- Electronic Supplementary Information -

Fabrication and Mechanical Properties of Knitted Dissimilar Polymeric Materials with Movable Cross-Links

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Contents

1. Experimental details

Materials

Ethyl acrylate (EA), butyl acrylate (BA), styrene (St), chloroform, toluene, and 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from Nacalai Tesque. Chloroform-*d* was purchased from Wako Pure Chemical Industries. Dodecyl acrylate (DA) and hexyl acrylate (HA) were purchased from Tokyo Chemical Industry Co., Ltd. 1-Hydroxy-cyclohexyl-phenyl-ketone (Ciba IRGACURE184) was purchased from BASF Japan Ltd. mono-6*O*-acrylamidomethyl-triicosaacetyl-γ-cyclodextrin (TAcγCDAAmMe) was prepared according to our previous works[1,2]. ZrO_2 balls (YTZ grade, φ = 1 mm) was purchased from AS One Corporation. Water was purified with a Milli-Q system. Other reagents and solvents were used without further purification.

Measurements

Nuclear magnetic resonance (NMR) spectroscopy: ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz with a ECA-500 NMR spectrometer (JEOL) at 25 °C. The solid state ^{1}H field gradient magic angle spinning (FGMAS) NMR spectra were recorded at 400 MHz with a JOEL ECA-400 NMR spectrometer at 25 °C. The ^{1}H-^{1}H nuclear Overhauser effect spectroscopy (NOESY) was performed at 600 MHz with an Agilent VNMR Ver.4.2 System. In all the NMR measurements, chemical shifts were referenced to an internal standard (δ = 0 ppm for tetramethylsilane).

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

Tensile test: Tensile tests of the polymers were performed using Autograph AG-X plus (Shimadzu Co.) at deformation rate of 1 mm/s. The dimension of dumbbell shaped specimen for tensile test is shown in **Fig. S1**. Toughness was calculated from the integral of the stress–strain curve.bi 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 Co.). The test pieces were continuously stretched and recovered without interval, where the maximum strains were set to 100%, 200%, 300%, 400%, 500%, 600%, 700%, 800%, 900%, and 1000% at deformation rate of 1.0 mm/s.

Stress relaxation test: Stress relaxation tests were performed using Autograph AG-X plus (Shimadzu Co.). Test pieces were stretched until 400%. Then, the strain was held and the stress was recorded for 1,0000 seconds.

Gel permeation chromatography (GPC): Number-average molecular weight (M_n), weight-average molecular weight (M_w) and molecular dispersity ($Đ = M_w/M_n$) were measured by GPC in chloroform at 40 °C with two columns (Tosoh TSK gel GMH_{HR} x2). The columns were connected to a Tosoh DP-8020 pump, a CO-8020 column oven, and an RI-8020 refractive index detector. The molecular weights of the samples were calculated based on calibration curve prepared using polystyrene standards.

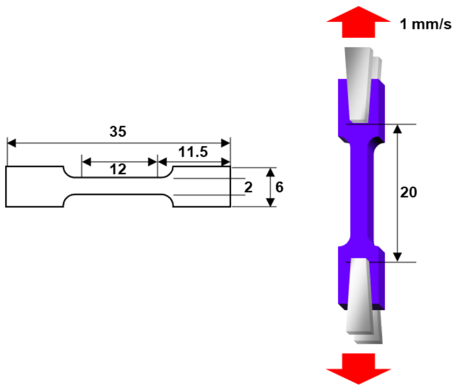


Fig. S1. The dimension of specimen for tensile.

Small angle X-ray scattering (SAXS) measurements: Internal structures of films were determined by SAXS at BL40B2 in SPring-8, Nishiharima, Japan. The wavelength of the incident X-ray beams was 0.10 nm. The sample-to-detector lengths for SAXS was 2m. The lengths of the scattering vector q in the SAXS measurements were 0.06–3.0, where $q = 4\pi \sin \theta/\lambda$ (2θ and λ are the scattering angle and the wavelength, respectively). Test pieces (40 mm×10 mm×1 mm) were stretched at 0.10 mm/s using TST 350 tensile stage (Linkam; 200 N load cell). SAXS profiles in the tensile direction and vertical directions were obtained from the 2D patterns in azimuthal angles φ = 255°~285° and φ = 165°~195°, respectively (**Fig. S2**).

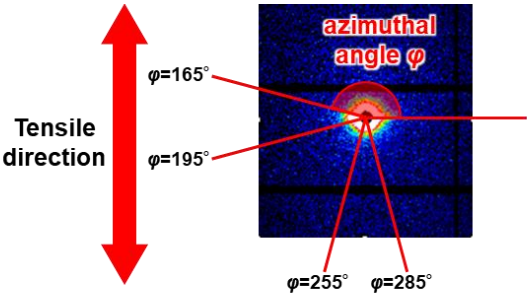


Fig. S2. Azimuthal angle φ.

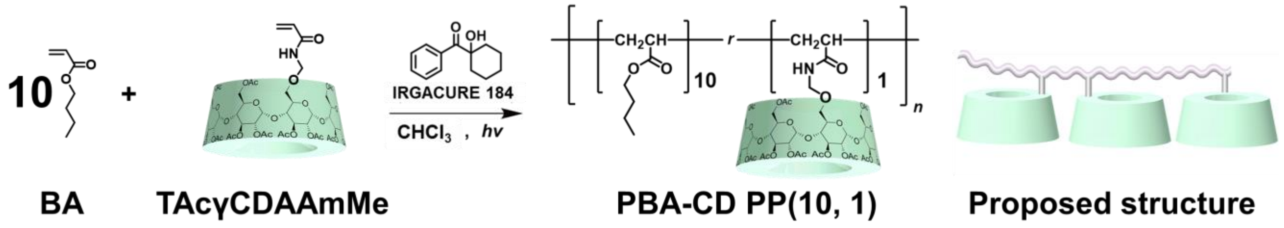
Differential scanning calorimetry (DSC): Glass transition temperatures (T_g) of the polymers were measured by DSC system (Hitachi High-Tech DSC 7020) with N_2 gas flow (50 mL/min.). Thermal transitions were measured in the temperature range of −100 to 150 °C heated 10 °C/min, once heated to 150 °C (10 °C/min) and cooled to −100 °C (10 °C/min) for removal of thermal history in advance.

Thermal gravimetric analysis (TGA): Thermal degradation of the polymers were measured by TGA system (PerkinElmer STA6000). Temperature increased 10 °C/min. from 30 °C to 550 °C with N_2 gas flow (20 mL/min).

Dynamic mechanical analysis (DMA): The viscoelastic properties were measured by DMA system using DVA-250 (IT-Keisoku Seigy Co., Ltd.). The polymer films were cut into 20 mm (width) ×5 mm (long)×0.5mm (thickness). The stretching strain for the samples was set to 0.1%, which is in the linear response regime. The storage modulus (E') and loss modulus (E'') were measured by applying sinusoidal strain at 13 different frequencies (f: 0.25, 0.40, 0.63, 1.0, 1.6, 2.5, 4.0, 6.3, 10, 16, 25, 40, and 63 Hz) at the isothermal condition. The same measurements were reported at several temperatures from −15 °C to 65 °C. The composite curves of E' and E'' were constructed following the time (angular frequency)-temperature superposition principle: each modulus was horizontally shifting moduli using the horizontal shift factor, α_T, setting 24 °C as the reference temperature. Since the time-temperature superposition principle held well, we will discuss the polymer chain dynamics using the composite curves.

2. Preparation and characterization of primary polymers

General preparative method of primary polymers (PBA-CD PP(*x*, *y*))



Scheme S1. Preparation of PBA-CD PP(10, 1).

Scheme S1 shows the preparation of PBA-CD PP(10, 1). BA (210 mg, 1.6 mmol), TAcγCDAAmMe (380 mg, 0.16 mmol), and 1-hydroxycyclohexyl phenyl ketone (Ciba IRGACURE 184 as a photoinitiator; 3.6 mg, 0.018 mmol) were dissolved in chloroform (2400 mg; equal to 4 times of monomers weight). Free radical copolymerization of the monomers was carried out under UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 2.0 hours in N_2 atmosphere. To complete the copolymerization, further IRGACURE 184 (3.6 mg, 0.018 mmol) was added in reaction mixture and UV irradiation was continued for additional 2.0 hours. After evaporation of solvent, the products were dried at 80 °C in vacuo for 12 hours. The other PBA-CD PP(*x*, *y*) primary polymers were also prepared by the same manner. **Table S1** summarize amounts of reagents in the reactions.

^{1}H NMR (500 MHz, chloroform-*d*) of PBA-CD PP(10, 1): δ = 5.47~5.27 (8H: C(3)*H* of CD), 5.27~5.03 (8H: C(1)*H* of CD), 5.00~4.62 (10H: C(2)*H* of CD and -NHCH_2O-), 4.62~4.17 (14H: C(6')*H* of CD), 4.17~3.58 (28H: C(5)*H* of CD and $CH_3CH_2CH_2C\mathit{H}_2$- of BA), 4.17~3.58 (10H: C(4, 6)*H* of CD), 2.56~2.20 (11H: -CH_2C*H*- of main chain), 2.13~2.03 (69H: CH_3 of acetyl), 1.96~1.21 (62H: -CH_2CH- of main chain and $CH_3C\mathit{H}_2C\mathit{H}_2CH_2$- of BA overlaps with water), 1.10~0.77 (30H: $C\mathit{H}_3CH_2CH_2CH_2$- of BA).

^{13}C NMR (125 MHz, chloroform-*d*) of PBA-CD PP(10, 1): δ = 175.2~174.2 (-*C*OO- and -*C*ONH-), 171.4~169.1 (CH_3-*C*O- in acetyl), 97.9~95.0 (*C*(1)H of CD), 76.5~73.8 (*C*(4)H of CD overlaps with $\mathit{C}DCl_3$), 73.0~68.1 (*C*(2, 3, 5)H of CD), 68.1~50.0 (*C*(6)H of CD, -NH$\mathit{C}H_2$O-, $CH_3CH_2CH_2\mathit{C}H_2$- of BA), 43.4~39.5 (-$CH_2\mathit{C}H$- of main chain), 38.4~33.2(-$\mathit{C}H_2CH$- of main chain), 33.2~28.5 ($CH_3CH_2\mathit{C}H_2CH_2$- of BA), 23.8~17.4 ($\mathit{C}H_3$-CO- in acetyl, $CH_3\mathit{C}H_2CH_2CH_2$- of BA), 15.7~11.4 ($\mathit{C}H_3CH_2CH_2CH_2$- of BA).

Table S1. Preparation of PBA-CD PP(x, y) polymers varying the mol% of BA and TAcγCD units (x, y).

PBA-CD PP(x, y)	BA			TAcγCDAAmMe			IRGACURE 184			Chloroform
	/mg	/mmol	/mol%	/mg	/mmol	/mol%	/mg	/mmol	/mol%	/mg
PBA-CD PP(10, 0.5)	210	1.6	10	190	0.08	0.5	3.5 → 3.5	0.017 → 0.017	1.0 → 1.0	1600
PBA-CD PP(10, 1)	210	1.6	10	380	0.16	1.0	3.6 → 3.6	0.018 → 0.018	1.0 → 1.0	2400
PBA-CD PP(10, 2)	210	1.6	10	770	0.33	2.0	4.0 → 4.0	0.020 → 0.020	1.0 → 1.0	3900

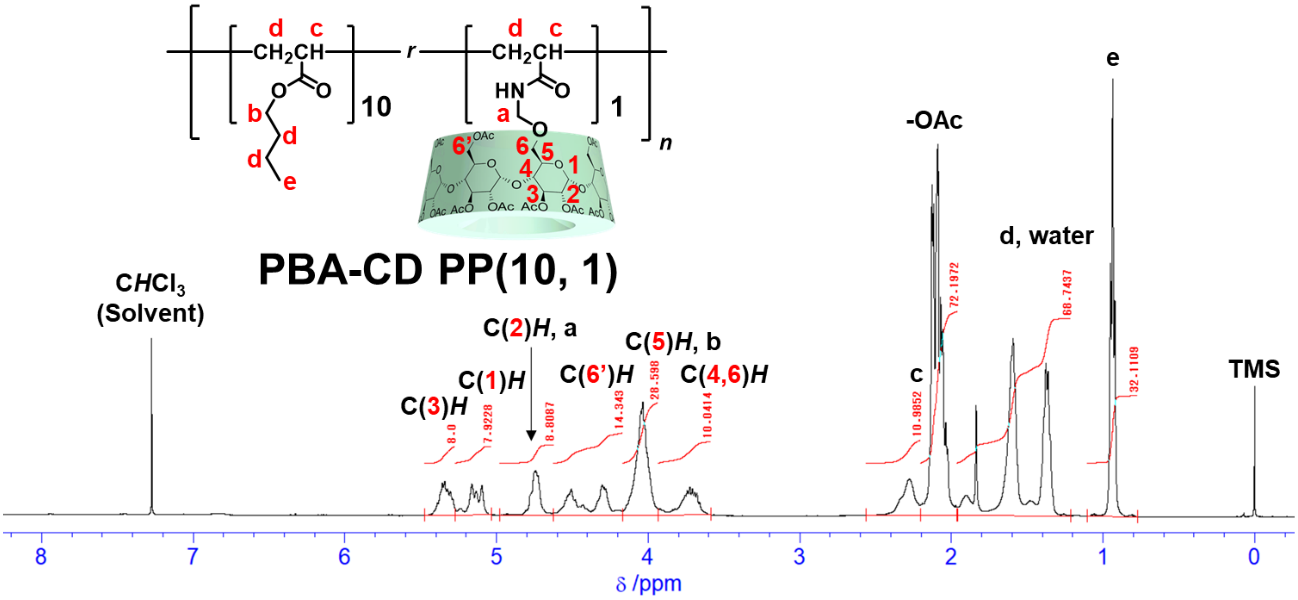


Fig. S3. 500 MHz ^{1}H NMR spectrum of PBA-CD PP(10, 1) in chloroform-d.

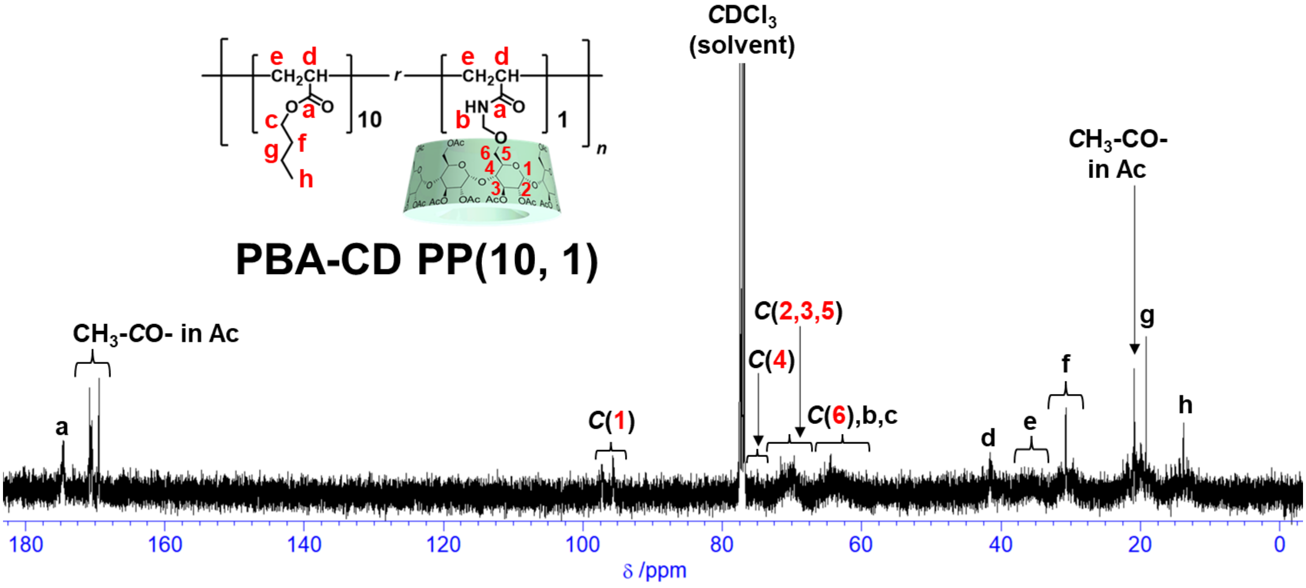
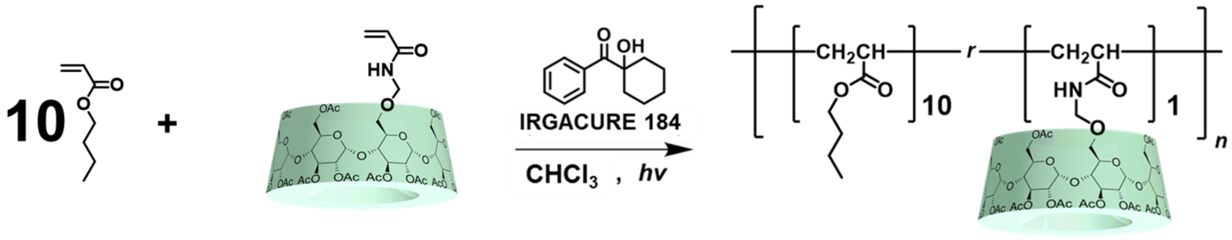


Fig. S4. 125 MHz ^{13}C NMR spectrum of PBA-CD PP(10, 1) in chloroform-d.



BA **TAcγCDAAmMe** **PBA-CD PP(10, 1)**

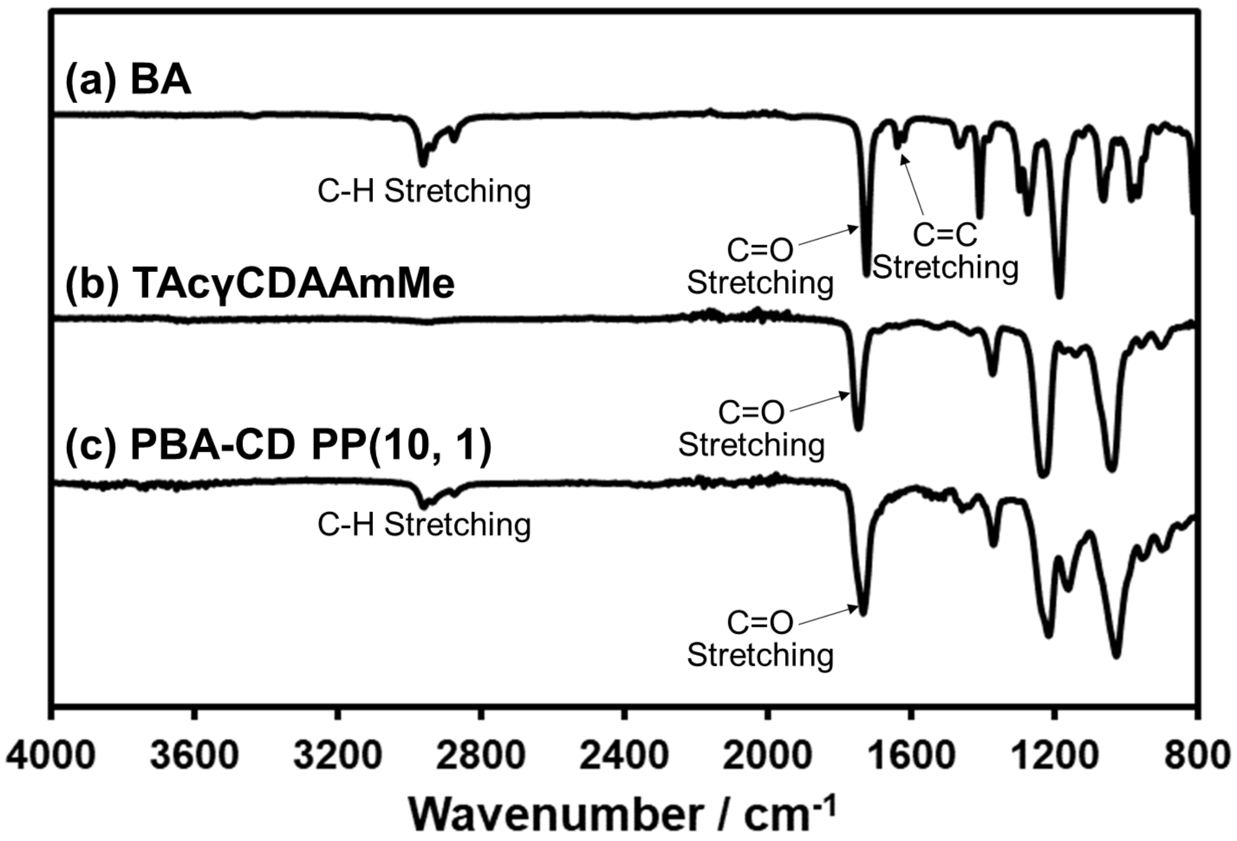
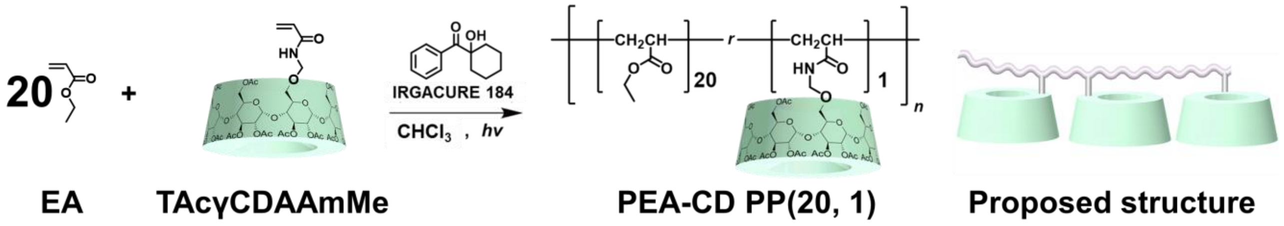


Fig. S5. FT-IR spectra (ATR method) of BA **(a)**, TAcγCDAAmMe **(b)**, and PBA-CD PP(10, 1) **(c)**.

General preparative method of primary polymers (PEA-CD PP(*x*, *y*))



Scheme S2. Preparation of PEA-CD PP(20, 1).

Scheme S2 shows the preparation of PEA-CD PP(20, 1). EA (300 mg, 3.0 mmol), TAcγCDAAmMe(390 mg, 0.17 mmol), and IRGACURE 184 (photoinitiator; 6.5 mg, 0.032 mmol) were dissolved in chloroform (2800 mg; equal to 4 times of monomers weight). Free radical copolymerization of the monomers was carried out under UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 2.0 hours in N_2 atmosphere. To complete the copolymerization, further IRGACURE 184 (6.5 mg, 0.032 mmol) was added in reaction mixture and UV irradiation was continued for additional 2.0 hours. After evaporation of solvent, the products were dried at 80 ^{o}C in vacuo for 12 hours. The other PEA-CD PP(*x*, *y*) primary polymers were also prepared by the same manner. **Table S2** summarize amounts of reagents in the reactions.

^{1}H NMR (500 MHz, chloroform-*d*) of PEA-CD PP(20, 1): δ = 5.57~5.26 (8H: C(3)*H* of CD), 5.27~5.03 (8H: C(1)*H* of CD), 5.01~4.62 (10H: C(2)*H* of CD and -NHCH_2O-), 4.62~4.23 (14H: C(6')*H* of CD), 4.23~3.36 (48H: C(5)*H* of CD and CH_3CH_2- of EA), 4.23~3.36 (10H: C(4, 6)*H* of CD), 2.60~2.20 (21H: -CH_2C*H*- of main chain), 2.20~1.98 (69H: CH_3 of acetyl), 1.98~1.34 (42H: -CH_2CH- of main chain overlaps with water), 1.34~0.92 (60H: C$H_3$$CH_2$- of EA).

