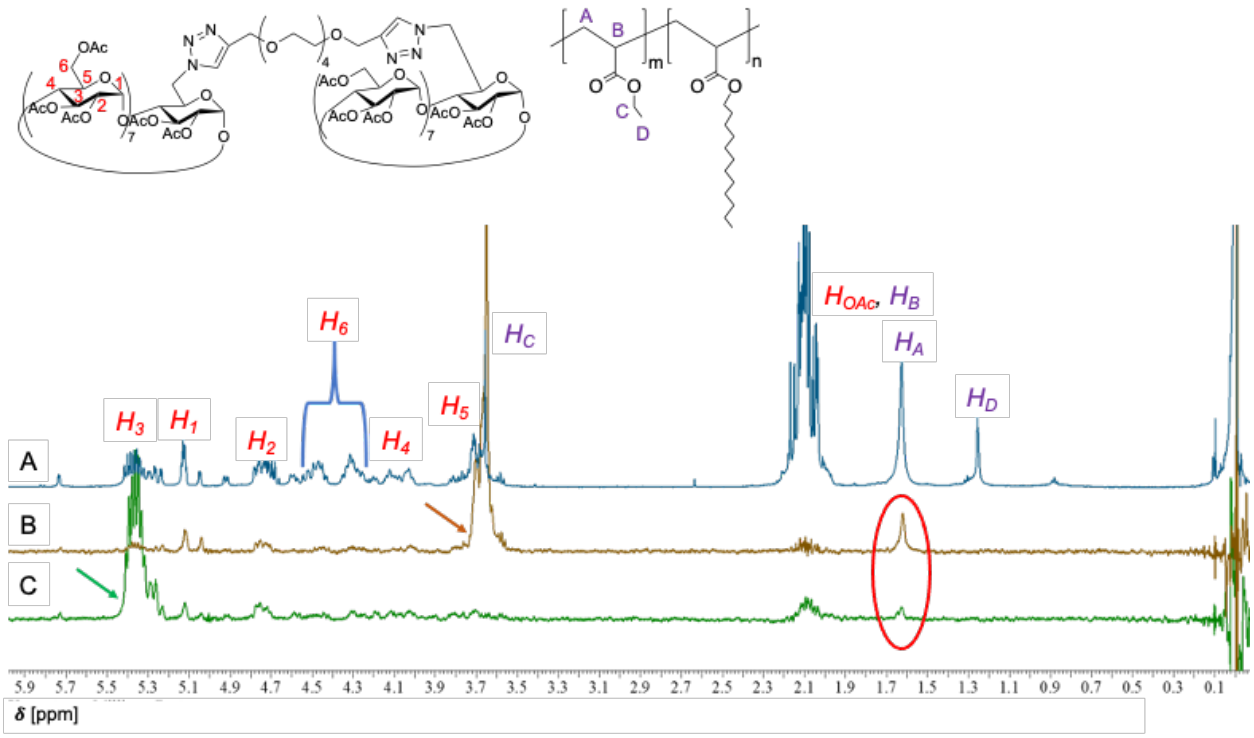


Fig. S17 NOE ^{1}H NMR (600 MHz, chloroform-d1) spectra of PEA-D1-1.25 with DA unit before irradiation (A) and after irradiation at H_5 (B) or H_3 (C) position.

3. Characterization of stress relaxation

Stress relaxation tests were conducted by tensile tests, using an Autograph AGS-J (Shimadzu) at a deformation rate of 1 mm/s and maintained at 100% strain. For comparison, the measured stress was normalized by the initial stress (**Fig. S18**).