^{13}C NMR (125 MHz, chloroform-*d*) of PEA-CD PP(20, 1): δ = 175.0~174.2 (-*C*OO- and -*C*ONH-), 171.4~169.3 (CH_3-*C*O- in acetyl), 98.0~95.3 (*C*(1)H of CD), 76.7~75.7 (*C*(4)H of CD overlaps with *C*DCl_3 and *C*HCl_3), 73.0~67.9 (*C*(2, 3, 5)H of CD), 65.3~57.6 (*C*(6)H of CD, NH*C*H_2O-, and CH_3*C*H_2- of EA), 44.2~38.2 (-CH_2*C*H- of main chain), 38.2~32.6 (-*C*H_2CH- of main chain), 23.7~18.6 (*C*H_3-CO- in acetyl), 17.7~11.1 (*C*$H_3$$CH_2$- of EA).

Table S2. Preparation of PEA-CD PP(*x*, *y*) polymers varying the mol% of EA and TAcγCD units (*x*, *y*).

PEA-CD PP(*x*, *y*)	EA			TAcγCDAAmMe			IRGACURE 184			Chloroform
	/mg	/mmol	/mol%	/mg	/mmol	/mol%	/mg	/mmol	/mol%	/mg
PEA-CD PP(20, 0.5)	300	3.0	20	200	0.08	0.5	6.4 → 6.4	0.031 → 0.031	1.0 → 1.0	2000
PEA-CD PP(20, 1)	300	3.0	20	390	0.17	1.0	6.5 → 6.5	0.032 → 0.032	1.0 → 1.0	2800
PEA-CD PP(20, 2)	310	3.1	20	790	0.34	2.0	7.0 → 7.0	0.034 → 0.034	1.0 → 1.0	4400

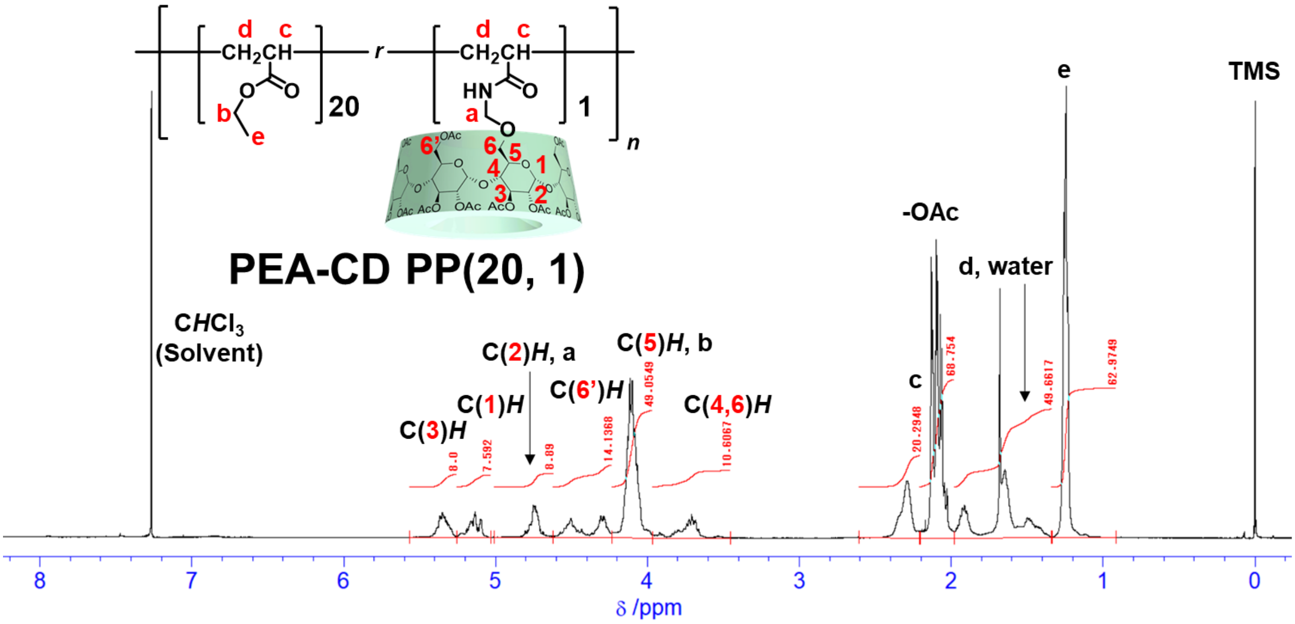


Fig. S6. 500 MHz ^{1}H NMR spectrum of PEA-CD PP(20, 1) in chloroform-*d*.

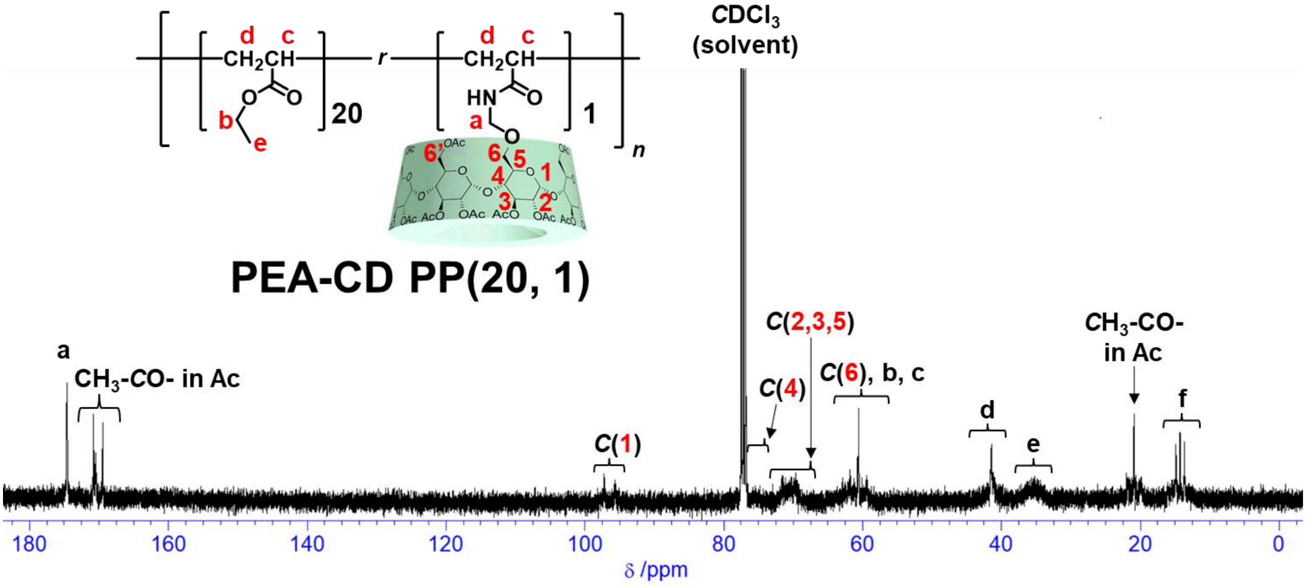


Fig. S7. 125 MHz ^{13}C NMR spectrum of PEA-CD PP(20, 1) in chloroform-*d*.

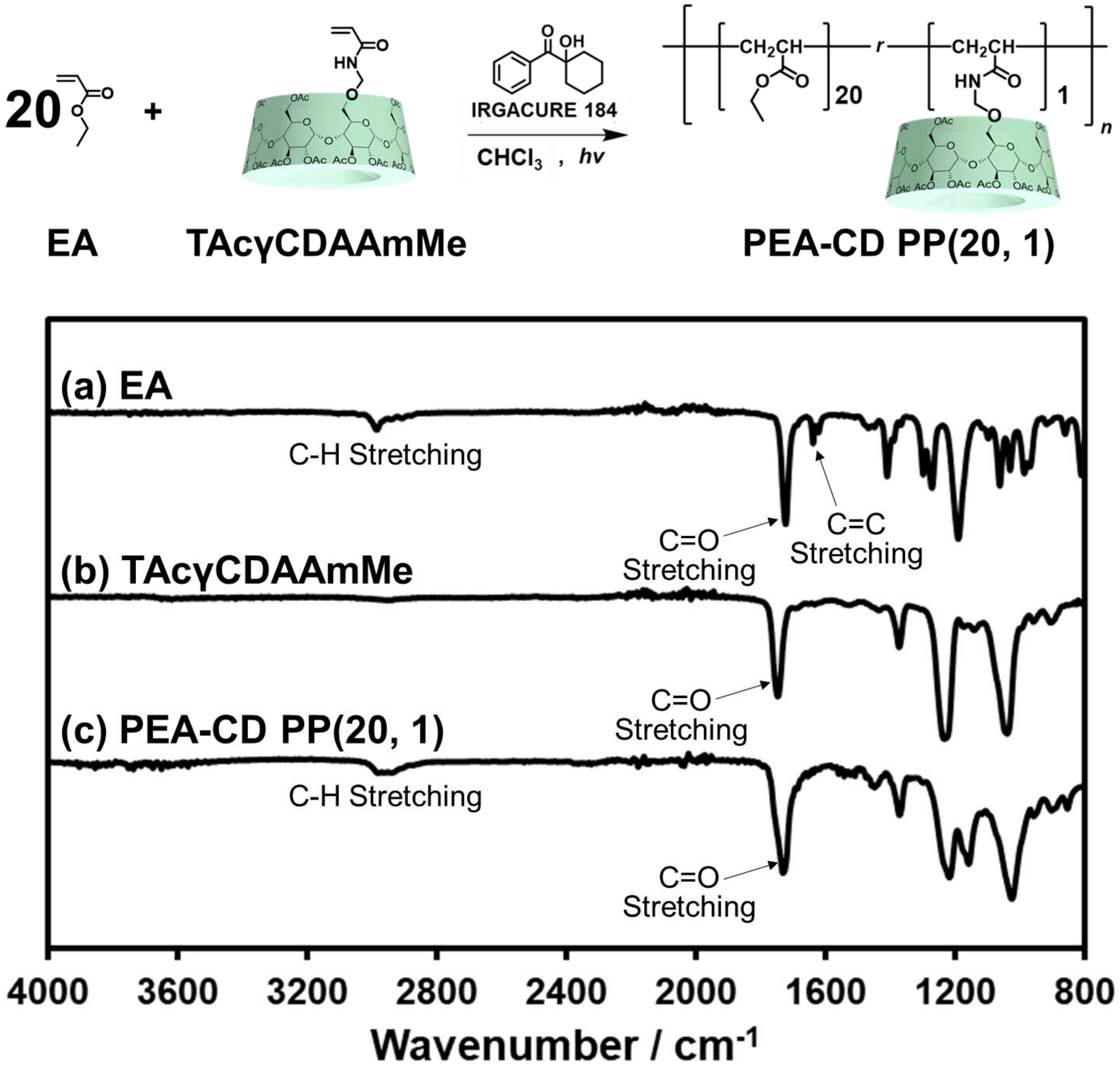
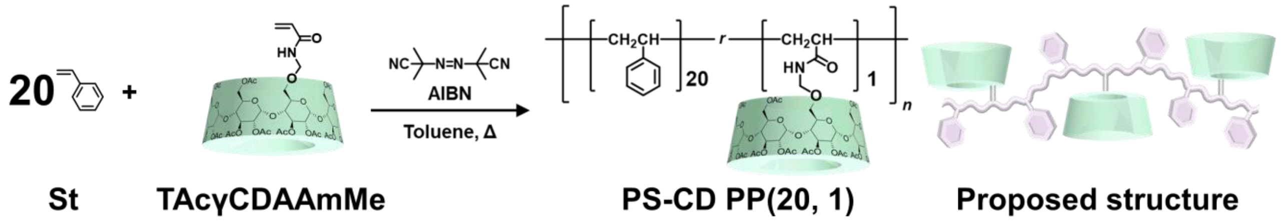


Fig. S8. FT-IR spectra (ATR method) of EA **(a)**, TAcγCDAAmMe **(b)**, and PEA-CD PP(20, 1) **(c)**.

General preparative method of primary polymers (PS-CD PP(*x*, *y*))



Scheme S3. Preparation of PS-CD PP(20, 1).

Scheme S3 shows the preparation of PS-CD PP(20, 1). TAcγCDAAmMe (390 mg, 0.17 mmol), St (340 mg, 3.3 mmol), and AIBN (5.7 mg, 0.035 mmol) were dissolved in toluene (740 mg; equal to monomers weight). Free radical copolymerization of the monomers was carried out at 80 ^{o}C for 24 hours in N_2 atmosphere. Further toluene (180 mg; 0.25 times of monomers weight) solution of AIBN (5.7 mg, 0.035 mmol) was added and stayed for 24 hours. Toluene (180 mg; 0.25 times of monomers weight) solution of AIBN (5.7 mg, 0.035 mmol) was added again and heated at 100 ^{o}C for 12 hours. After evaporation of solvent, the products were dried at 100 ^{o}C in vacuo for 12 hours. The other PS-CD PP(*x*, *y*) primary polymers were also prepared by the same manner. **Table S3** summarize amounts of reagents and solvents in the reactions.

^{1}H NMR (500 MHz, chloroform-*d*) of PS-CD PP(20, 1): δ = 7.21~6.82 (60H: *m*,*p*-protons of phenyl), 6.82~6.22 (40H: *o*-protons of phenyl), 5.45~5.25 (8H: C(3)*H* of CD), 5.25~5.05 (8H: C(1)*H* of CD), 5.05~4.63 (10H: C(2)*H* of CD and -NHCH_2O-), 4.63~4.19 (14H: C(6')*H* of CD), 4.19~3.95 (8H: C(5)*H* of CD), 3.95~3.57 (10H: C(4, 6)*H* of CD), 2.36 (1H: -CH_2C*H*- of main chain in CD units), 2.32~2.04 (69H: CH_3 of acetyl), 2.04~1.66 (20H: -CH_2C*H*- of main chain in St units), 1.66~1.20 (42H: -CH_2CH- of main chain overlaps with water).

^{13}C NMR (125 MHz, chloroform-*d*) of PS-CD PP(20, 1): δ = 171.5~168.4 (CH_3-*C*O- in acetyl), 147.0~144.7 (*ipso*-carbon of phenyl), 130.6~125.9 (*o*,*m*-carbons of phenyl), 125.9~123.6 (*p*-carbons of phenyl), 99.2~94.8 (*C*(1)H of CD), 76.6~74.9 (*C*(4)H of CD overlaps with *C*DCl_3), 73.3~67.0 (*C*(2, 3, 5)H of CD), 64.7~60.6 (*C*(6)H of CD), 44.8~41.7 (-CH_2*C*H- of main chain in St units), 41.7~35.3 (-*C*H_2CH- of main chain in St units and -*C*H_2*C*H- of main chain in CD units), 24.1~17.8 (*C*H_3-CO- in acetyl).

Table S3. Preparation of PS-CD PP(*x*, *y*) polymers varying the mol% of St and TAcγCD units (*x*, *y*).

PS-CD PP(*x*, *y*)	St			TAcγCDAAmMe			AIBN			Toluene
	/mg	/mmol	/mol%	/mg	/mmol	/mol%	/mg	/mmol	/mol%	/mg
PS-CD PP(20, 0.5)	340	3.3	20	190	0.08	0.5	5.6 → 5.6 → 5.6	0.034 → 0.034 → 0.034	1.0 → 1.0 → 1.0	540 → 140 → 140
PS-CD PP(20, 1)	340	3.3	20	390	0.17	1.0	5.7 → 5.7 → 5.7	0.035 → 0.035 → 0.035	1.0 → 1.0 → 1.0	740 → 180 → 180
PS-CD PP(20, 2)	350	3.3	20	780	0.33	2.0	6.0 → 6.0 → 6.0	0.037 → 0.037 → 0.037	1.0 → 1.0 → 1.0	1100 → 280 → 280

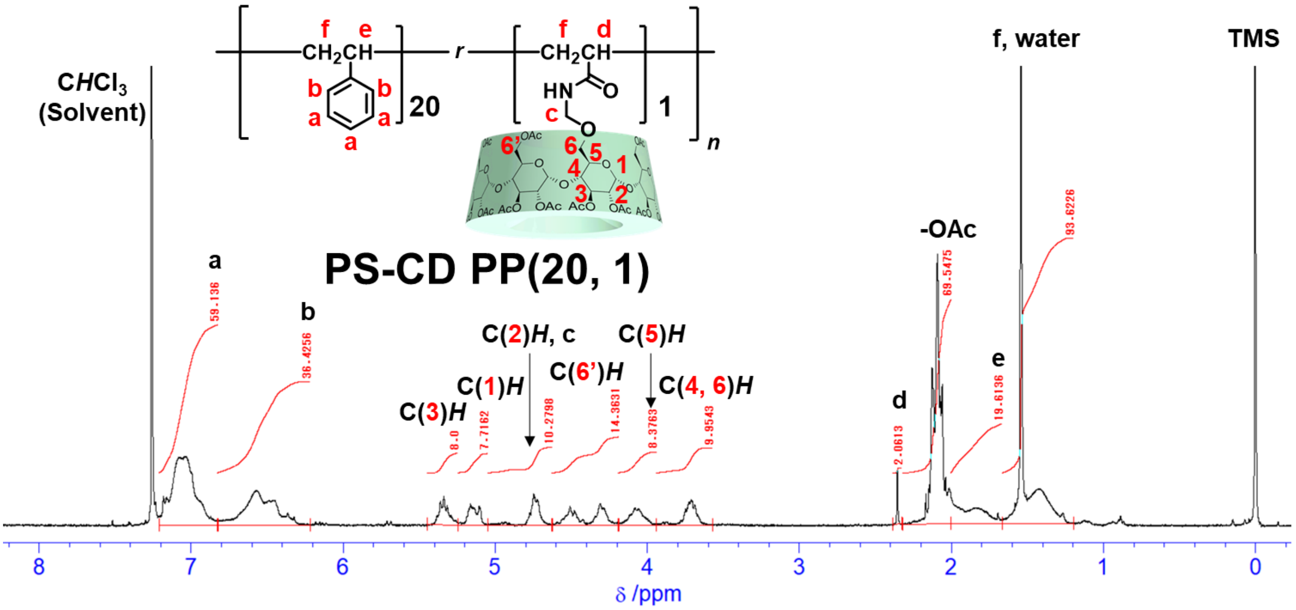


Fig. S9. 500 MHz ^{1}H NMR spectrum of PS-CD PP(20, 1) in chloroform-*d*.

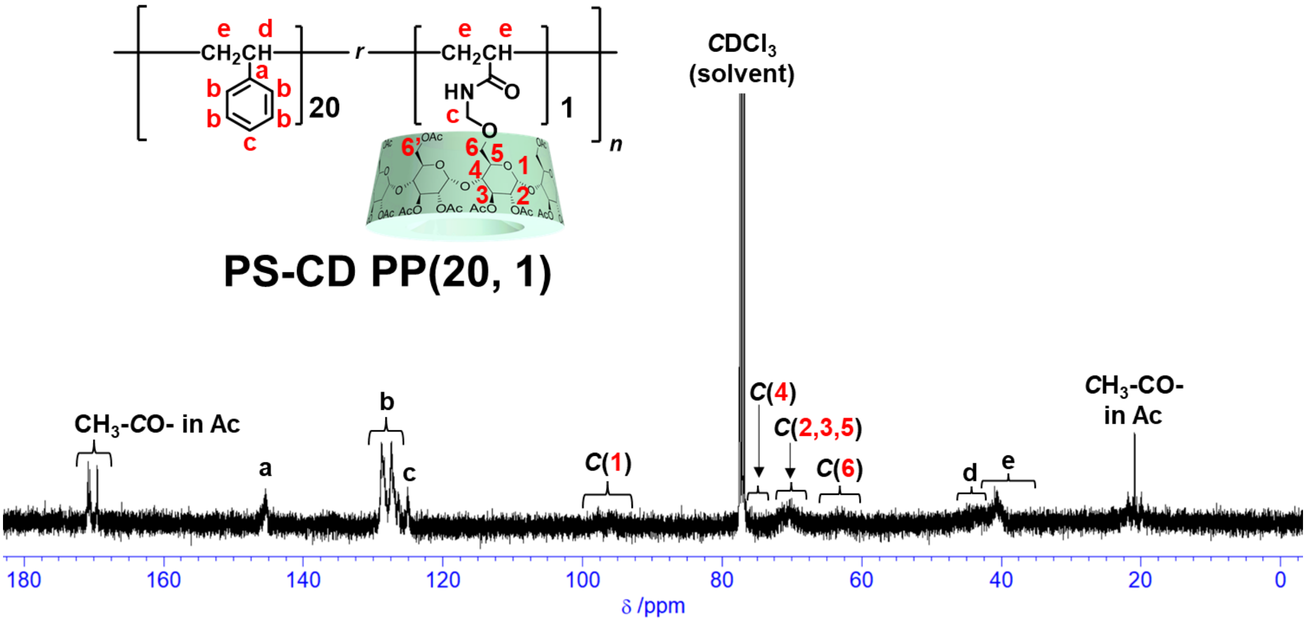
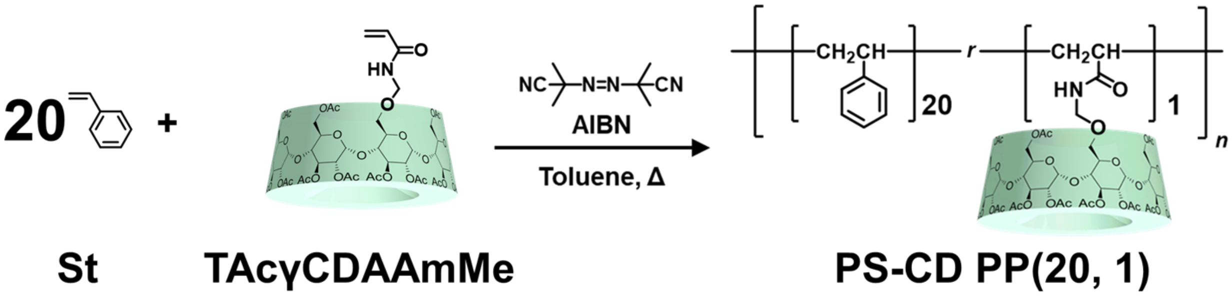


Fig. S10. 125 MHz ^{13}C NMR spectrum of PS-CD PP(20, 1) in chloroform-*d*.



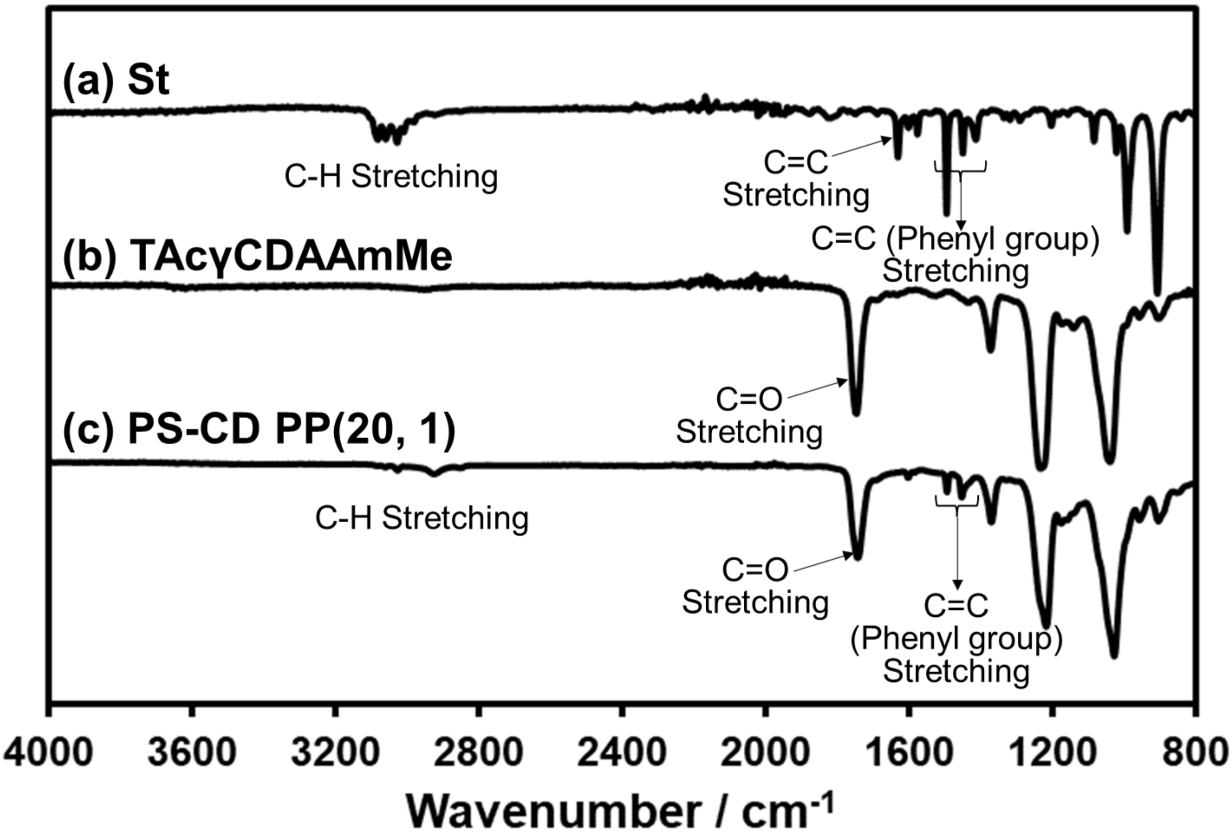
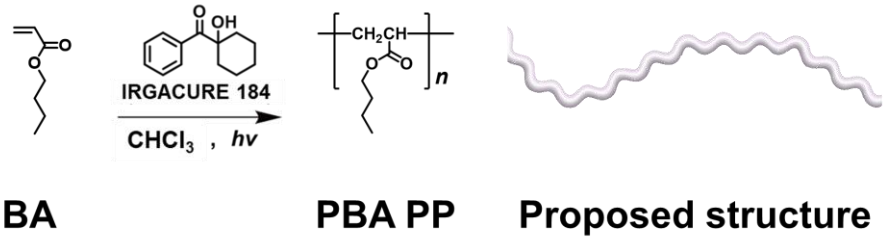


Fig. S11. FT-IR spectra (ATR method) of St **(a)**, TAcγCDAAmMe **(b)**, and PS-CD PP(20, 1) **(c)**.

General preparative method of primary polymer (PBA PP)



Scheme S4. Preparation of PBA PP.

Scheme S4 shows the preparation of PBA PP. BA (210 mg, 1.6 mmol) and IRGACURE 184 (photoinitiator; 3.3 mg, 0.016 mmol) were dissolved in chloroform (630 mg; equal to 4 times of monomers weight). Free radical copolymerization of the monomers was carried out under UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 2 hours in N_2 atmosphere. To complete the copolymerization, further IRGACURE 184 (3.3 mg, 0.016 mmol) was added in reaction mixture and UV irradiation was continued for additional 2 hours. After evaporation of solvent, the products were dried at 80 ^{o}C in vacuo for 12 hours.

^{1}H NMR (500 MHz, chloroform-*d*) of PBA PP: δ = 4.28~3.75 (2H: $CH_3CH_2CH_2CH_2$- of BA), 2.57~2.08 (1H: -CH_2CH- of main chain), 2.08~1.13 (6H: -CH_2CH- of main chain and $CH_3CH_2CH_2CH_2$- of BA), 1.12~0.73 (3H: $CH_3CH_2CH_2CH_2$- of BA).

^{13}C NMR (125 MHz, chloroform-*d*) of PBA PP: δ = 174.7~174.0 (-COO-), 60.8~60.3 ($CH_3CH_2CH_2CH_2$- of BA), 42.3~40.5 (-CH_2CH- of main chain), 37.6~33.1(-CH_2CH- of main chain), 30.8~30.4 ($CH_3CH_2CH_2CH_2$- of BA), 19.4~18.8 ($CH_3CH_2CH_2CH_2$- of BA), 14.7~13.4 ($CH_3CH_2CH_2CH_2$- of BA).

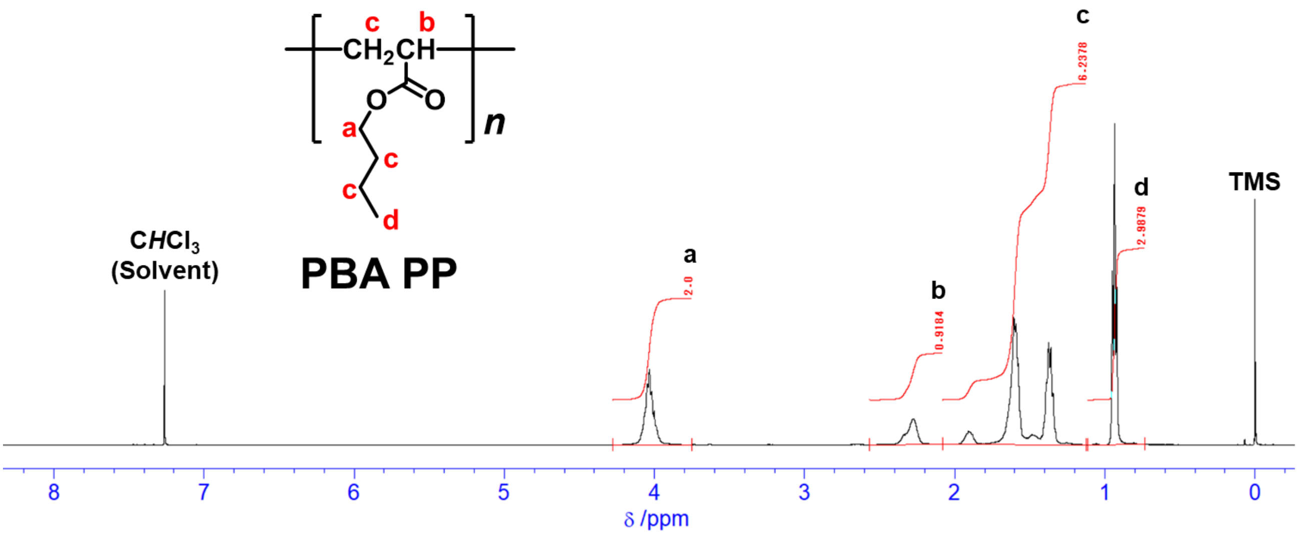


Fig. S12. 500 MHz ^{1}H NMR spectrum of PBA PP in chloroform-*d*.

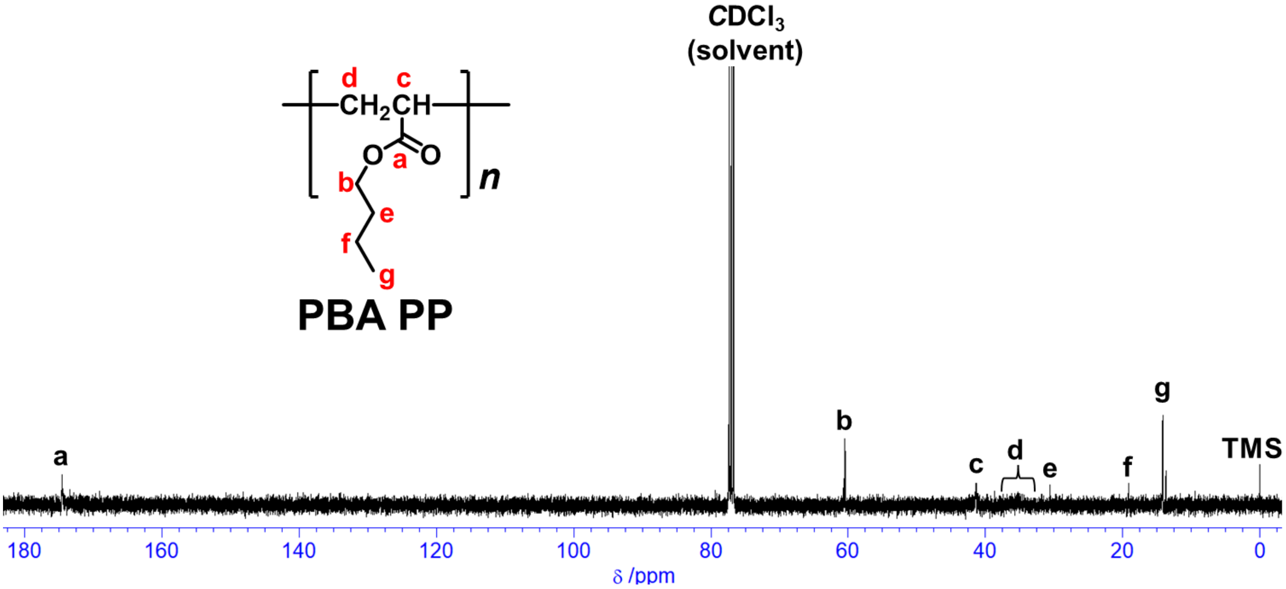
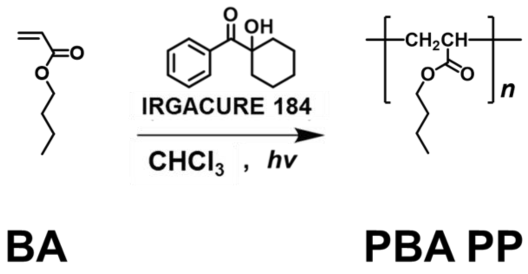


Fig. S13. 125 MHz ^{13}C NMR spectrum of PBA PP in chloroform-*d*.



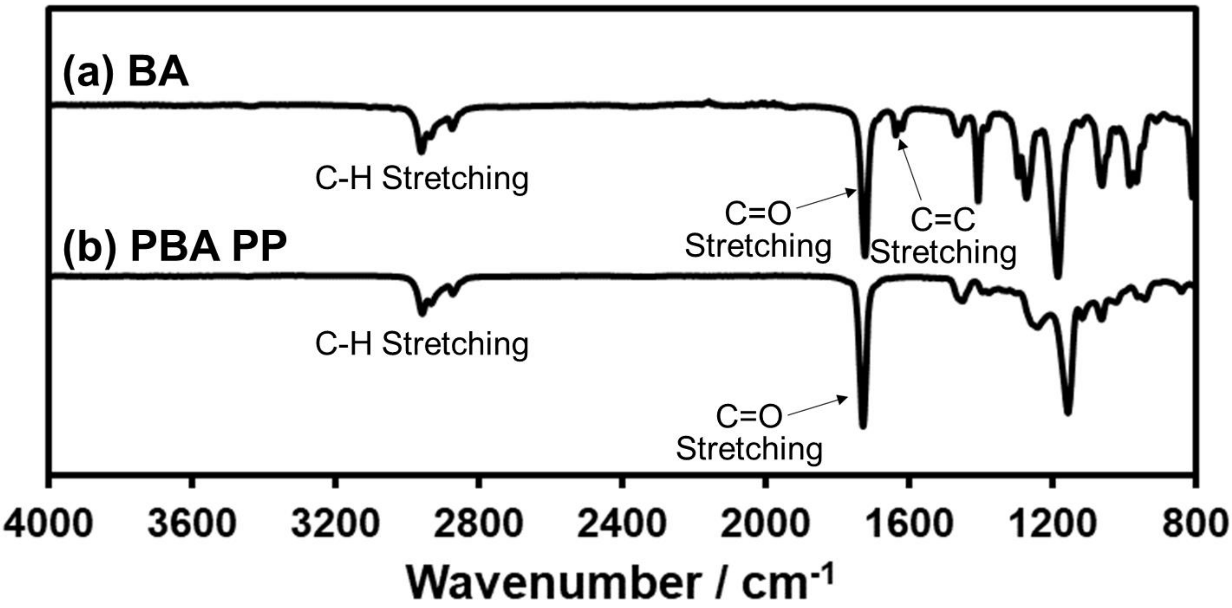
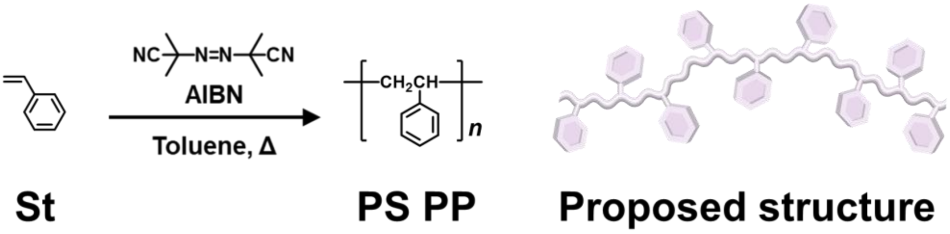


Fig. S14. FT-IR spectra (ATR method) of BA **(a)** and PBA PP **(b)**.

General preparative method of primary polymer (PS PP)



Scheme S5. Preparation of PS PP.

Scheme S5 shows the preparation of PS PP. St (340 mg, 3.3 mmol) and AIBN (5.4 mg, 0.033 mmol) were dissolved in toluene (350 mg; equal to monomers weight). Free radical copolymerization of the monomers was carried out at 80 ^{o}C for 24 hours in N_2 atmosphere. Toluene (90 mg; 0.25 times of monomers weight) solution of AIBN (5.4 mg, 0.033 mmol) was added and stayed for 24 hours. Further toluene (90 mg; 0.25 times of monomers weight) solution of AIBN (5.4 mg, 0.033 mmol) was added again and heated at 100 ^{o}C for 12 hours. After evaporation of solvent, the products were dried at 100 ^{o}C in vacuo for 12 hours.

^{1}H NMR (500 MHz, chloroform-*d*) of PS PP: δ = 7.21~6.86 (3H: *m*,*p*-protons of phenyl), 6.86~6.14 (2H: *o*-protons of phenyl), 2.30~1.66 (1H: $-CH_2C\mathit{H}-$ of main chain), 1.66~0.66 (2H: $-C\mathit{H}_2CH-$ of main chain overlaps with water).

^{13}C NMR (125 MHz, chloroform-*d*) of PS PP: δ = 146.8~143.4 (*ipso*-carbon of phenyl), 129.7~125.6 (*o,m*-carbons of phenyl), 125.6~124.0 (*p*-carbons of phenyl), 45.4~41.4 ($-CH_2\mathit{C}H-$ of main chain), 41.4~39.2 ($-\mathit{C}H_2CH-$ of main chain).

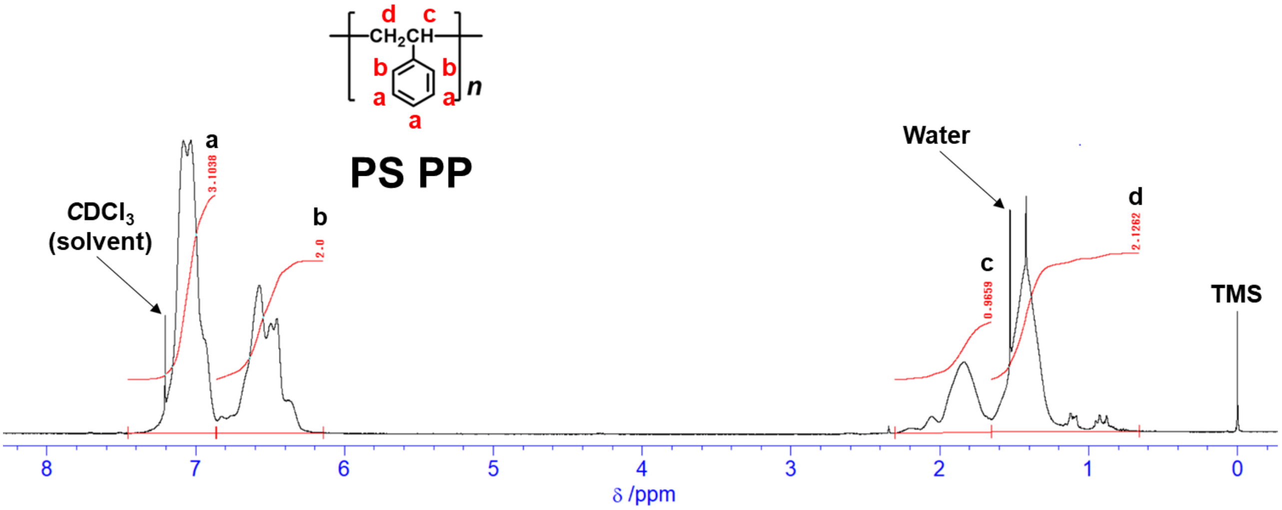


Fig. S15. 500 MHz ^{1}H NMR spectrum of PS PP in chloroform-*d*.

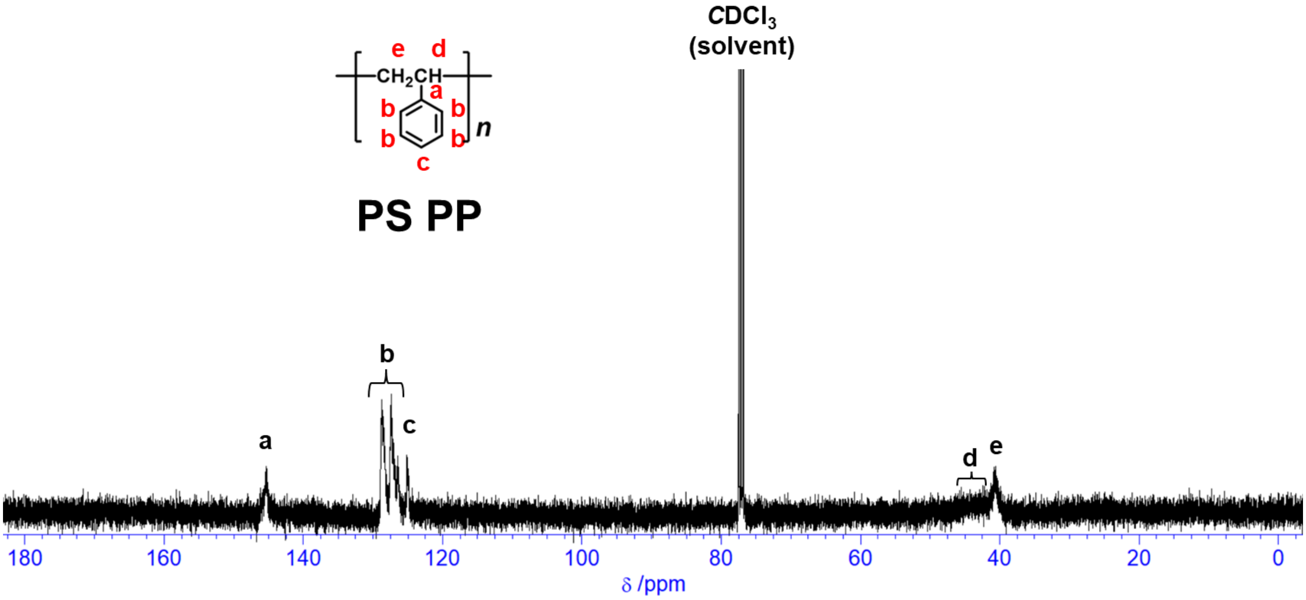
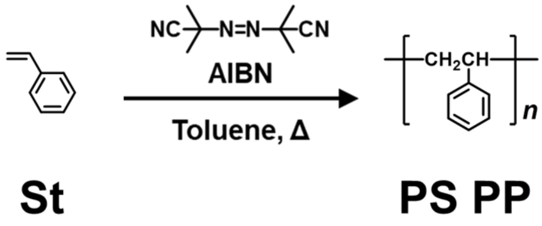


Fig. S16. 125 MHz ^{13}C NMR spectrum of PS PP in chloroform-*d*.



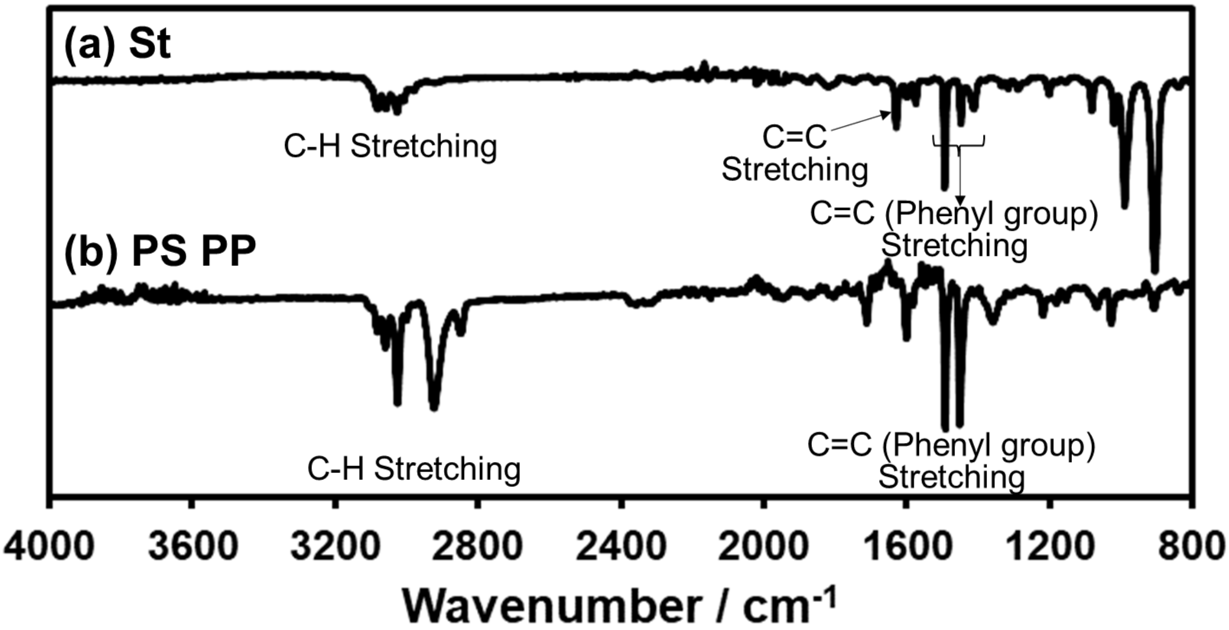
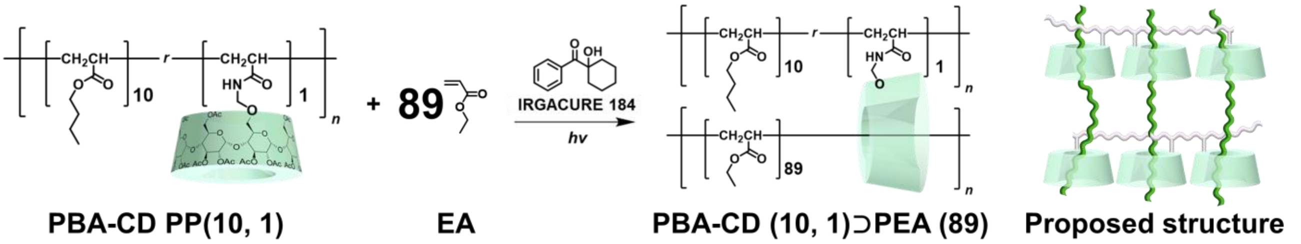


Fig. S17. FT-IR spectra (ATR method) of St **(a)** and PS PP **(b)**.