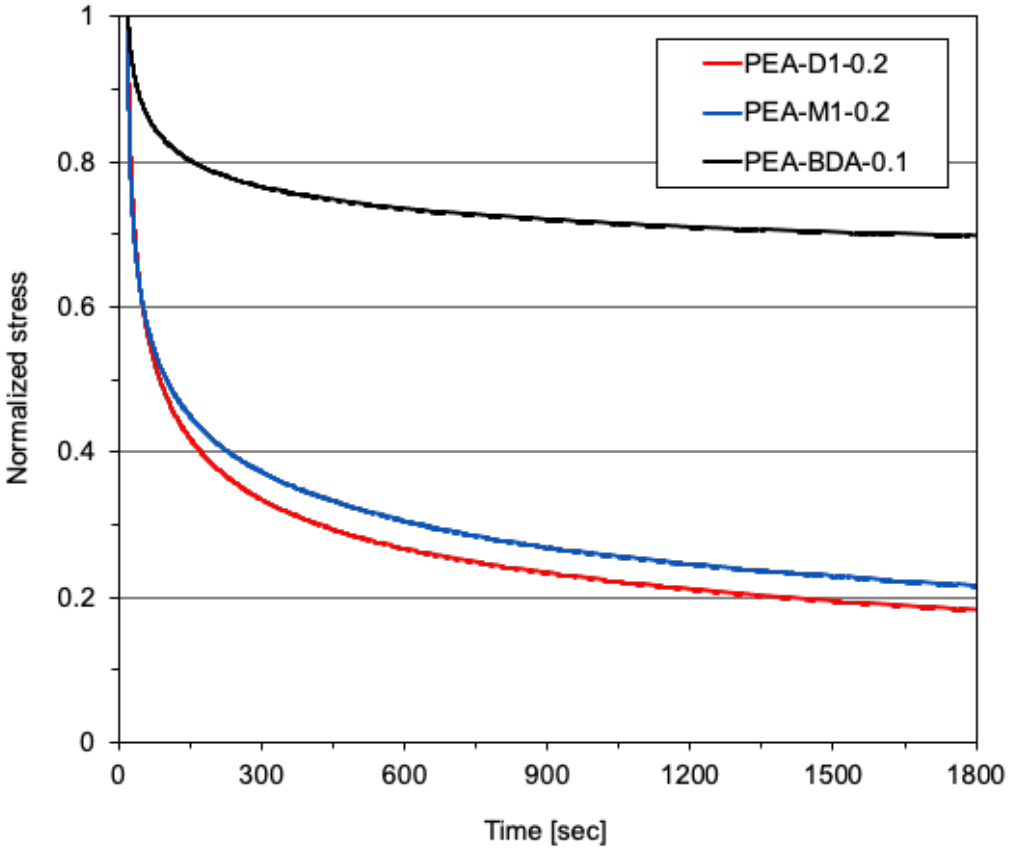


Fig. S18 Stress relaxation of PEA-D1-0.2, PEA-M1-0.2, and PEA-BDA-0.1 at 100% strain.

4. Characterization of self-healing property

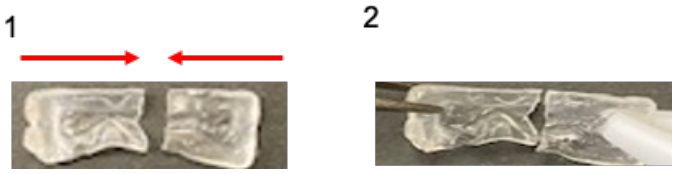


Fig. S19 Photographs of self-healing of PEA–BDA-0.1 elastomer; PEA–BDA-0.1 was cut into two pieces with scissors (1), and then the two pieces were attached together; however, the two pieces did not adhere to each other and separated easily after pulling them in opposing directions (2).