3. Preparation of movable cross-network elastomers knitting dissimilar polymers (KP)

General preparative method of movable cross-network elastomers knitting dissimilar polymers (PBA-CD (*x*, *y*)$\supset$PEA (*z*))



Scheme S6. Preparation of PBA-CD (10, 1)$\supset$PEA (89) and proposed structure.

Scheme S6 shows the preparation of PBA-CD (10, 1)$\supset$pEA (89). PBA-CD PP(10, 1) (590 mg) and IRGACURE 184 (photoinitiator; 5.9 mg, 0.029 mmol) were dissolved in EA (1400 mg, 14 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 ^{o}C in vacuo for 12 hours. The other PBA-CD (*x*, *y*)$\supset$pEA (*z*) KP elastomers were also prepared by same manner. **Table S4** summarize amounts of reagents in the reactions.

^{1}H NMR (500 MHz, chloroform-*d*) of PBA-CD (10, 1)$\supset$PEA (89): δ = 5.53~5.25 (8H: C(3)*H* of CD), 5.25~5.00 (8H: C(1)*H* of CD), 5.00~4.62 (10H: C(2)*H* of CD and $\mathrm{-NHC}\mathit{H}_2\mathrm{O}$-), 4.60~4.22 (14H: C(6')*H* of CD), 4.17~3.85 (206H: C(5)*H* of CD, $\mathrm{CH_3CH_2CH_2C}\mathit{H}_2$- of BA, and $\mathrm{CH_3C}\mathit{H}_2$- of EA), 3.85~3.48 (10H: C(4,6)*H* of CD), 2.61~2.21 (100H: $\mathrm{-CH_2C}\mathit{H}$- of main chain), 2.21~2.00 (69H: $\mathrm{C}\mathit{H}_3$ of acetyl), 2.00~1.30 (240H: $\mathrm{-C}\mathit{H}_2\mathrm{CH}$- of main chain and $\mathrm{CH_3C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2}$- of BA overlaps with water), 1.30~1.04 (267H: $\mathrm{C}\mathit{H}_3\mathrm{CH_2}$- of EA), 1.04~0.69 (30H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2CH_2}$- of BA).

^{13}C NMR (125 MHz, chloroform-*d*) of PBA-CD (10, 1)$\supset$PEA (89): δ = 175.6~174.0 (-*C*OO- and -*C*ONH-), 171.0~169.2 ($\mathrm{CH_3}$-*C*O- in acetyl), 96.7~96.1 (*C*(1)H of CD), 76.5~75.1 (*C*(4)H of CD overlaps with *C*$\mathrm{DCl_3}$), 72.2~67.9 (*C*(2, 3, 5)H of CD), 65.0~64.1 (*C*(6)H of CD), 63.1~62.0 ($\mathrm{-NH}\mathit{C}\mathrm{H_2O}$-), 61.3~60.1 ($\mathrm{CH_3CH_2CH_2}\mathit{C}\mathrm{H_2}$- of BA, and $\mathrm{CH_3}\mathit{C}\mathrm{H_2}$- of EA), 42.4~40.4 ($\mathrm{-CH_2}\mathit{C}\mathrm{H}$- of main chain), 36.9~33.3(-$\mathit{C}\mathrm{H_2CH}$- of main chain), 31.0~30.2 ($\mathrm{CH_3CH_2}\mathit{C}\mathrm{H_2CH_2}$- of BA), 21.2~20.5 ($\mathit{C}\mathrm{H_3}$-CO- in acetyl), 19.7~18.6 ($\mathrm{CH_3}\mathit{C}\mathrm{H_2CH_2CH_2}$- of BA), 14.7~13.3 ($\mathit{C}\mathrm{H_3CH_2CH_2CH_2}$- of BA and $\mathit{C}\mathrm{H_3CH_2}$- of EA).

Table S4. Preparation of PBA-CD (x, y)⊃PEA (z) elastomers varying the mol% of BA, TAcγCD, and EA units (x, y, z).

PBA-CD(x , y)⊃PEA(z)	EA			IRGACURE 184			Primary polymer	
	/mg	/mmol	/mol%	/mg	/mmol	/mol%	Name	/mg
PBA-CD(10, 0.5)⊃PEA(89)	1400	14	89	5.9	0.029	0.2	PBA-CD PP(10, 0.5)	400
PBA-CD(10, 1)⊃PEA(89)	1400	14	89	5.9	0.029	0.2	PBA-CD PP(10, 1)	590
PBA-CD(10, 2)⊃PEA(89)	1400	14	88	5.9	0.029	0.2	PBA-CD PP(10, 2)	980

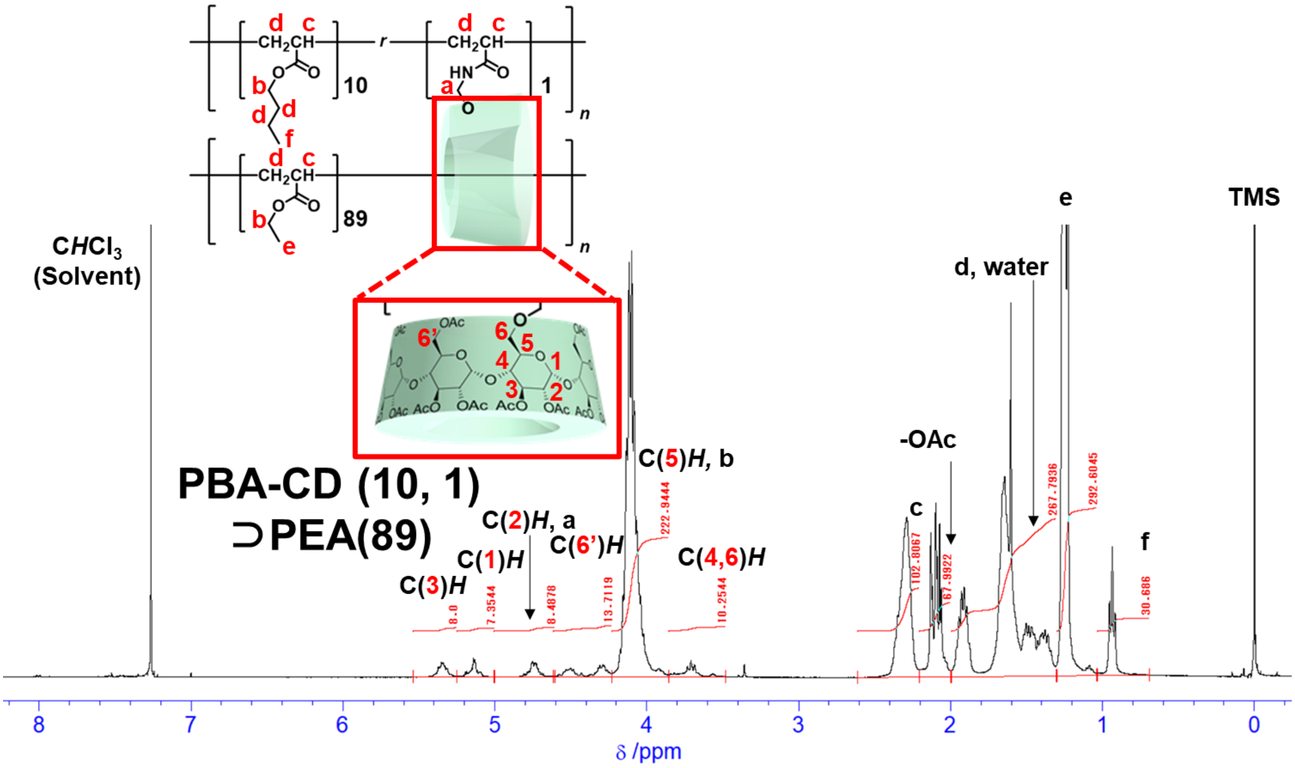


Fig. S18. 500 MHz ^{1}H NMR spectrum of PBA-CD (10, 1)⊃PEA (89) in chloroform-*d*.

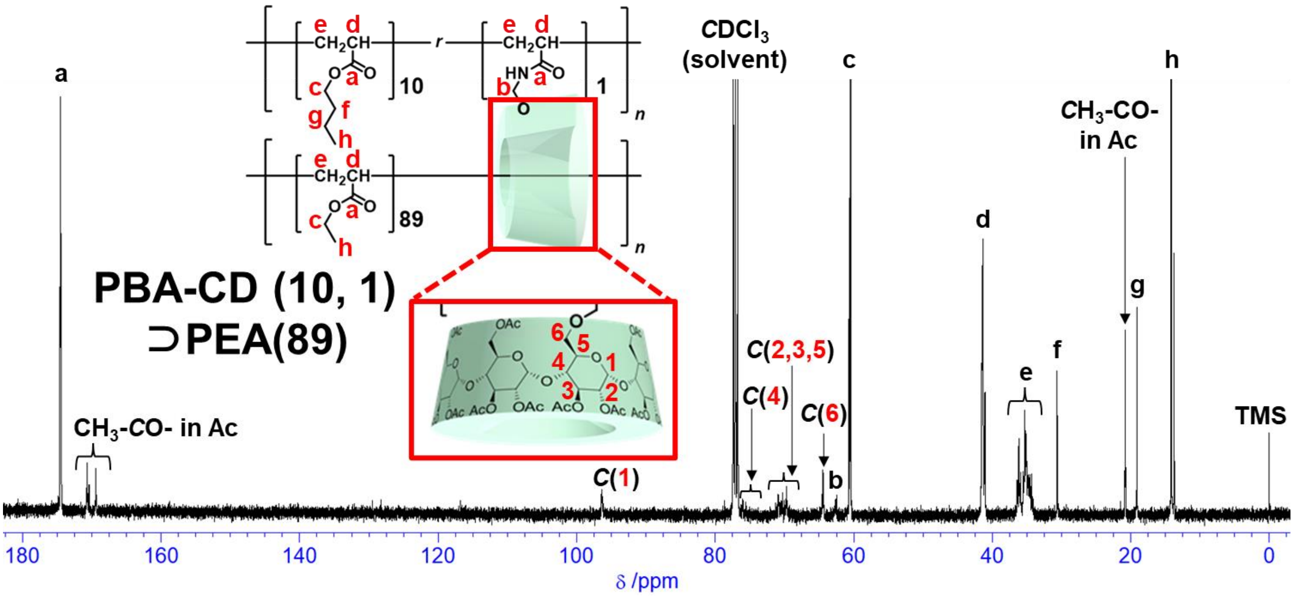


Fig. S19. 125 MHz ^{13}C NMR spectrum of PBA-CD (10, 1)⊃PEA (89) in chloroform-*d*.

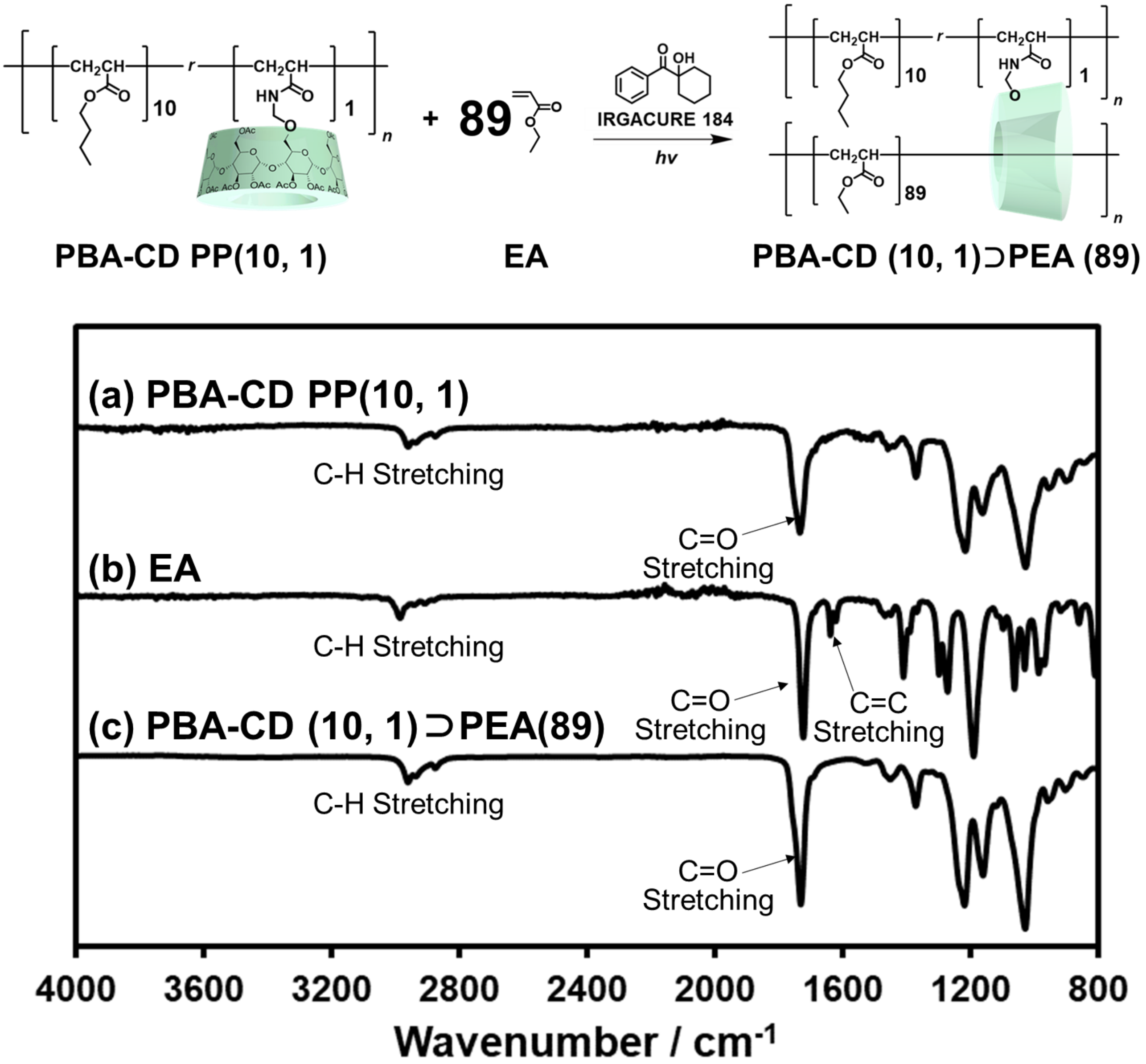
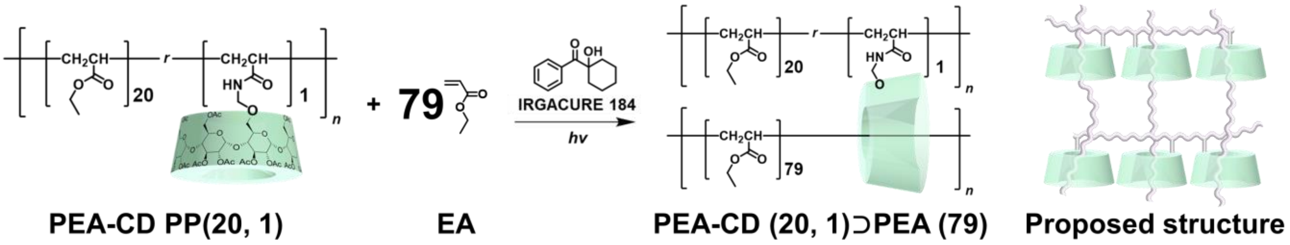


Fig. S20. FT-IR spectra (ATR method) of PBA-CD PP(10, 1) **(a)**, EA **(b)**, and PBA-CD (10, 1)⊃PEA (89) **(c)**.

General preparative method of movable cross-network elastomers knitting similar polymers (PEA-CD (*x*, *y*)⊃PEA (*z*))



Scheme S7. Preparation of PEA-CD (20, 1)⊃PEA (79) and proposed structure.

Scheme S7 shows the preparation of PEA-CD (20, 1)⊃PEA (89). PEA-CD PP(20, 1) (730 mg) and IRGACURE 184 (photoinitiator; 5.4 mg, 0.026 mmol) were dissolved in EA (1300 mg, 13 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 ^{o}C in vacuo for 12 hours. The other PEA-CD (*x*, *y*)⊃pEA (*z*) KP elastomers were also prepared by same manner. **Table S5** summarize amounts of reagents in the reactions.

^{1}H NMR (500 MHz, chloroform-*d*) of PEA-CD (20, 1)⊃PEA (79): δ = 5.47~5.24 (8H: C(3)*H* of CD), 5.24~5.03 (8H: C(1)*H* of CD), 5.03~4.60 (10H: C(2)*H* of CD and -NHCH_2O-), 4.60~4.24 (14H: C(6')*H* of CD), 4.24~3.93 (206H: C(5)*H* of CD, $\mathrm{CH_3C}H_2$- of EA), 3.93~3.41 (10H: C(4,6)*H* of CD), 2.52~2.21 (100H: $\mathrm{-CH_2C}H$- of main chain), 2.21~2.01 (69H: CH_3 of acetyl), 2.01~1.34 (200H: -CH_2CH- of main chain), 1.34~1.09 (297H: C$H_3$$\mathrm{CH_2}$- of EA).

^{13}C NMR (125 MHz, chloroform-*d*) of PEA-CD (20, 1)⊃PEA (79): δ = 175.1~174.2 (-*C*OO- and -*C*ONH-), 172.8~169.0 ($\mathrm{CH_3}$-*C*O- in acetyl), 97.8~94.0 (*C*(1)H of CD), 76.7~75.7 (*C*(4)H of CD overlaps with *C*$\mathrm{DCl_3}$ and *C*$\mathrm{HCl_3}$), 72.6~66.4 (*C*(2, 3, 5)H of CD), 63.4~56.8 (*C*(6)H of CD, NH*C*$\mathrm{H_2}$O-, and $\mathrm{CH_3}$*C*$\mathrm{H_2}$- of EA), 43.7~37.8 (-$\mathrm{CH_2}$*C*H- of main chain), 37.8~31.1 (-*C*$\mathrm{H_2}$CH- of main chain), 21.5~20.6 (*C*$\mathrm{H_3}$-CO- in acetyl), 17.0~10.6 (*C*$\mathrm{H_3CH_2}$- of EA).

Table S5. Preparation of PEA-CD (*x*, *y*)⊃PEA (*z*) elastomers varying the mol% of EA, TAcγCD, and EA units (*x*, *y*, *z*).

PEA-CD(*x*, *y*)⊃PEA(*z*)	EA			IRGACURE 184			Primary polymer	
	/mg	/mmol	/mol%	/mg	/mmol	/mol%	Name	/mg
PEA-CD(20, 0.5)⊃PEA(79)	1300	13	79	5.4	0.026	0.2	PEA-CD PP(20, 0.5)	540
PEA-CD(20, 1)⊃PEA(79)	1300	13	79	5.4	0.026	0.2	PEA-CD PP(20, 1)	730
PEA-CD(20, 2)⊃PEA(78)	1300	13	78	5.4	0.026	0.2	PEA-CD PP(20, 2)	1100

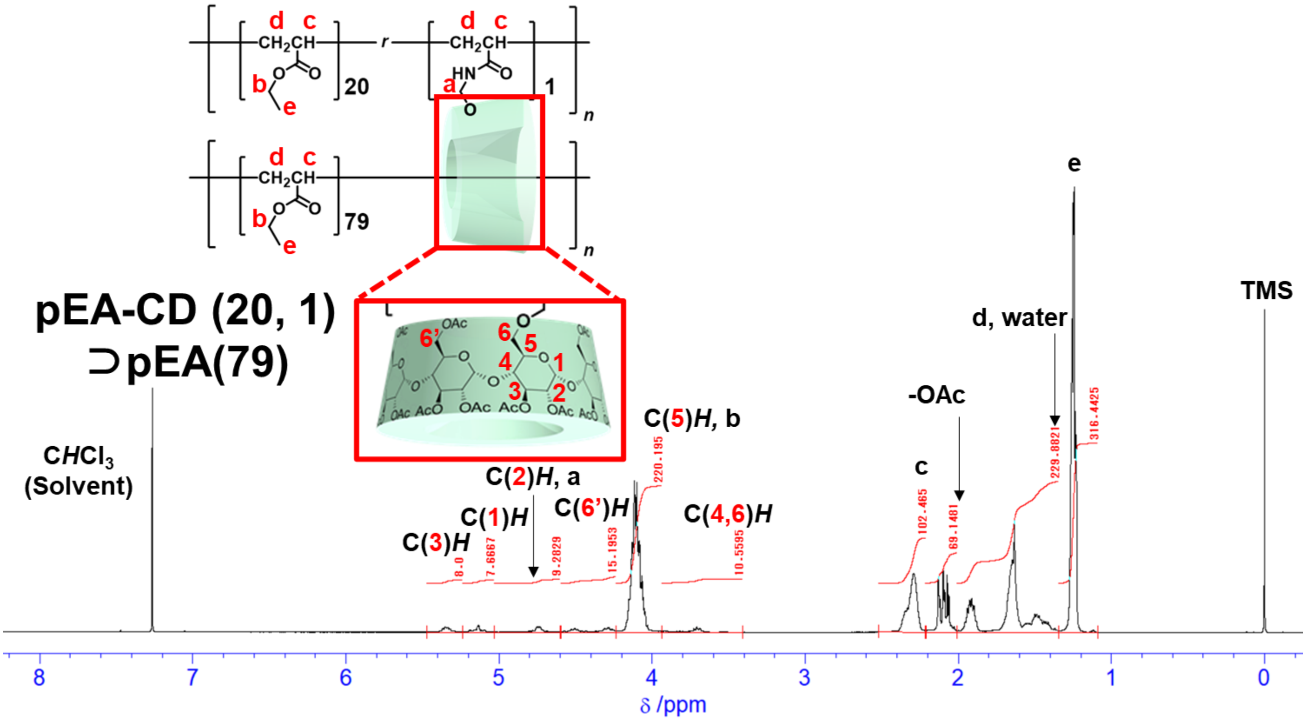


Fig. S21. 500 MHz ^{1}H NMR spectrum of PEA-CD (20, 1)⊃PEA (79) in chloroform-*d*.

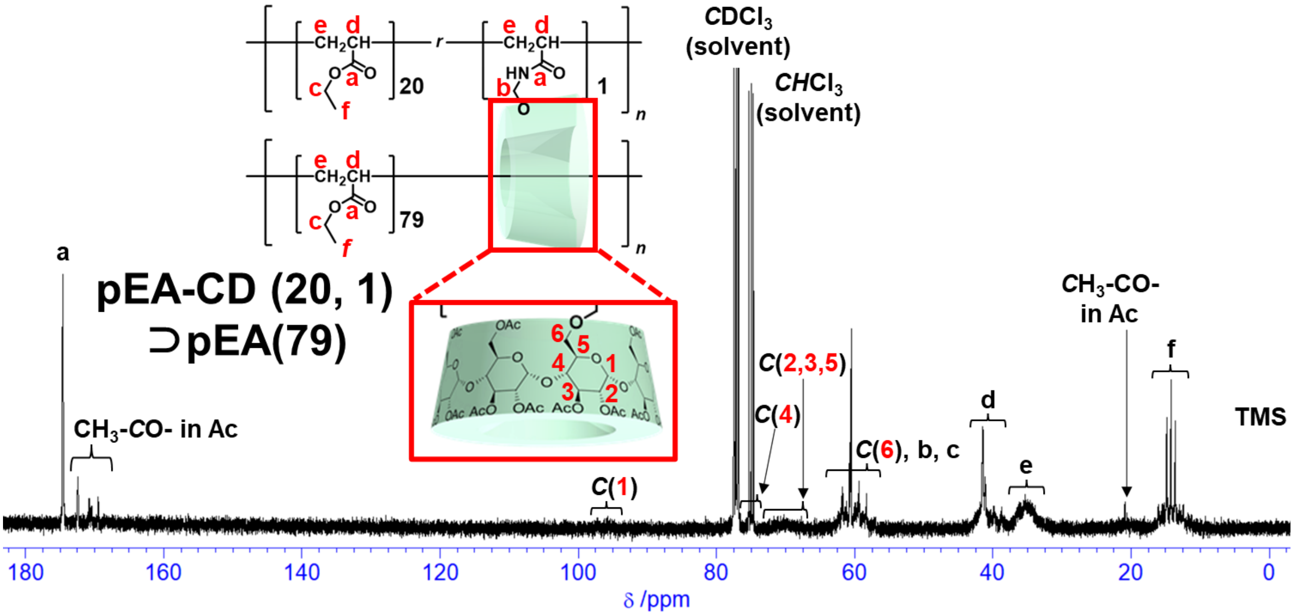
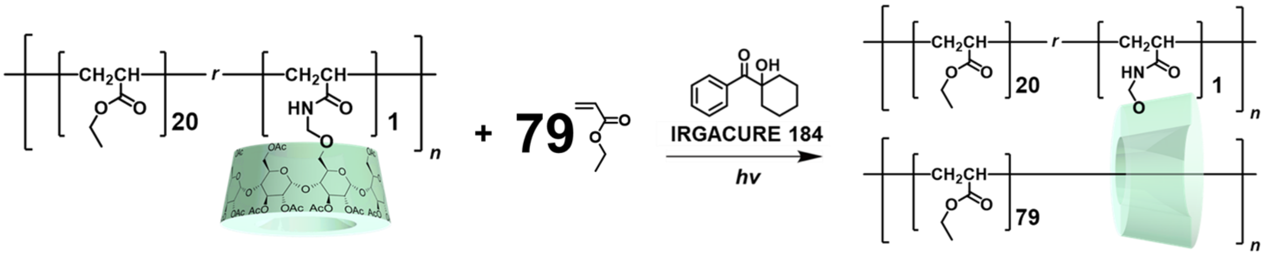


Fig. S22. 125 MHz ^{13}C NMR spectrum of PEA-CD (20, 1)⊃PEA (79) in chloroform-*d*.



PEA-CD PP(20, 1) **EA** **PEA-CD (20, 1)⊃PEA (79)**

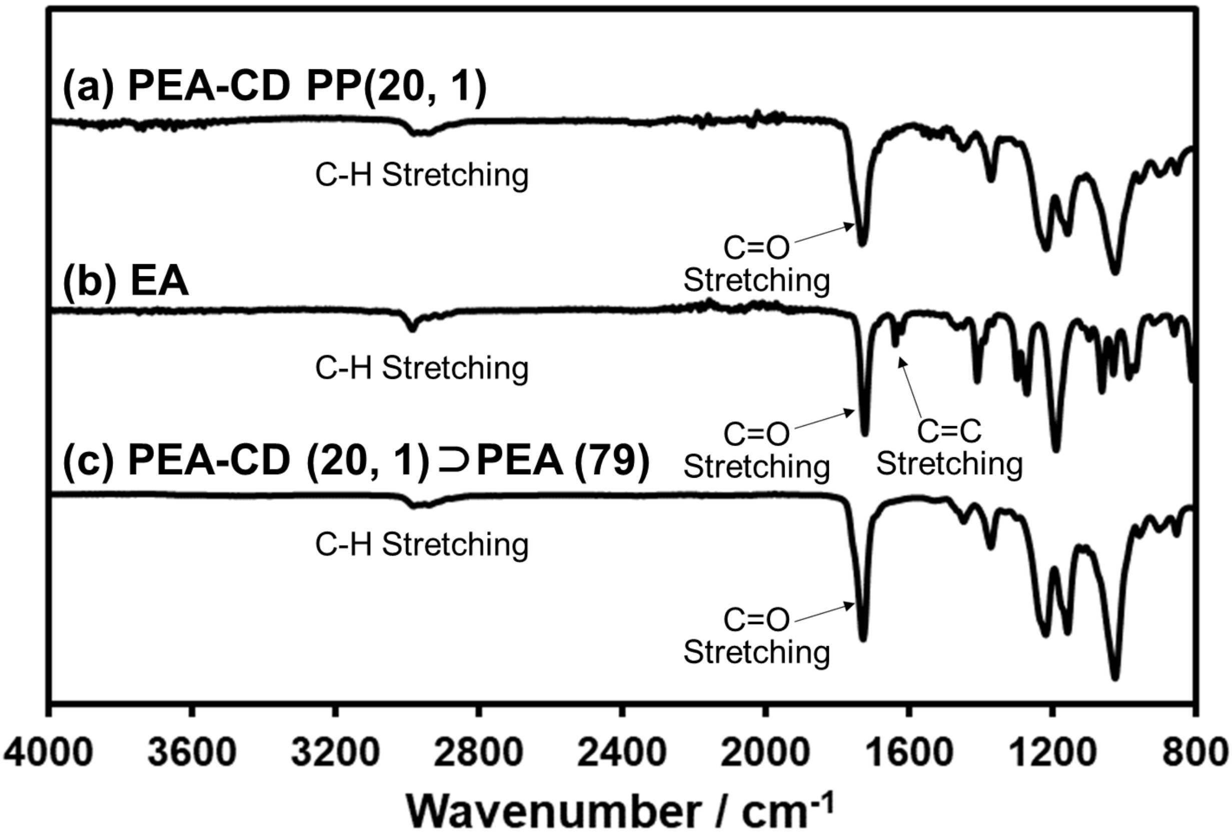
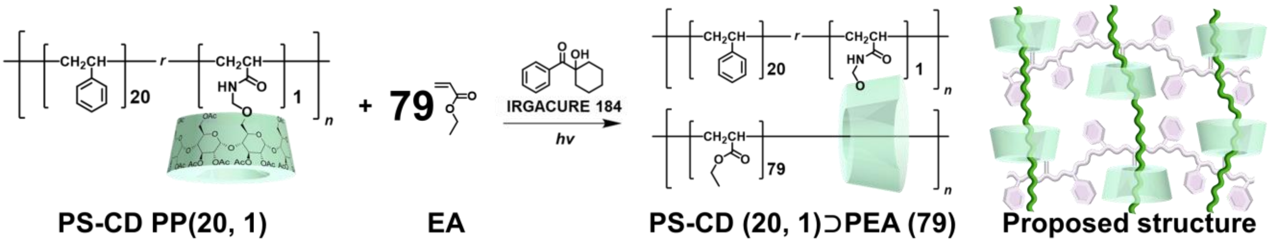


Fig. S23. FT-IR spectra (ATR method) of PEA-CD PP(20, 1) **(a)**, EA **(b)**, and PEA-CD (20, 1)⊃PEA (79) **(c)**.

General preparative method of movable cross-network elastomers knitting immiscible polymers (PS-CD (*x*, *y*)⊃PEA (*z*))



Scheme S8. Preparation of PS-CD (20, 1)⊃PEA (79) and proposed structure.

Scheme S8 shows the preparation of PS-CD (20, 1)⊃pEA (79). PEA-CD PP(20, 1) (740 mg) and IRGACURE 184 (photoinitiator; 5.3 mg, 0.026 mmol) were dissolved in EA (1300 mg, 13 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 ^{o}C in vacuo for 12 hours. The other PS-CD (*x*, *y*)⊃pEA (*z*) KP elastomers were also prepared by same manner. **Table S6** summarize amounts of reagents in the reaction.

^{1}H NMR (500 MHz, chloroform-*d*) of PS-CD (20, 1)⊃PEA (79): δ = 7.21~6.85 (60H: *m*,*p*-protons of phenyl), 6.85~6.24 (60H: *o*-protons of phenyl), 5.43~5.24 (8H: C(3)*H* of CD), 5.24~5.03 (8H: C(1)*H* of CD), 5.03~4.60 (10H: C(2)*H* of CD and -NHCH_2O-), 4.60~4.21 (14H: C(6')*H* of CD), 4.21~3.84 (168H: C(5)*H* of CD and CH_3CH_2- of EA), 3.84~3.34 (10H: C(4,6)*H* of CD), 2.48~2.18 (80H: -CH_2CH- of main chain of EA units), 2.18~1.98 (69H: CH_3 of acetyl), 1.98~0.81 (457H: -CH_2CH- of main chain of St units, -CH_2CH- of main chain of EA/St units, and CH_3CH$_2$- of EA overlaps with water).

^{13}C NMR (125 MHz, chloroform-*d*) of PS-CD (10, 1)⊃PEA (79): δ = 175.1~173.8 (-*C*OO- and -*C*ONH-), 171.5~168.7 (CH_3-*C*O- in acetyl), 146.8~144.2 (*ipso*-carbon of phenyl), 129.6~126.9 (*o*,*m*-carbons of phenyl), 126.8~125.0 (*p*-carbons of phenyl), 96.9~95.8 (*C*(1)H of CD), 76.4~75.0 (*C*(4)H of CD overlaps with *C*DCl$_3$), 72.4~68.1 (*C*(2, 3, 5)H of CD), 63.2~61.7 (*C*(6)H of CD), 61.4~59.8 (CH_3*C*H_2- of EA), 44.1~41.8 (-CH_2*C*H- of main chain in St units), 41.8~39.9 (-*C*H_2CH- of main chain in St units and -CH_2*C*H- of main chain in EA/CD units), 36.9~33.5 (-*C*H_2CH- of main chain in EA/CD units), 21.2~20.4 (*C*H_3-CO- in acetyl), 14.6~13.6 (*C*H_3CH$_2$- of EA).

Table S6. Preparation of PS-CD (x, y)⊃PEA (z) elastomers varying the mol% of St, TAcγCD, and EA units (x, y, z).

PS-CD(x, y)⊃PEA(z)	EA			IRGACURE 184			Primary polymer	
	/mg	/mmol	/mol%	/mg	/mmol	/mol%	Name	/mg
PS-CD(20, 0.5)⊃PEA(79)	1300	13	79	5.3	0.026	0.2	PS-CD PP(20, 0.5)	540
PS-CD(20, 1)⊃PEA(79)	1300	13	79	5.3	0.026	0.2	PS-CD PP(20, 1)	740
PS-CD(20, 2)⊃PEA(79)	1300	13	78	5.3	0.026	0.2	PS-CD PP(20, 2)	1100

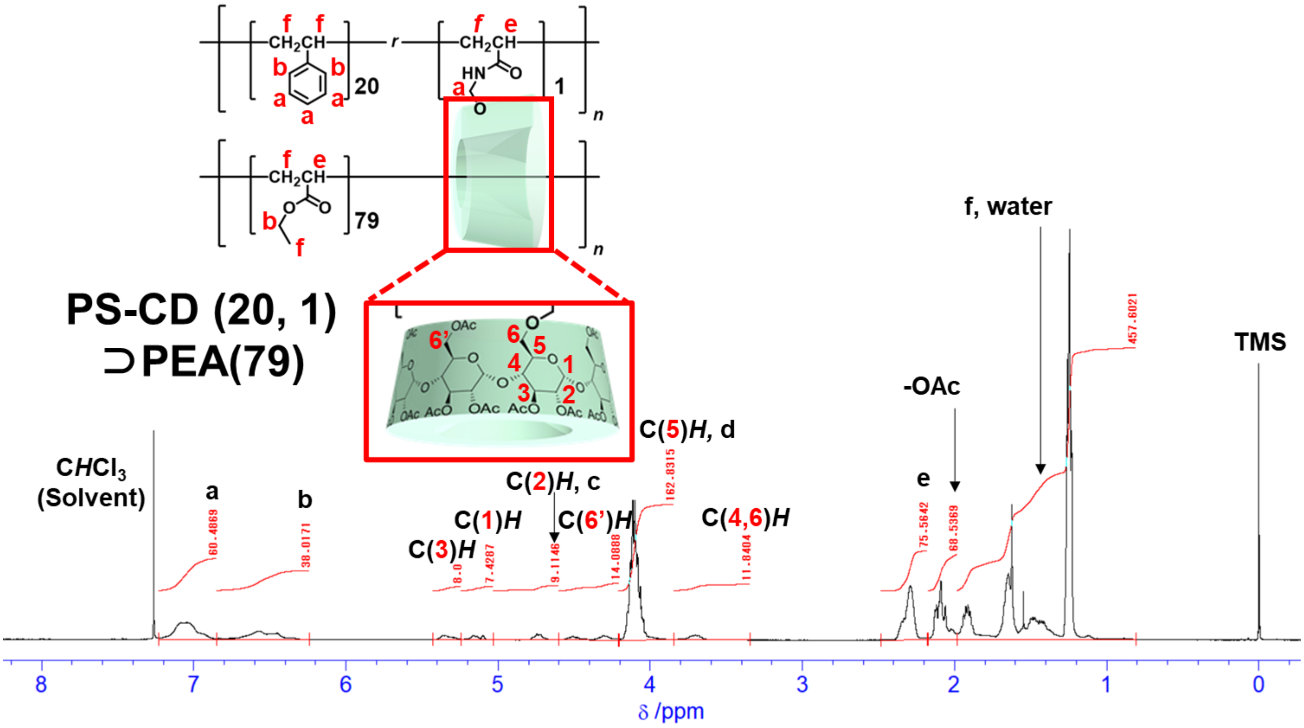


Fig. S24. 500 MHz ^{1}H NMR spectrum of PS-CD (20, 1)⊃PEA (79) in chloroform-d.

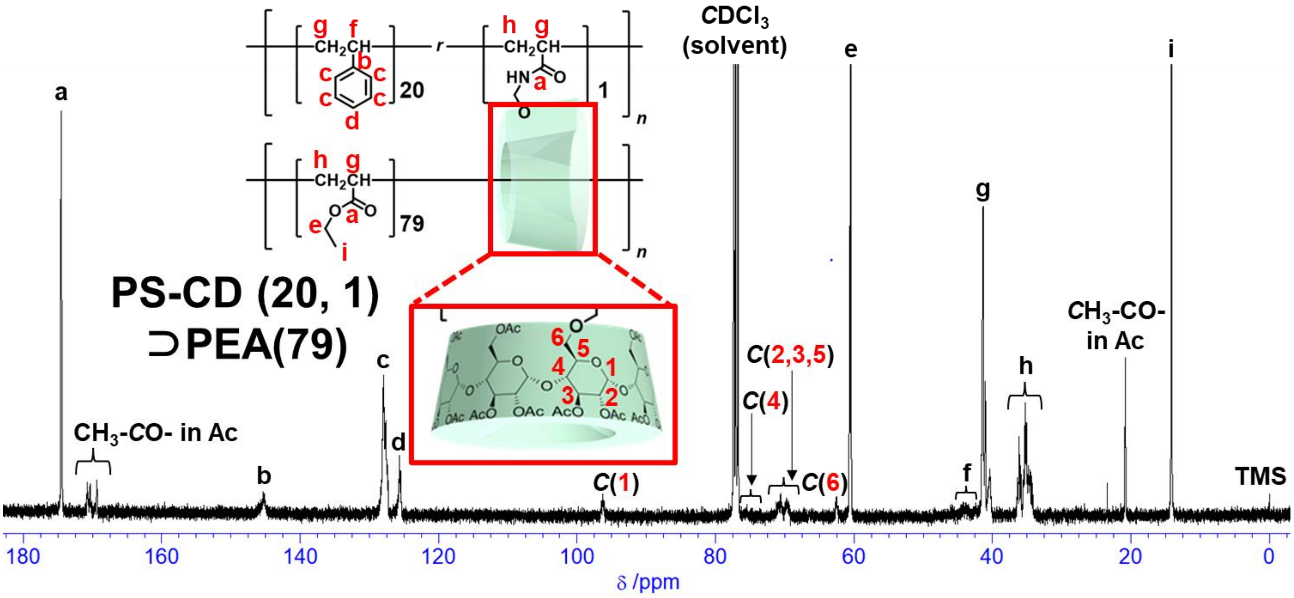
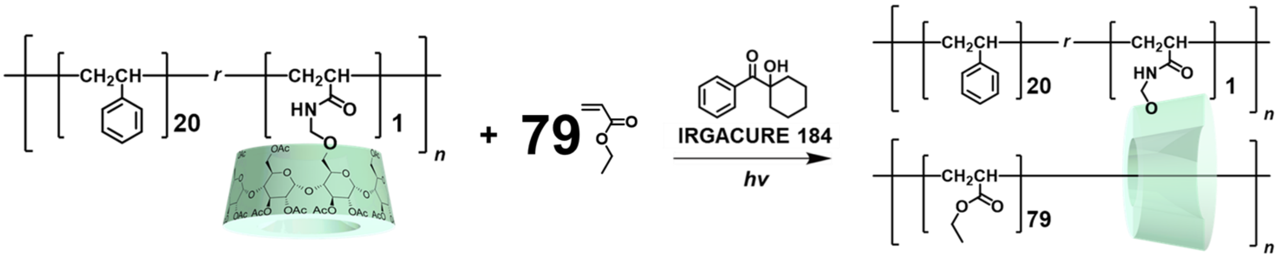


Fig. S25. 125 MHz ^{13}C NMR spectrum of PS-CD (20, 1)⊃PEA (79) in chloroform-d.



PS-CD PP(20, 1) **EA** **PS-CD (20, 1)⊃PEA (79)**

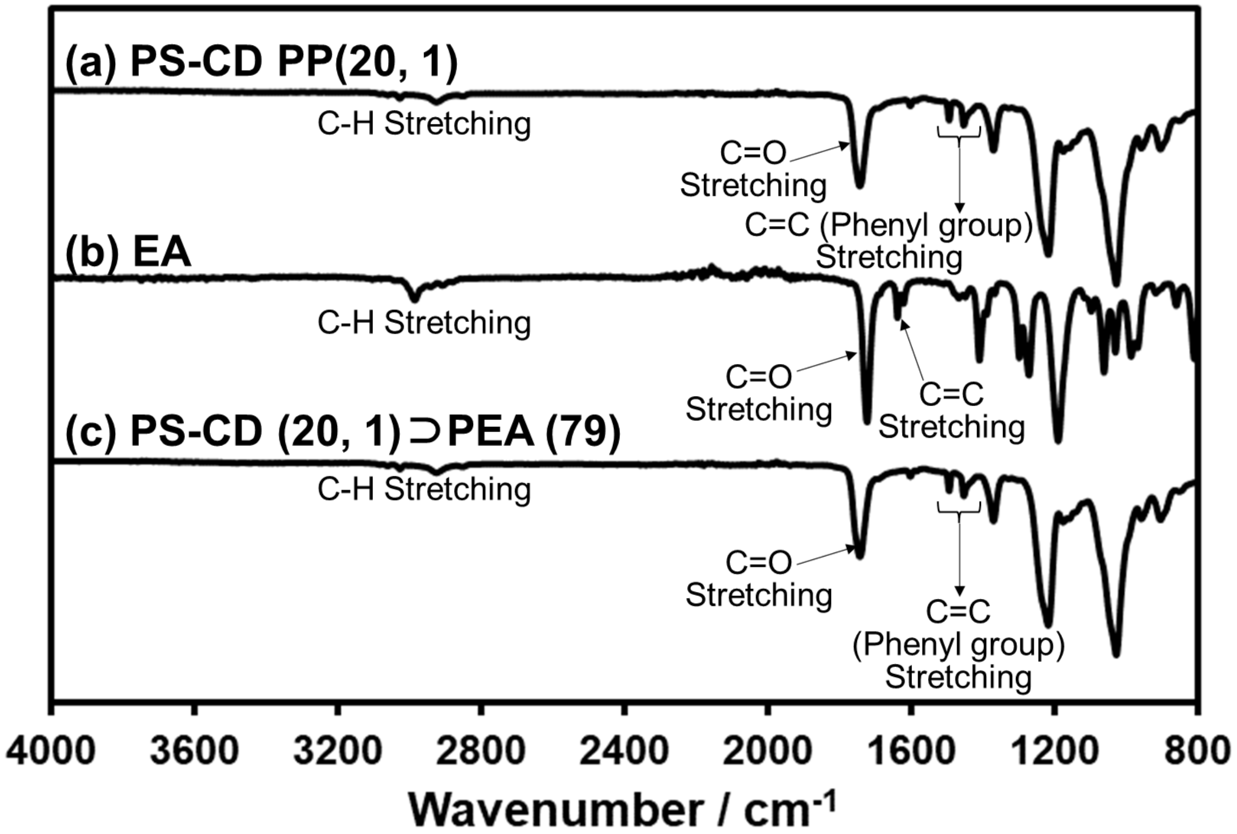
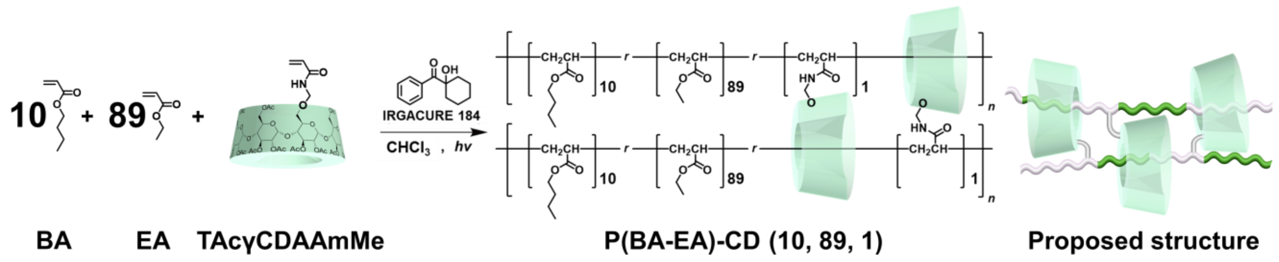


Fig. S26. FT-IR spectra (ATR method) of PS-CD PP(20, 1) **(a)**, EA **(b)**, and PS-CD (20, 1)⊃PEA (79) **(c)**.

4. Preparation of reference samples

General preparative method of single movable cross-network elastomer (SC) (P(BA-EA)-PAcγCD (10, 89, 1))



Scheme S9. Preparation of P(BA-EA)-CD (10, 89, 1) and proposed structure.

Scheme S9 shows the preparation of P(BA-EA)-CD (10, 89, 1). BA (210 mg, 1.6 mmol), TAcγCDAAmMe (380 mg, 0.16 mmol), and IRGACURE 184 (photoinitiator; 3.6 mg, 0.018 mmol) were dissolved in EA (1400 mg, 14 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 $^{\mathrm{o}}$C in vacuo for 12 hours. The other P(BA-EA)-CD (10, 89, 1) SC elastomers were also prepared by same manner. **Table S7** summarize amounts of reagents in the reactions.

^{1}H NMR (500 MHz, chloroform-*d*) of P(BA-EA)-CD (10, 89, 1): δ = 5.53~5.25 (8H: C(3)*H* of CD), 5.25~5.00 (8H: C(1)*H* of CD), 5.00~4.62 (10H: C(2)*H* of CD and -$NHC\mathit{H}_2O$-), 4.60~4.22 (14H: C(6')*H* of CD), 4.17~3.85 (206H: C(5)*H* of CD, $CH_3CH_2CH_2C\mathit{H}_2$- of BA, and $CH_3C\mathit{H}_2$- of EA), 3.85~3.48 (10H: C(4,6)*H* of CD), 2.61~2.21 (100H: -$CH_2C\mathit{H}$- of main chain), 2.21~2.00 (69H: $C\mathit{H}_3$ of acetyl), 2.00~1.30 (240H: -$C\mathit{H}_2CH$- of main chain and $CH_3C\mathit{H}_2C\mathit{H}_2CH_2$- of BA overlaps with water), 1.30~1.04 (267H: $C\mathit{H}_3CH_2$- of EA), 1.04~0.69 (30H, $C\mathit{H}_3CH_2CH_2CH_2$- of BA).