5. Characterization of recyclability

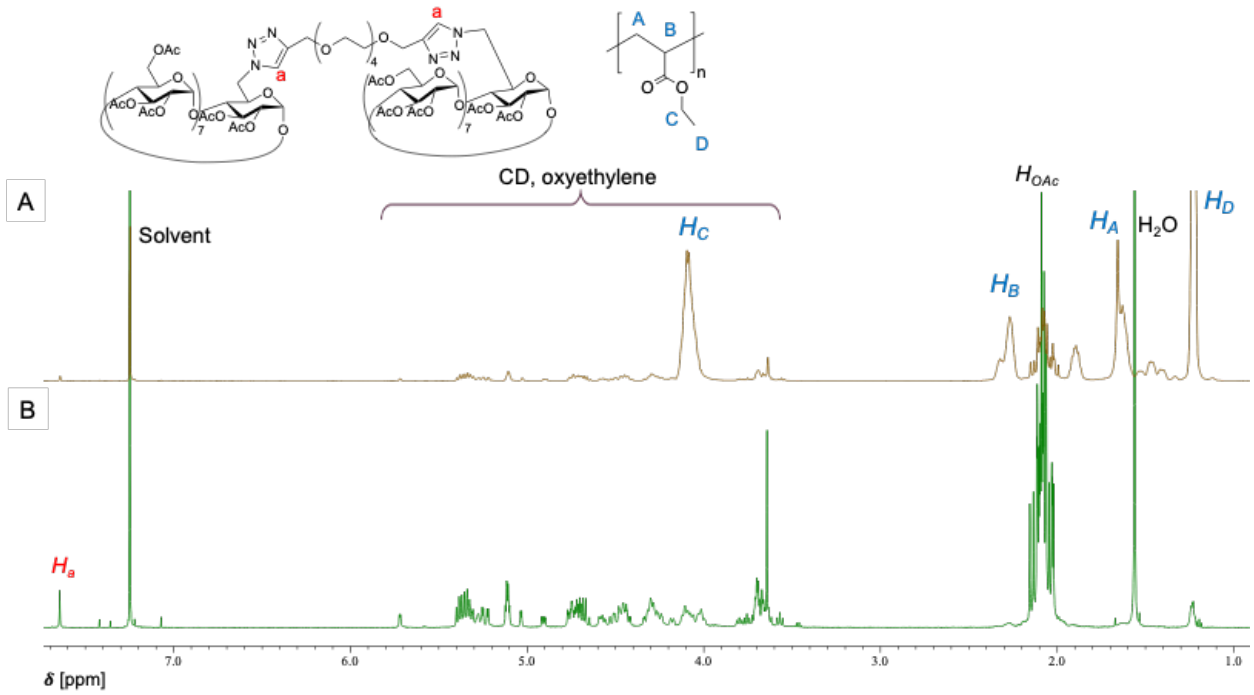


Fig. S20 ^{1}H NMR spectra: (A) PEA-D1-0.5 elastomer, (B) purified product after separation by using diethylether [δ= 0.0 ppm (TMS standard), 600 MHz, $CDCl_3$].

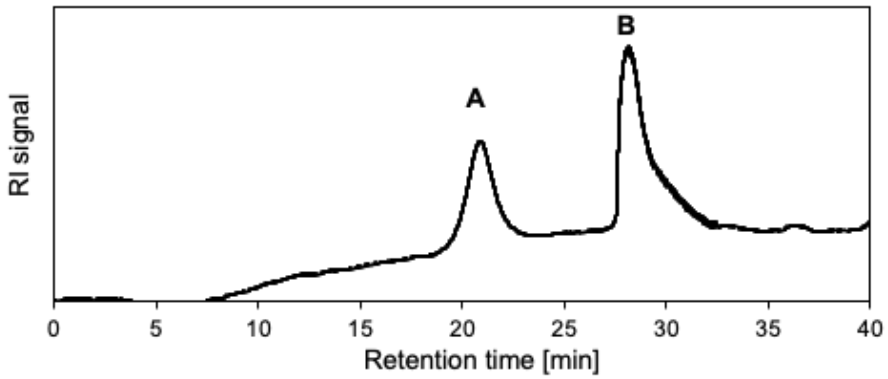


Fig. S21 Preparative GPC chart of continuously separated products corresponding to PEA (A) and D1 (B) after simple dilution of PEA-D1-0.5 elastomer in chloroform. Both compounds were collected by preparative GPC through the simultaneous elution.