^{13}C NMR (125 MHz, chloroform-*d*) of P(BA-EA)-CD (10, 89, 1): δ = 175.6~174.0 (-*C*OO- and -*C*ONH-), 171.0~169.2 (CH_3-*C*O- in acetyl), 96.7~96.1 (*C*(1)H of CD), 76.5~75.1 (*C*(4)H of CD overlaps with $\mathit{C}DCl_3$), 72.2~67.9 (*C*(2, 3, 5)H of CD), 65.0~64.1 (*C*(6)H of CD), 63.1~62.0 (-$NH\mathit{C}H_2O$-), 61.3~60.1 ($CH_3CH_2CH_2\mathit{C}H_2$- of BA, and $CH_3\mathit{C}H_2$- of EA), 42.4~40.4 (-$CH_2\mathit{C}H$- of main chain), 36.9~33.3(-$\mathit{C}H_2CH$- of main chain), 31.0~30.2 ($CH_3CH_2\mathit{C}H_2CH_2$- of BA), 21.2~20.5 ($\mathit{C}H_3$-CO- in acetyl), 19.7~18.6 ($CH_3\mathit{C}H_2CH_2CH_2$- of BA), 14.7~13.3 ($\mathit{C}H_3CH_2CH_2CH_2$- of BA and $\mathit{C}H_3CH_2$- of EA).

Table S7. Preparation of pEA-PAcγCD (x, y)⊃pEA (z) elastomers varying the mol% of BA, EA, and TAcγCD units (x, y, z).

P(BA-EA)-CD (x, y, z)	BA			EA			TAcγCDAAmMe			IRGACURE 184		
	/mg	/mmol	/mol%	/mg	/mmol	/mol%	/mg	/mmol	/mol%	/mg	/mmol	/mol%
P(BA-EA)-CD (10, 89, 0.5)	210	1.6	10	1400	14	89	190	0.08	0.5	6.6	0.032	0.20
P(BA-EA)-CD (10, 89, 1)	210	1.6	10	1400	14	89	380	0.16	1.0	6.6	0.033	0.20
P(BA-EA)-CD (10, 89, 2)	210	1.6	10	1400	14	88	770	0.33	2.0	6.7	0.033	0.20

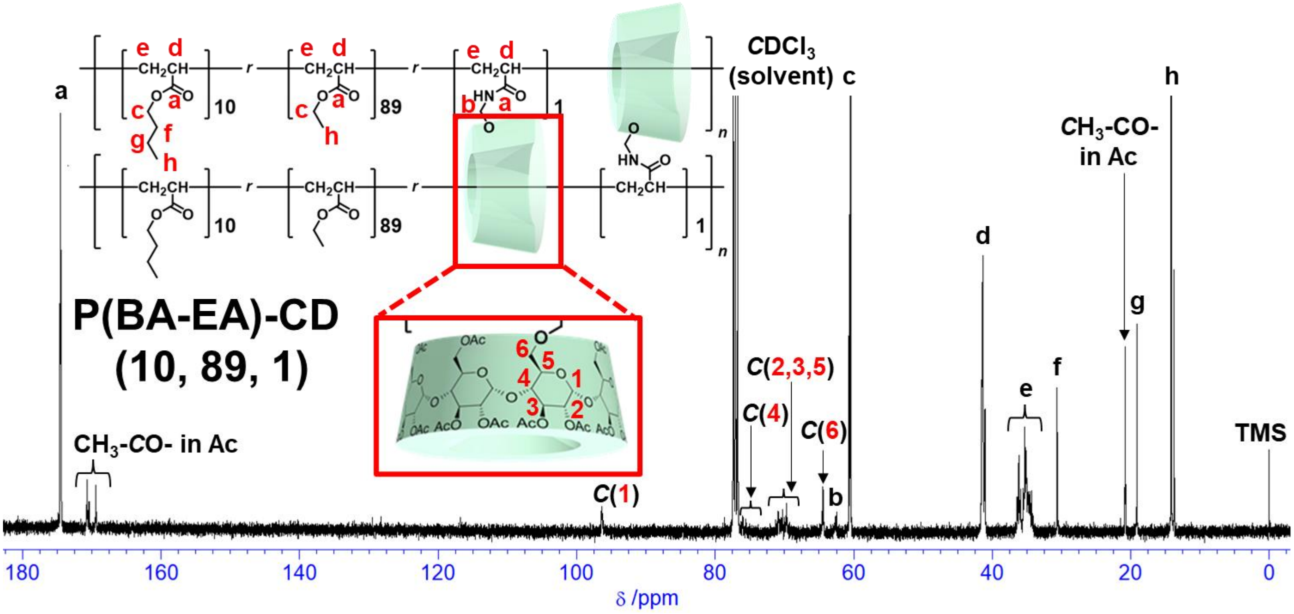


Fig. S27. 500 MHz ^{1}H FGMAS NMR spectrum of P(BA-EA)-CD (10, 89, 1) in chloroform-d (rotation frequency = 7k Hz).

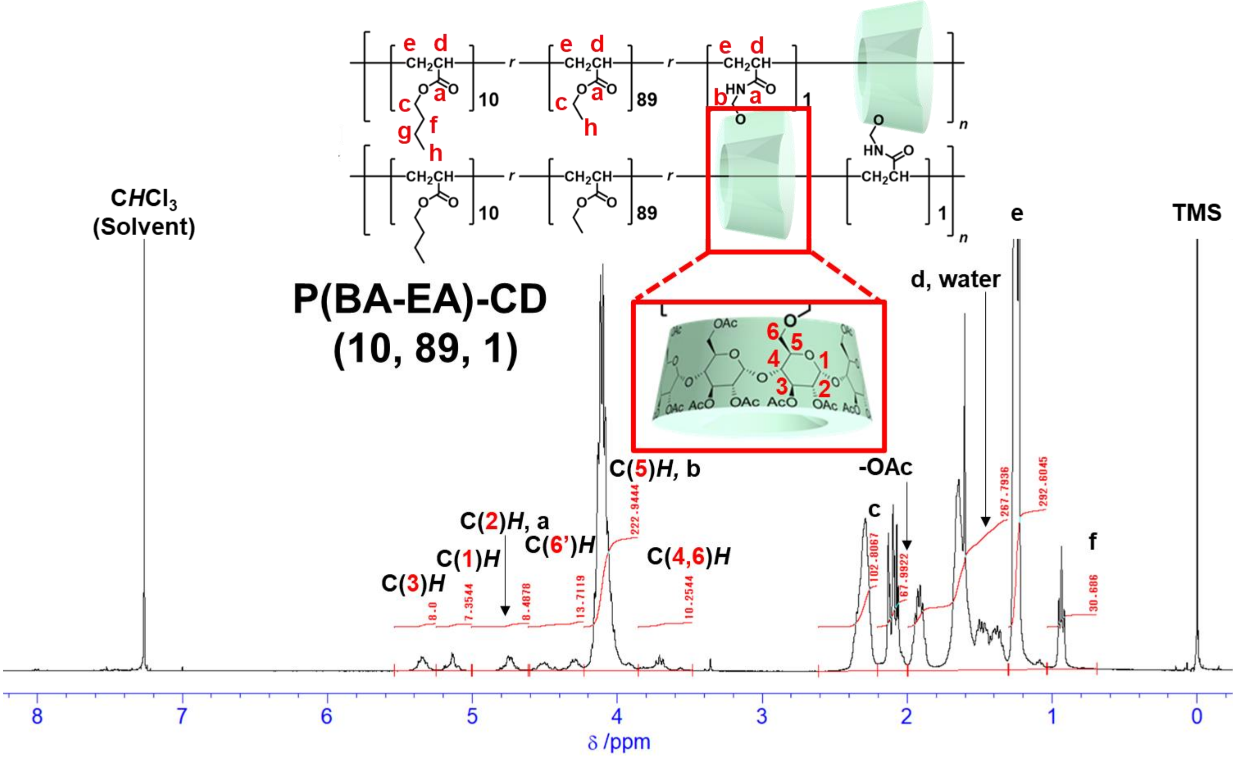
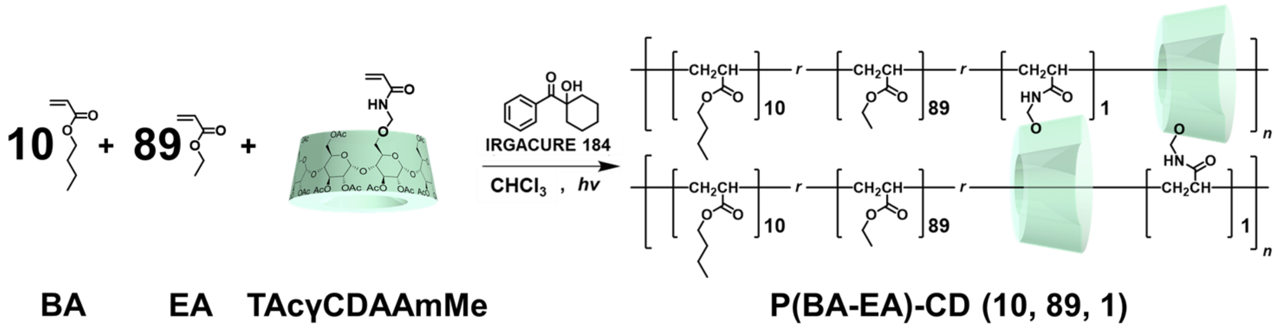


Fig. S28. 125 MHz ^{13}C FGMAS NMR spectrum of P(BA-EA)-CD (10, 89, 1) in chloroform-d (rotation frequency = 7k Hz).



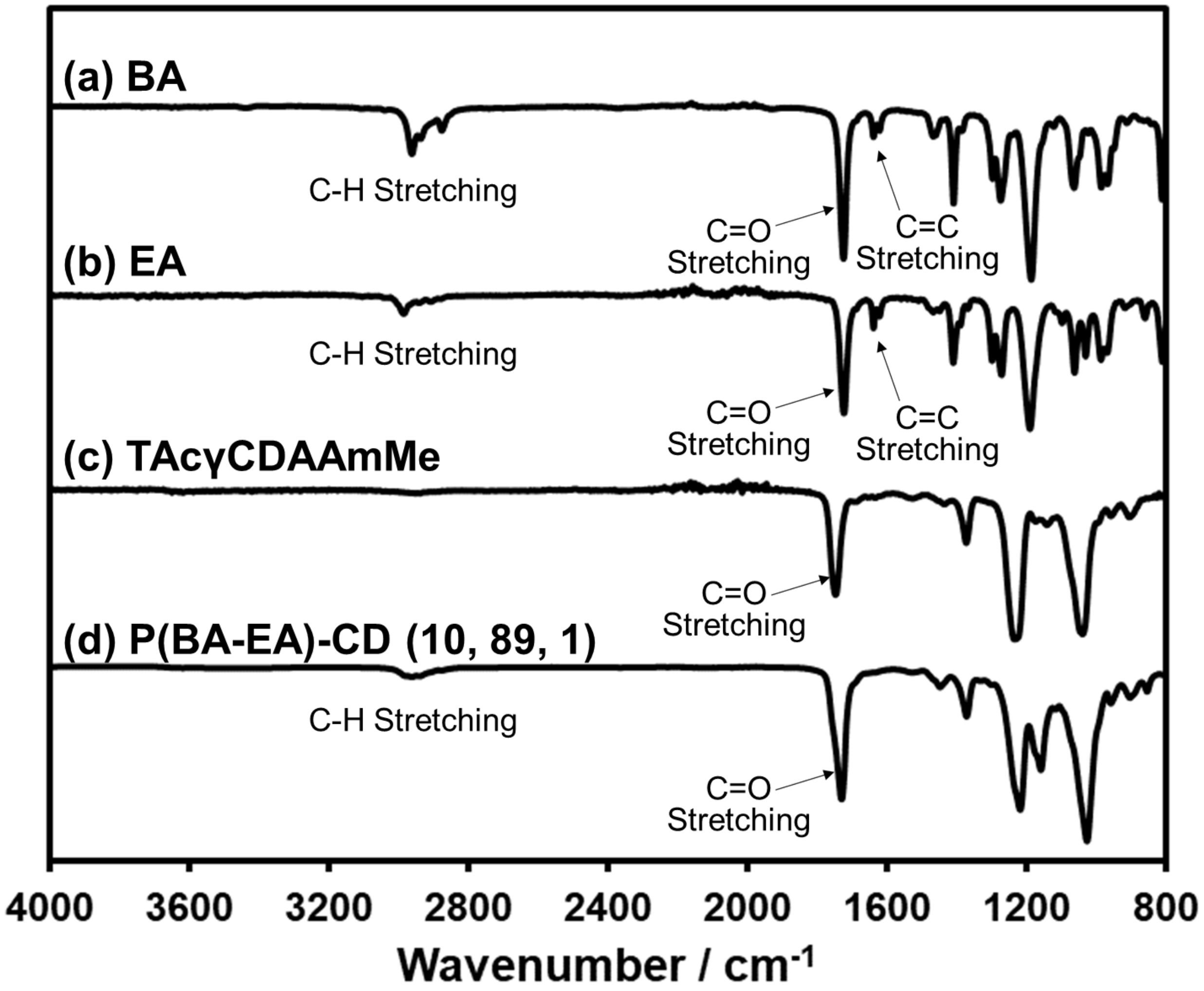
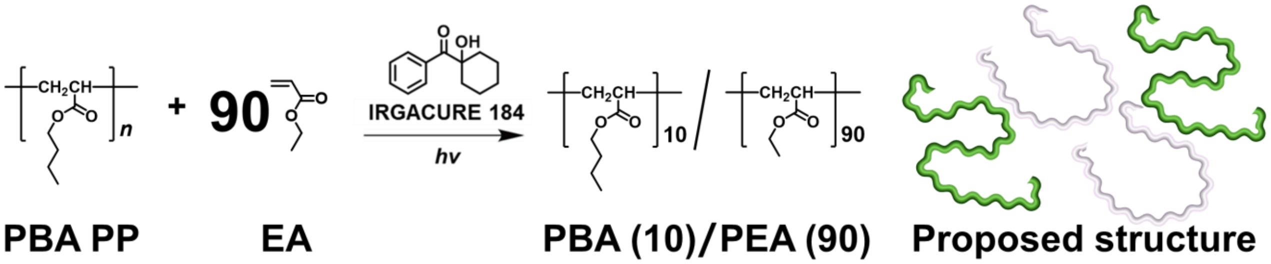


Fig. S29. FT-IR spectra (ATR method) of BA **(a)**, EA **(b)**, TAcγCDAAmMe **(c)**, and P(BA-EA)-CD (10, 89, 1) **(d)**.

General preparative method of polymer blend materials (PBA(10)/PEA(90))



Scheme S10. Preparation of PBA(10)/PEA(90).

Scheme S10 shows the preparation of PBA(10)/PEA(90). PBA PP (210 mg) and IRGACURE 184 (photoinitiator; 5.9 mg, 0.029 mmol) were dissolved in EA (1400 mg, 14 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 ^{o}C in vacuo for 12 hours.

^{1}H NMR (500 MHz, chloroform-*d*) of PBA(10)/PEA(90): δ = 4.40~3.79 (200H: $CH_3CH_2CH_2C\mathit{H}_2$- of BA and $CH_3C\mathit{H}_2$- of EA), 2.47~2.16 (100H: -$CH_2C\mathit{H}$- of main chain), 2.08~1.31 (240H: -$C\mathit{H}_2CH$- of main chain and $CH_3C\mathit{H}_2C\mathit{H}_2CH_2$- of BA overlaps with water), 1.31~1.01 (270H: $C\mathit{H}_3CH_2$- of EA), 1.01~0.81 (30H, $C\mathit{H}_3CH_2CH_2CH_2$- of BA).

^{13}C NMR (125 MHz, chloroform-*d*) of PBA(10)/PEA(90): δ = 174.8~174.1 (-$\mathit{C}OO$-), 61.0~60.3 ($CH_3CH_2CH_2\mathit{C}H_2$- of BA, and $CH_3\mathit{C}H_2$- of EA), 42.4~40.9 (-$CH_2\mathit{C}H$- of main chain), 37.6~33.8 (-$\mathit{C}H_2CH$- of main chain), 31.0~30.5 ($CH_3CH_2\mathit{C}H_2CH_2$- of BA), 19.6~19.0 ($CH_3\mathit{C}H_2CH_2CH_2$- of BA), 15.4~13.7 ($\mathit{C}H_3CH_2CH_2CH_2$- of BA and $\mathit{C}H_3CH_2$- of EA).

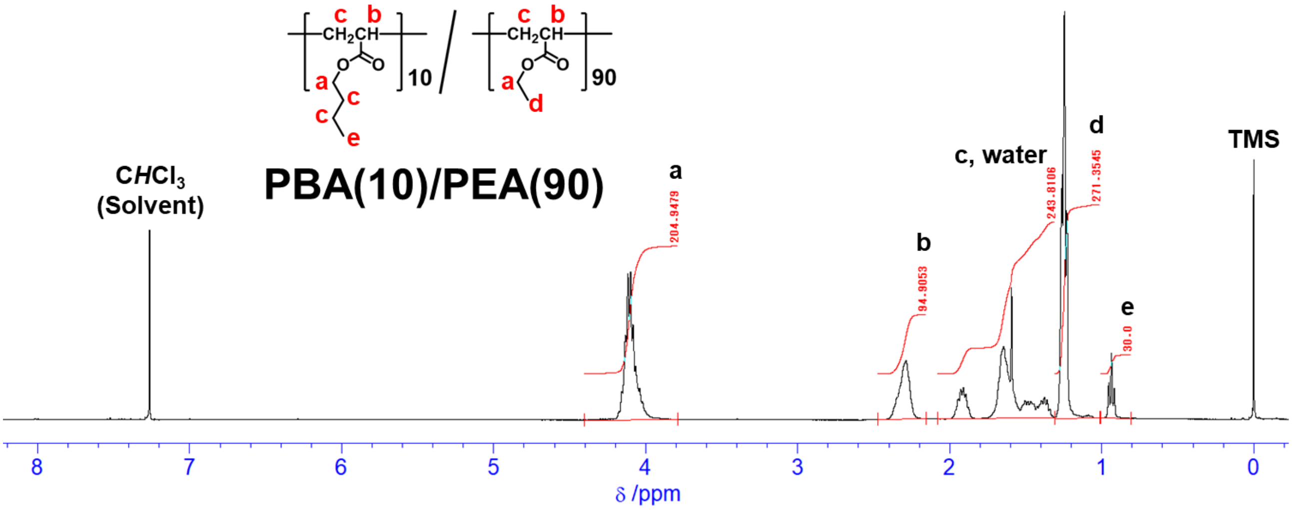


Fig. S30. 500 MHz ^{1}H NMR spectrum of PBA(10)/PEA(90) in chloroform-*d*.

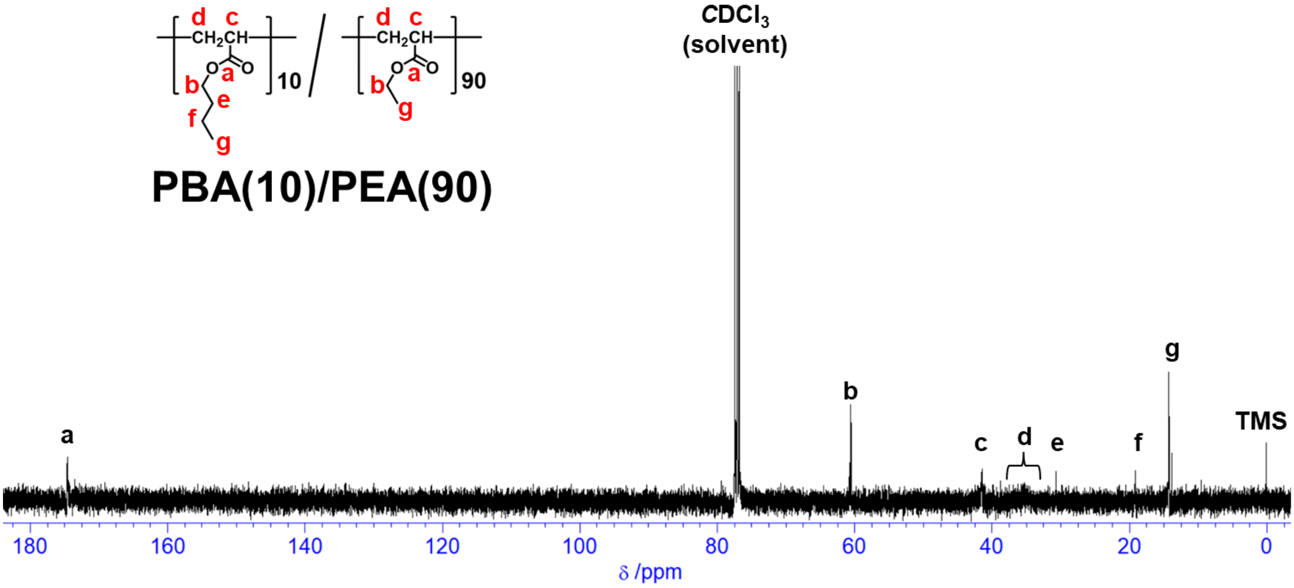
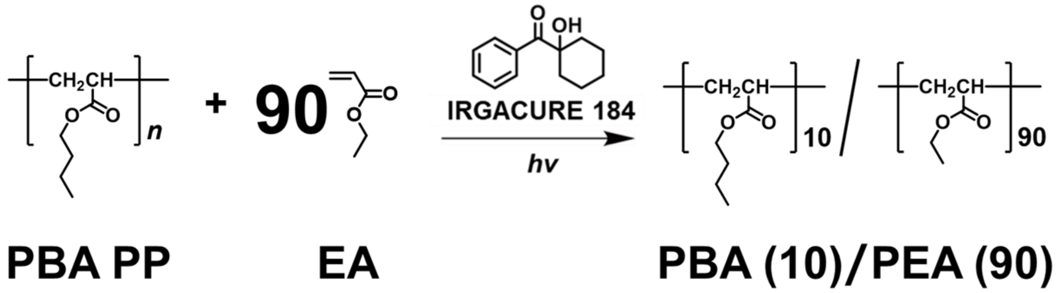


Fig. S31. 125 MHz ^{13}C NMR spectrum of PBA(10)/PEA(90) in chloroform-*d*.



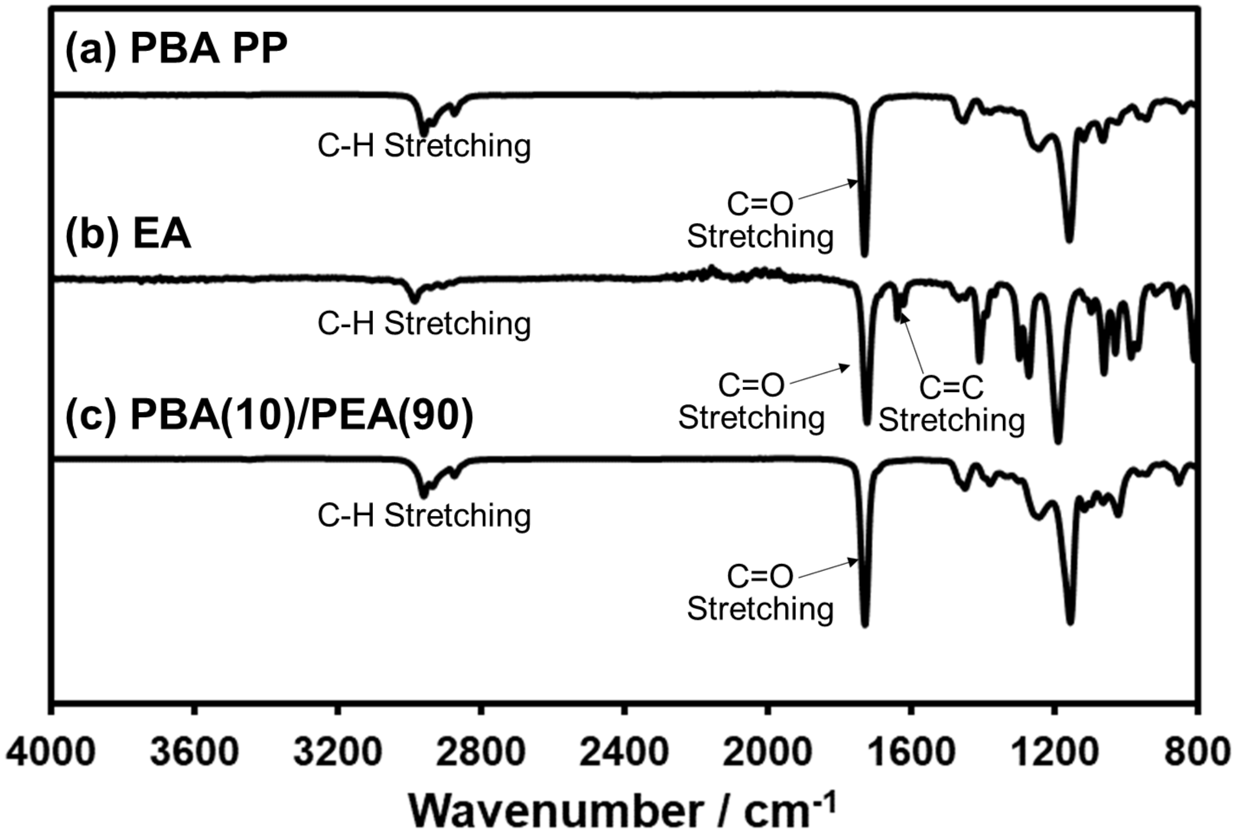
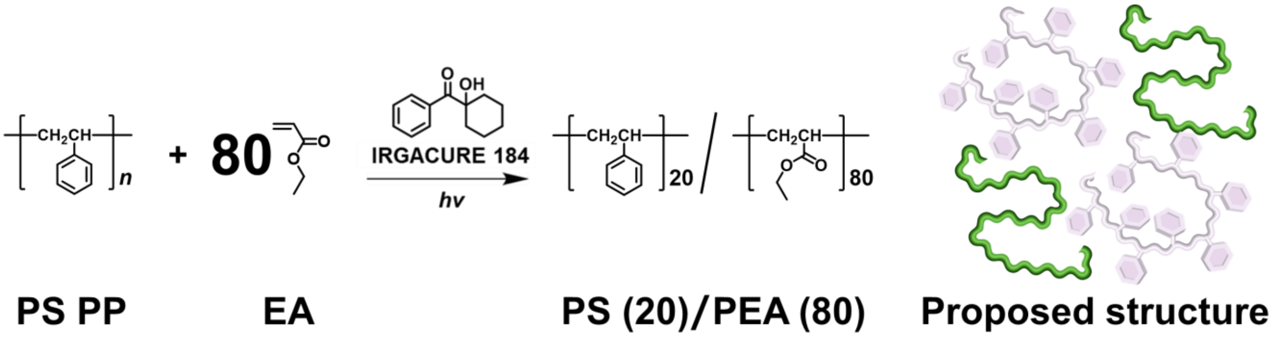


Fig. S32. FT-IR spectra (ATR method) of PBA PP **(a)**, EA **(b)**, and PBA(10)/PEA(90) **(c)**.

General preparative method of polymer blend materials (PS(20)/PEA(80))



Scheme S11. Preparation of PS(20)/PEA(80).

Scheme S11 shows the preparation of PS(20)/PEA(80). PS PP (350 mg) and IRGACURE 184 (photoinitiator; 5.4 mg, 0.026 mmol) were dissolved in EA (1300 mg, 13 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 °C in vacuo for 12 hours.

^{1}H NMR (500 MHz, chloroform-*d*) of PS(20)/PEA(80): δ = 7.25~6.87 (60H: *m*,*p*-protons of phenyl), 6.87~6.24 (40H: *o*-protons of phenyl), 4.33~3.83 (160H: $CH_3C\mathit{H}_2$- of EA), 2.56-2.12 (80H: -$CH_2C\mathit{H}$- of main chain in EA units), 2.12-0.80 ($CH_2C\mathit{H}$- of main chain in St units, $C\mathit{H}_2CH$- of main chain in St/EA units, and $C\mathit{H}_3CH_2$- of EA).

^{13}C NMR (125 MHz, chloroform-*d*) of PS(20)/PEA(80): δ = 175.0~174.2 (-*C*OO-), 145.8~144.9 (*ipso*-carbon of phenyl), 129.5~125.7 (*o*,*m*,*p*-carbons of phenyl), 63.2~58.4 ($CH_3\mathit{C}H_2$- of EA), 45.1~42.6 (-$CH_2\mathit{C}H$- of main chain in St units), 42.6~39.3 (-$\mathit{C}H_2CH$- of main chain in St units and -$CH_2\mathit{C}H$- of main chain in EA units), 37.8~33.5 (-$\mathit{C}H_2CH$- of main chain in EA units), 16.5~12.0 ($\mathit{C}H_3CH_2$- of EA).

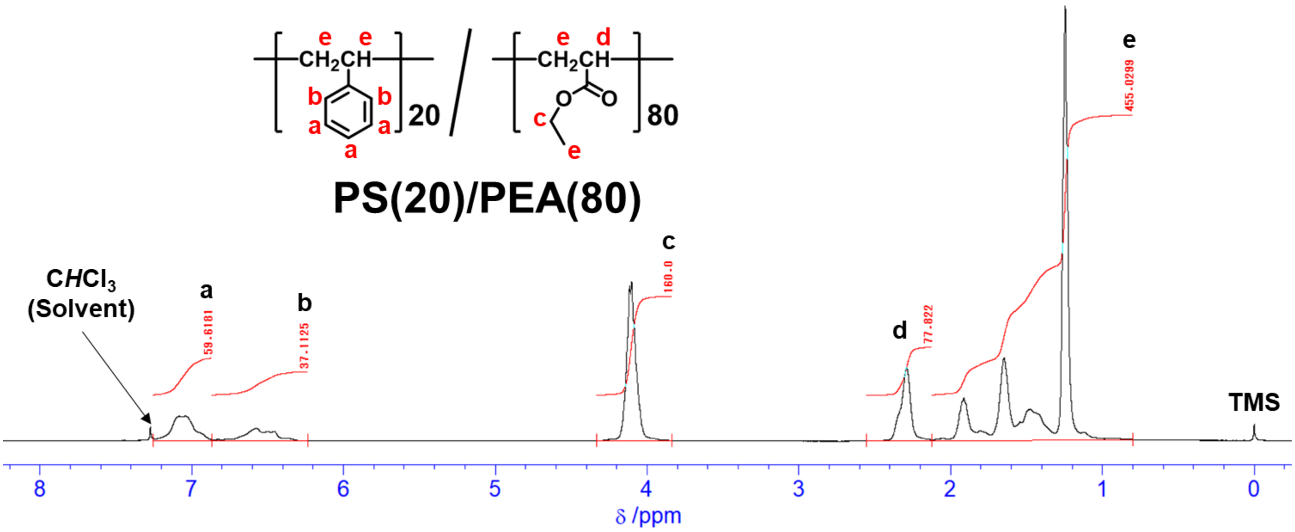


Fig. S33. 500 MHz ^{1}H NMR spectrum of PS(20)/PEA(80) in chloroform-*d*.

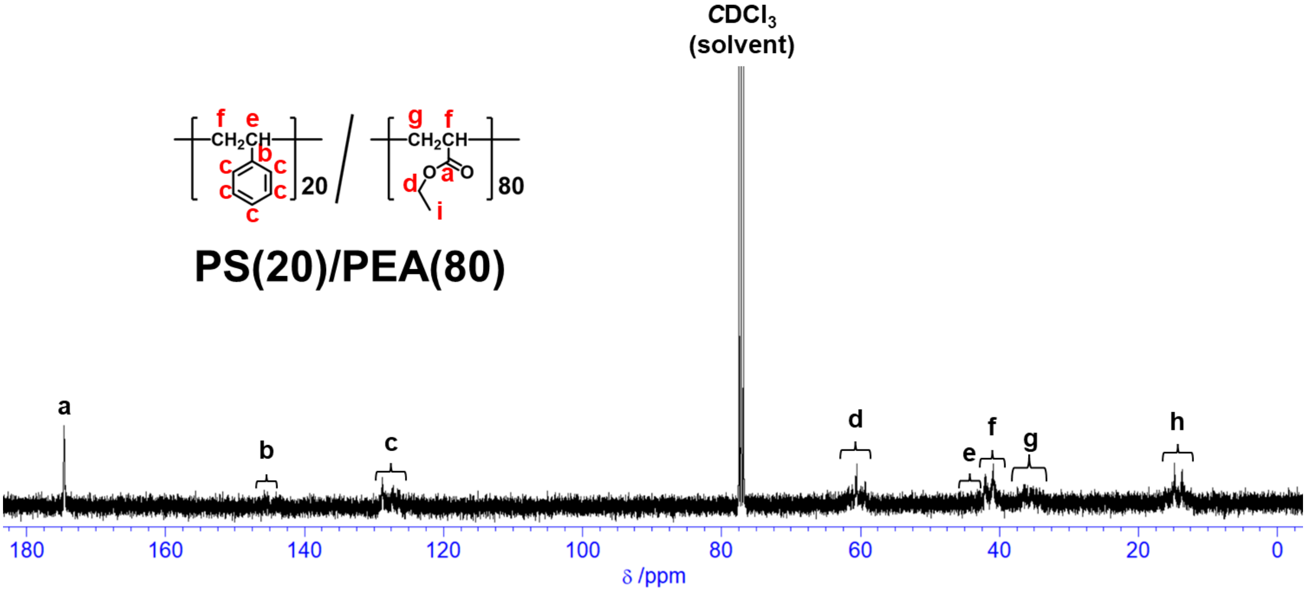


Fig. S34. 125 MHz ^{13}C NMR spectrum of PS(20)/PEA(80) in chloroform-*d*.

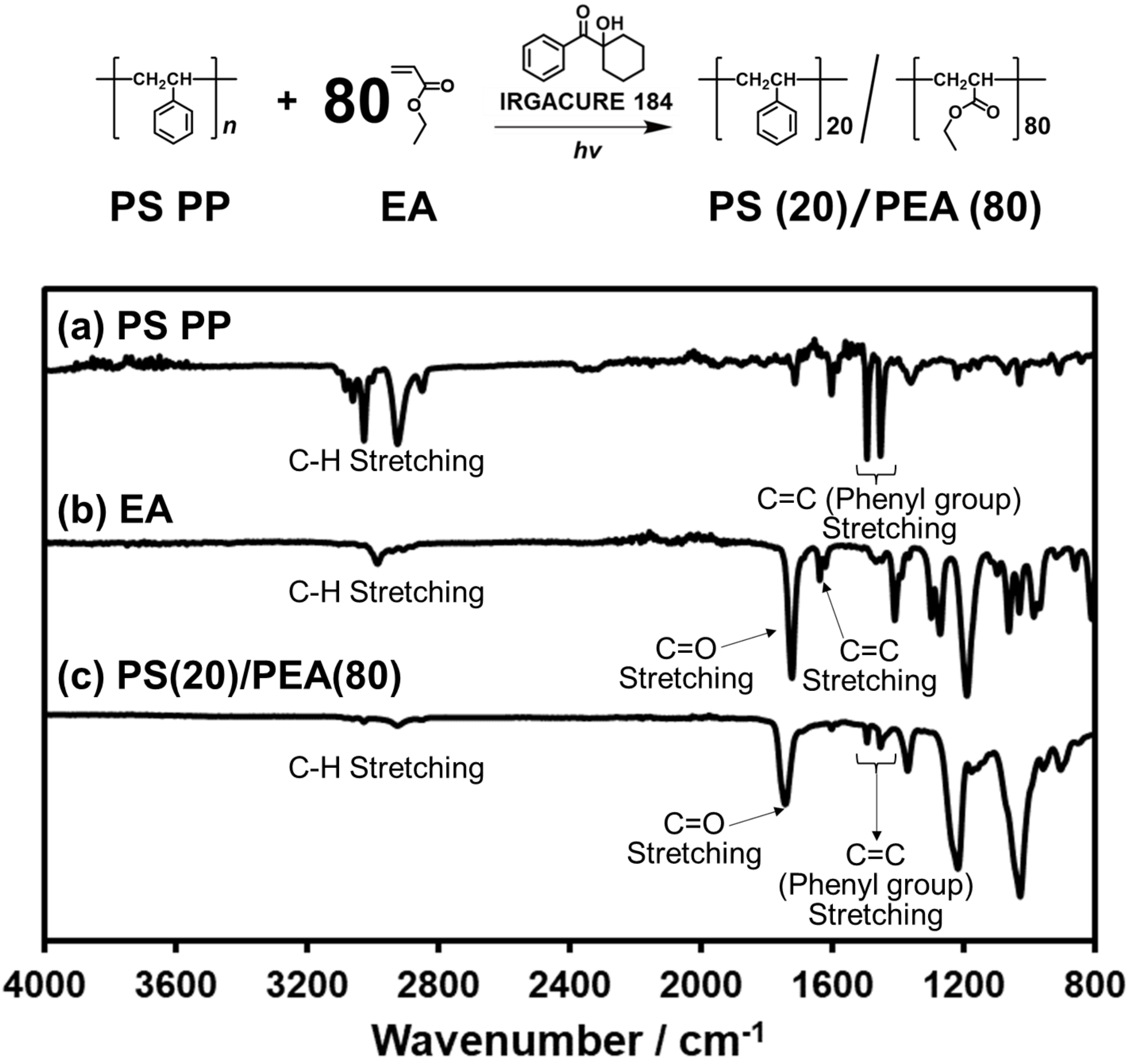


Fig. S35. FT-IR spectra (ATR method) of PS PP **(a)**, EA **(b)**, and PS(20)/PEA(80) **(c)**.

5. Determination of molecular weight by GPC

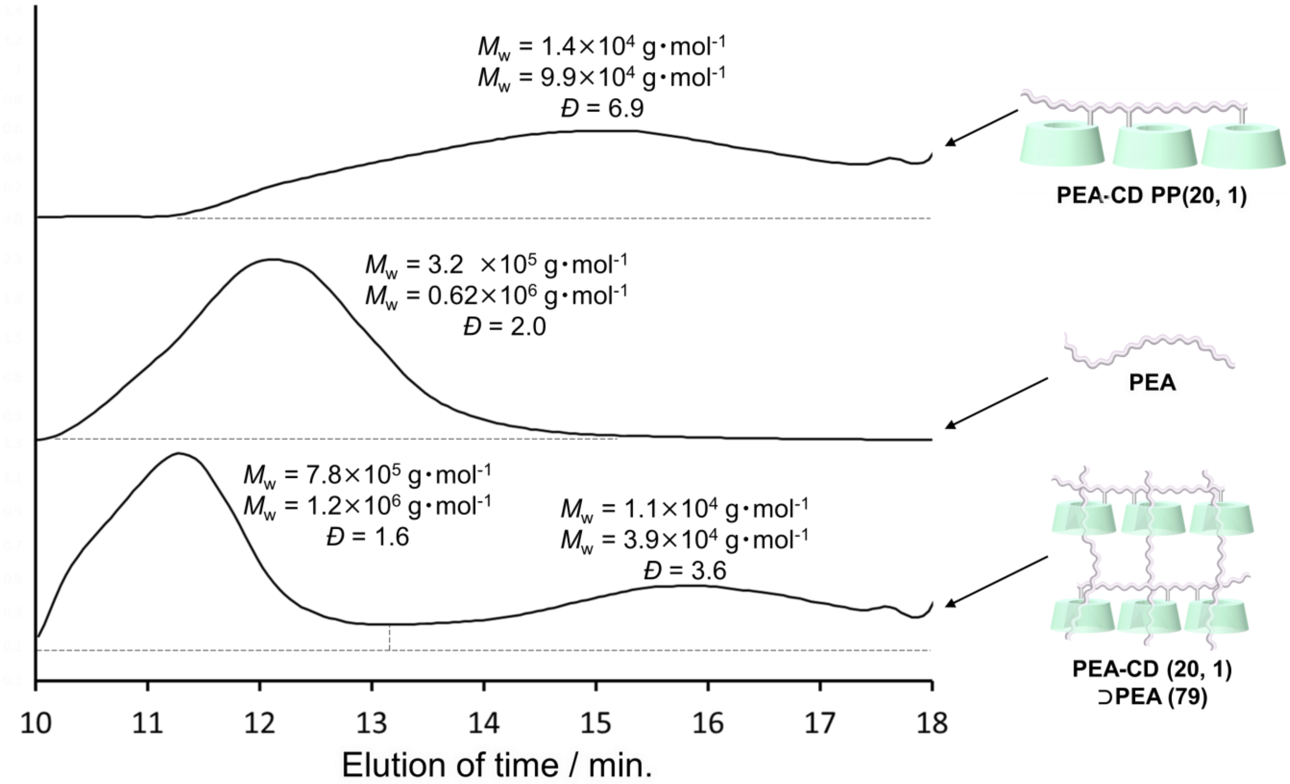


Fig. S36. GPC profiles of PEA-CD PP(20, 1), PEA, and PEA-CD (20, 1)⊃PEA (79) in chloroform eluant. M_n, M_w and Đ were determined by the calibration using PS standards.

The KP elastomers without DA units were dissolved in chloroform. These solubilities allowed the GPC measurements of the KP elastomers. The GPC profiles of PEA-CD (20, 1)⊃PEA (79) showed two peaks (**Fig. S36**). The peak at 11 min. showed the orders of M_n and M_w comparable to PEA obtained by the bulk polymerization. The peak at 16 min. showed the orders of M_n and M_w comparable to PEA-CD PP(20, 1). These results suggest that the dethreading of the secondary polymer from the TAcγCD units caused the elastomers to dissolve. The other primary polymers and KP elastomers showed the similar tendency. **Table S8 and S9** summarize M_n, M_w, and Đ of them.

Table S8. Molecular weight and distribution of the primary polymers by GPC.

Name	Peak of primary polymer		
	$M_n{}^a$ /mg·mol^{-1}	$M_w{}^a$ /mg·mol^{-1}	$Đ^a$
PBA-CD PP(10, 1)	1.1×10^4	4.8×10^4	4.2
PBA PP	1.0×10^4	4.6×10^4	4.4
PEA-CD PP(20, 1)	1.4×10^4	9.9×10^4	6.9
PS-CD PP(20, 1)	1.3×10^4	3.0×10^4	2.3
PS PP	0.88×10^4	2.5×10^4	2.8

[a] Determined by GPC using PS standards for calibration in chloroform as an eluent.

Table S9. Molecular weight and distribution of the elastomers by GPC.

Name	Peak of primary polymer			Peak of secondary polymer		
	$M_n{}^a$ /mg·mol^{-1}	$M_w{}^a$ /mg·mol^{-1}	$Đ^a$	$M_n{}^a$ /mg·mol^{-1}	$M_w{}^a$ /mg·mol^{-1}	$Đ^a$
PBA-CD(10, 1)⊃PEA(89)	1.8×10^4	4.0×10^4	2.9	7.8×10^5	1.2×10^6	1.6
PBA(10)/PEA(90)	1.6×10^4	4.8×10^4	2.9	5.5×10^5	0.87×10^5	1.6
PEA-CD(20, 1)⊃PEA(79)	1.1×10^4	3.9×10^4	3.6	7.8×10^5	1.2×10^6	1.6
PEA	-	-	-	3.2×10^5	0.62×10^6	2.0
PS-CD(20, 1)⊃PEA(79)	1.4×10^4	2.9×10^4	2.1	5.5×10^5	1.1×10^6	2.0
PS(20)/PEA(80)	1.0×10^4	2.7×10^4	2.6	4.0×10^5	0.71×10^6	1.8

[a] Determined by GPC using PS standards for calibration in chloroform as an eluent.

6. Evaluation of mechanical properties by tensile test (stress-strain curves)

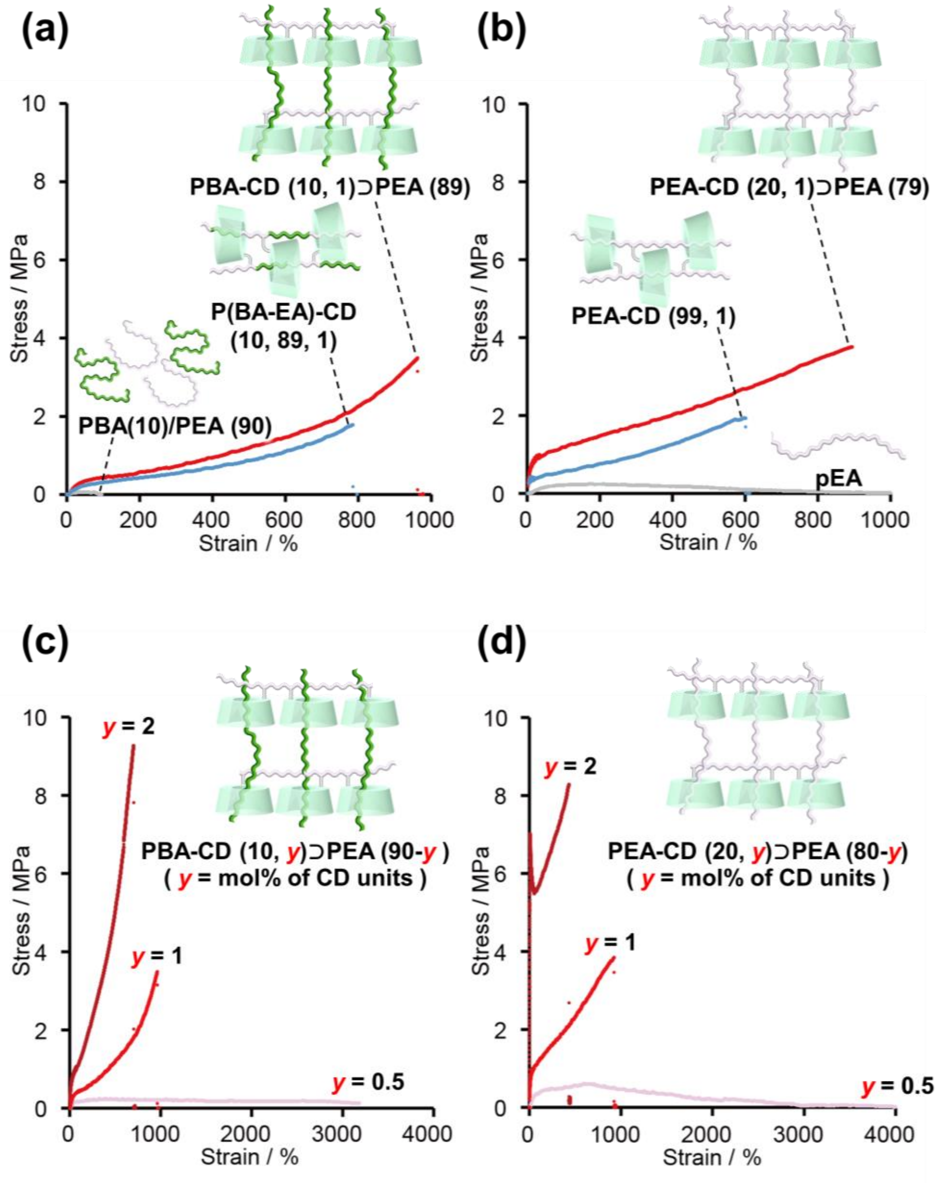


Fig. S37. Stress-strain curves for **(a)** PBA-CD (10, 1)⊃PEA (89) (red line), P(BA-EA)-CD (10, 89, 1) (blue line), PBA(10)/PEA(90) (gray line), **(b)** PEA-CD (20, 1)⊃PEA (79) (red line), PEA-CD (99, 1) (blue line), PEA (gray line), **(c)** PBA-CD (10, y)⊃PEA (10-y) (y = 0.5 : pale red filled line, y = 1 : red filled line, and y =2 : dark red filled line), **(d)** PEA-CD (20, y)⊃PEA (80-y) (y = 0.5 : pale red filled line, y = 1 : red filled line, and y =2 : dark red filled line).

Table S10. Mechanical properties of PBA-CD (10, y)⊃PEA (90-y) (y = 0.5, 1, and 2), P(BA-EA)-CD (10, 89, 1), PBA(10)/PEA(90), PEA-CD (20, y)⊃PEA (80-y) (y = 0.5, 1, and 2), PEA-CD (99, 1), and PEA.

Name	Maximum stress	Maximum strain	Toughness	Young's modulus
	/MPa	/%	/MJm^{-3}	/MPa
PBA-CD(10, 0.5)⊃PEA(89)	0.25±0.09	3180±637	1.9±0.4	0.47±0.23
PBA-CD(10, 1)⊃PEA(89)	3.3±0.8	927±77	12±3	1.7±0.4
PBA-CD(10, 2)⊃PEA(89)	9.2±1.7	695±29	27±3	3.4±0.4
P(BA-EA)-CD (10, 89, 1)	1.9±0.2	754±27	6.2±0.8	1.4±0.2
PBA(10)/PEA(90)	0.058±0.010	76±19	0.019±0.011	0.28±0.16
PEA-CD(20, 0.5)PEA(79)	0.58±0.04	3640±514	9.5±2.4	1.2±0.2
PEA-CD(20, 1)⊃PEA(79)	3.7±0.1	1016±80	22±2	4.1±1.6
PEA-CD(20, 2)⊃PEA(78)	8.1±0.7	451±28	28±1	95±25
PEA-CD (99, 1)	2.0±0.1	575±26	6.2±0.5	4.7±0.6
PEA	0.32±0.10	860±170	1.4±0.7	0.75±0.32

7. Evaluation of mechanical properties by tensile test (relationship between Young's modulus and toughness)

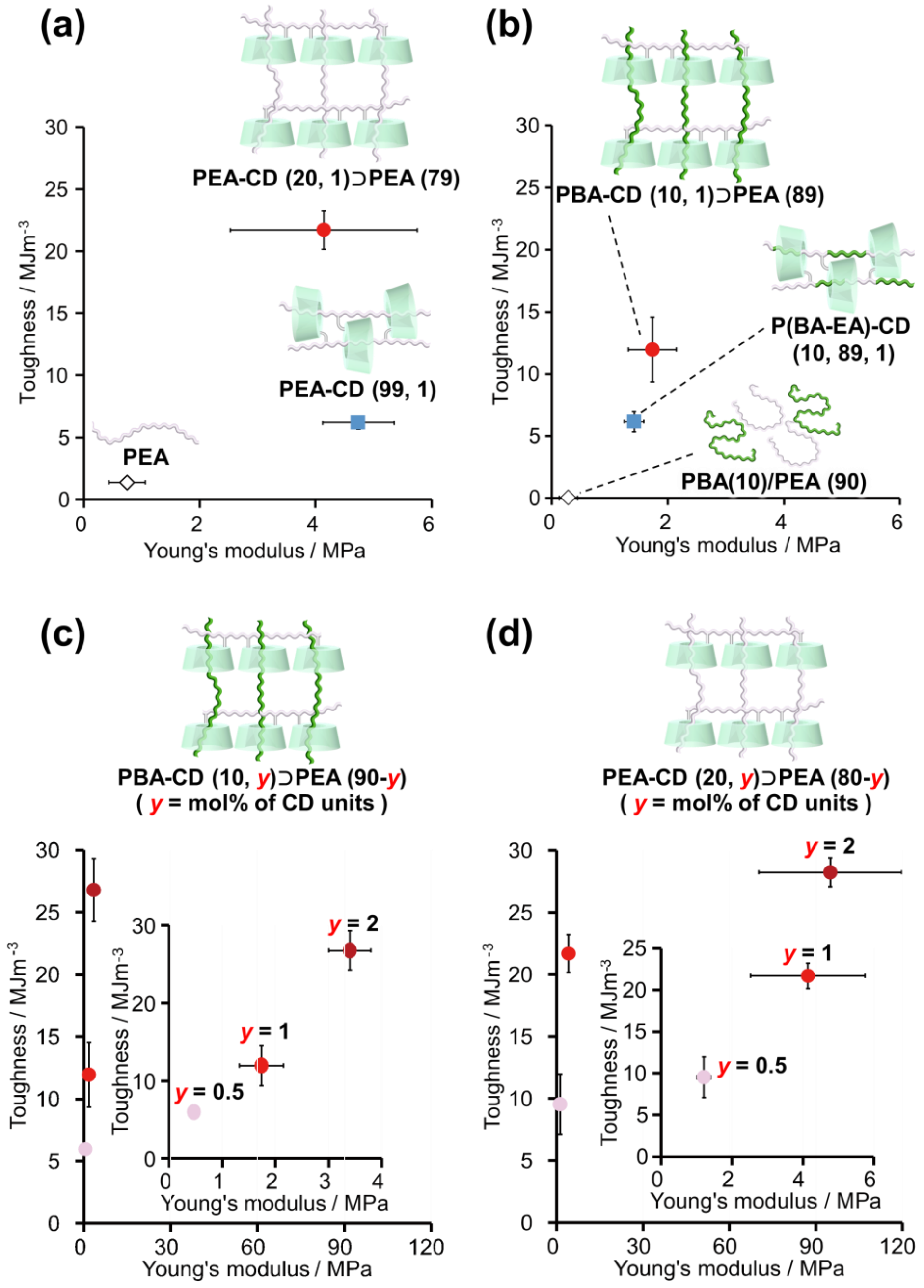
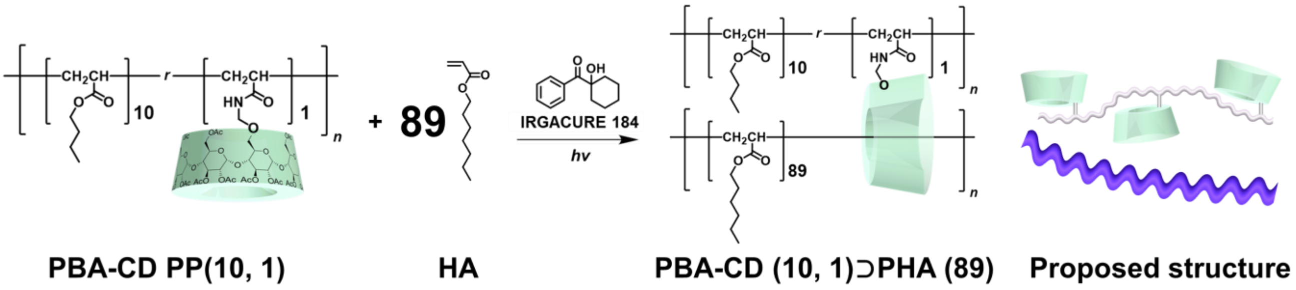


Fig. S38. Plots of toughness energy and Young's modulus for **(a)** PBA-CD (10, 1)⊃PEA (89) (red filled circle), P(BA-EA)-CD (10, 89, 1) (blue filled circle), PBA(10)/PEA(90) (gray filled circle), **(b)** PEA-CD (20, 1)⊃PEA (79) (red filled circle), PEA-CD (99, 1) (blue filled circle), PEA (gray filled circle), **(c)** PBA-CD (10, *y*)⊃PEA (90-*y*) (*y* = 0.5 : pale red filled circle, *y* = 1 : red filled circle, and *y* =2 : dark red filled circle), **(d)** PEA-CD (20, *y*)⊃PEA (80-*y*) (*y* = 0.5 : pale red filled circle, *y* = 1 : red filled circle, and *y* =2 : dark red filled circle).

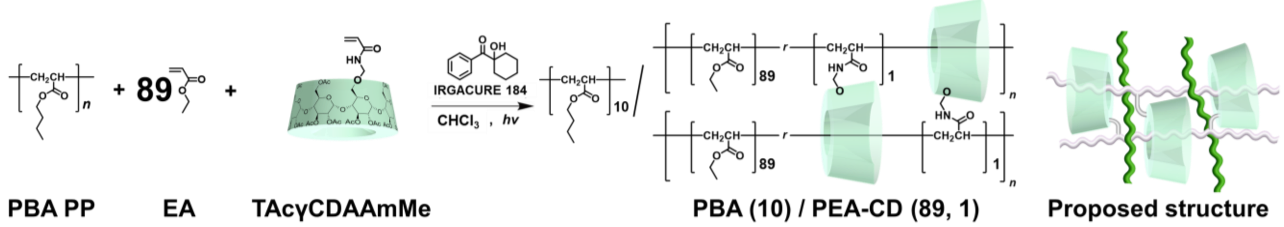
8. Preparation of KP elastomer with bulky secondary polymer (PBA-CD (10, 1)⊃PHA (89))



Scheme S12. Preparation of PBA-CD (10, 1)⊃PHA (89).

Scheme S12 shows the preparation of PBA-CD (10, 1)⊃PHA (89). PBA-CD PP(10, 1) (380 mg) and IRGACURE 184 (photoinitiator; 3.8 mg, 0.019 mmol) were dissolved in HA (1500 mg, 9.4 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 ^{o}C in vacuo for 12 hours.

9. Preparation of SC in presence of poly(BA) linear polymer (PBA(10)/PEA-CD(89, 1))



Scheme S13. Stress-strain curves of PBA(10)/PEA-CD(89, 1).

Scheme S13 shows the preparation of PBA(10)/PEA-CD(89, 1). PBA PP (210 mg), TAcγCDAAmMe (380 mg, 0.16 mmol), and IRGACURE 184 (photoinitiator; 5.9 mg, 0.029 mmol) were dissolved in EA (1400 mg, 14 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 ^{o}C in vacuo for 12 hours.

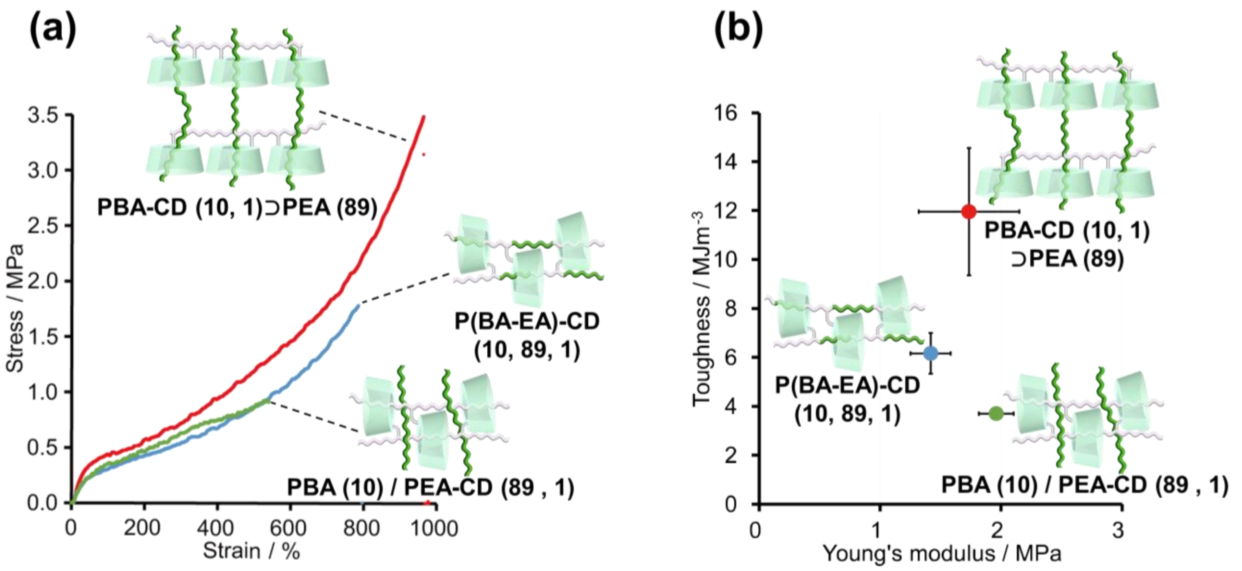
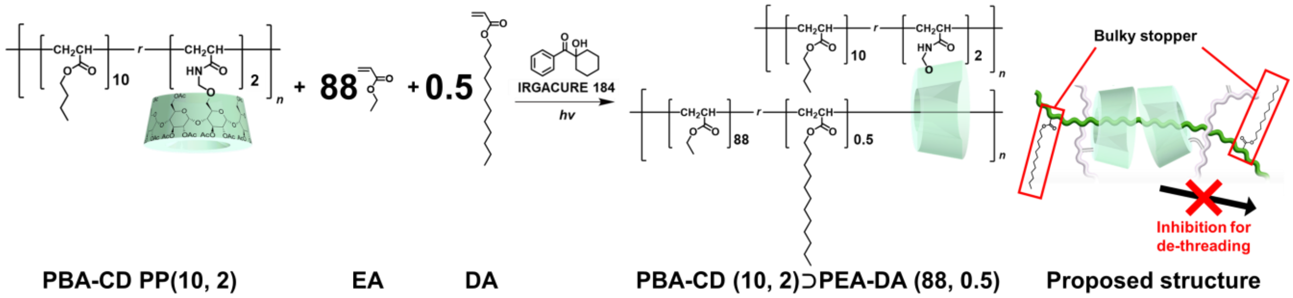


Fig. S39. **(a)** Stress-strain curves for PBA-CD (10, 1)⊃PEA (89) (red line), P(BA-EA)-CD (10, 89, 1) (blue line), and PBA(10)/pEA-CD(89, 1) (green line). **(b)** Plots of toughness and Young's modulus for PBA-CD (10, 1)⊃PEA (89) (red filled circle), P(BA-EA)-CD (10, 89, 1) (blue filled circle), and PBA(10)/pEA-CD(89, 1) (green filled circle).

10. Preparation of KP elastomer where secondary polymers have bulky stoppers (PBA-CD (10, 2)⊃PEA-DA (88, 0.5))



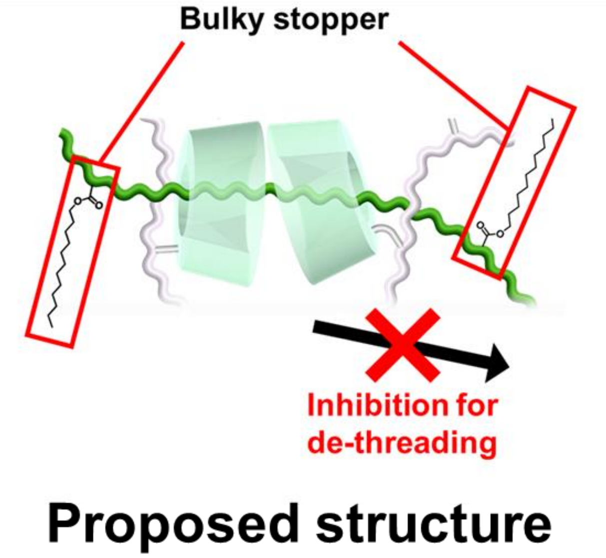
Scheme S14. Preparation of PBA-CD (10, 2)⊃PEA-DA (88, 0.5).

Scheme S14 shows the preparation of PBA-CD (10, 2)⊃PEA-DA (88, 0.5). PBA-CD PP(10, 2) (590 mg), DA (12 mg, 0.049 mmol), and IRGACURE 184 (photoinitiator; 5.9 mg, 0.029 mmol) were dissolved in EA (1400 mg, 14 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 ºC in vacuo for 12 hours.

11. Evaluation of inclusion complexation with NOESY NMR spectroscopies

2D NOESY NMR measurement of KP elastomer where secondary polymers have bulky stoppers (PBA-CD (10, 2)⊃PEA-DA (88, 0.5))

Measurement



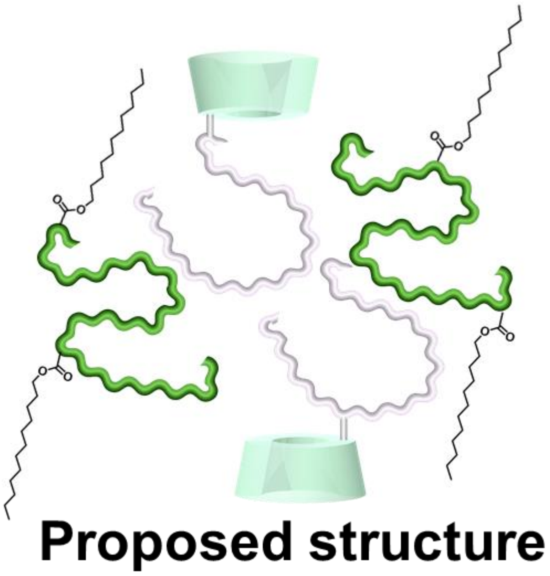
PBA-CD (10, 2)⊃PEA-DA (88, 0.5) (350 mg) were immersed in excess methanol. The swollen samples were frozen using liquid N_2, and then the frozen samples were crushed into powder in a mortar. After evaporation of methanol, the products were dried at 100 ^{o}C in vacuo for 12 hours. After immersing the obtained powder (320 mg) in chloroform-*d* (10 mL) for 24 hours, the mixtures were mixed at 2000 rpm for 5 minutes with ZrO_2 balls (φ = 1mm, 14 g) using a ball miller (Thinky NP-100). After mixing, ZrO_2 balls were removed by filtration. 600 MHz 2D ^{1}H-^{1}H NOESY-NMR spectrum of the obtained slurries (600 µL) were measured (mixing time τ = 1000 ms) (**Fig. S39a**).

Discussion

The spectrum exhibits NOE correlation signals between the protons in CD units and PEA chains. In particular, C(3)H protons locate on internal side of CD rings, showing that PEA main chains penetrated CD units.

2D NOESY NMR measurement of mixture of P(EA-DA) and PBA-CD PP(20, 1) (Control)

Measurement



DA (12 mg, 0.049 mmol) and IRGACURE 184 (photoinitiator; 5.9 mg, 0.029 mmol) were dissolved in EA (1400 mg, 14 mmol). The homogeneous mixture of monomers was sonicated for 1.0 h. Free radical bulk copolymerization of the monomers was carried out by UV irradiation with a high-pressure Hg lamp (λ = 253 and 365 nm) for 30 min. The products were dried at 80 °C in vacuo for 12 hours. The obtained elastomer P(EA-DA) (13.5 mg) and PBA-CD PP(10, 2) (5.7 mg) were dissolved in chloroform-*d* (600 μL). 600 MHz 2D ^{1}H-^{1}H NOESY-NMR spectrum for the mixture of the solutions were measured (mixing time τ = 1000 ms) (**Fig. S39b**).

Discussion

The spectrum only exhibits NOE correlation signals between the protons in external side of CD rings and PEA chains. The absence of NOE signals of C(3)H indicates that TAcγCD units did not form inclusion complex although PAcγCD was accessible to side chains of pEA-DA. These results indicate that PAcγCD units form inclusion complex with pEA secondary polymer chains in PBA-CD (10, 2)⊐PEA-DA (88, 0.5).

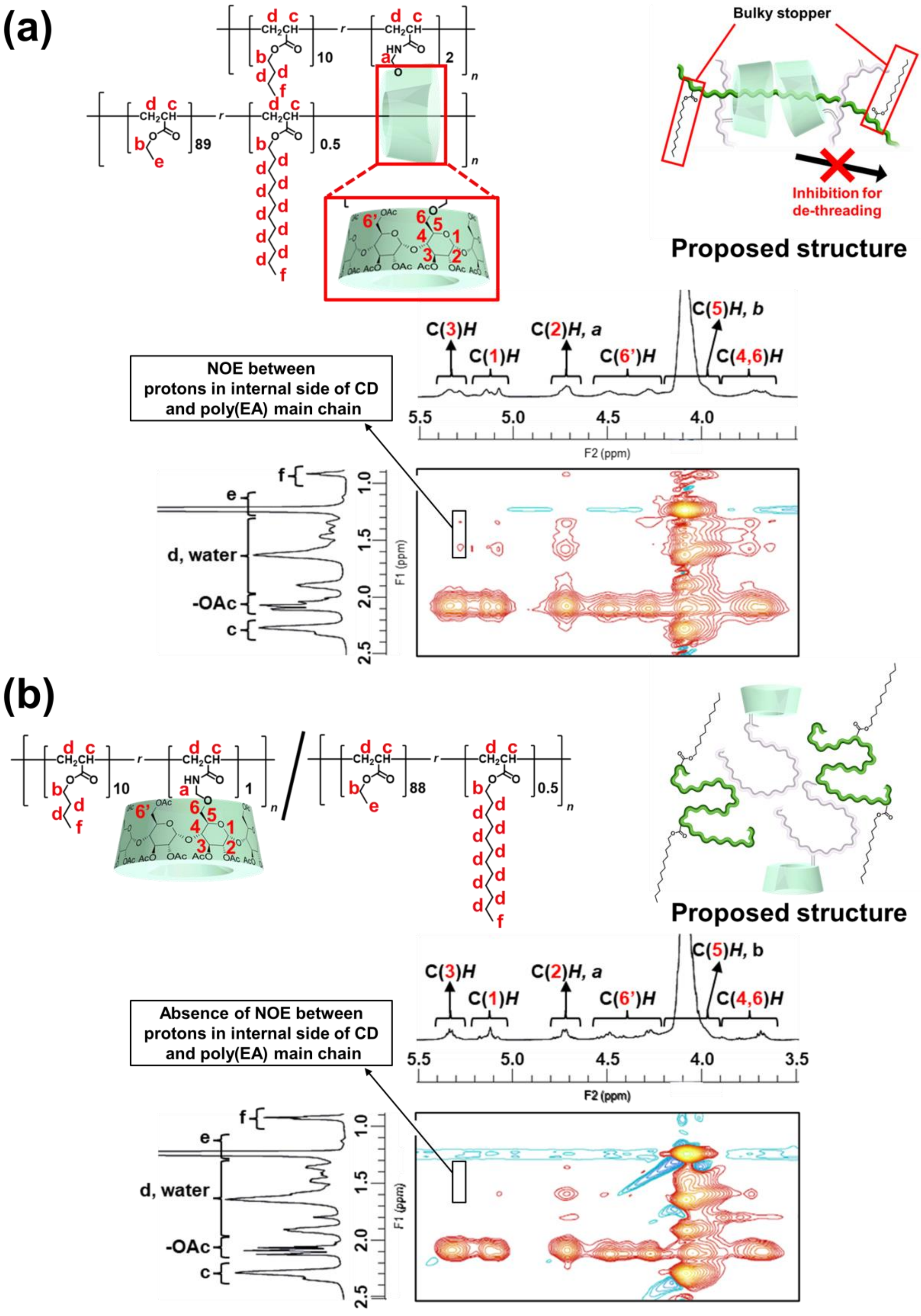


Fig. S40. Chemical structures, proposed structures, and 600 MHz 2D ^{1}H-^{1}H NOESY NMR spectra for **(a)** the ball-milled PBA-CD (10, 2)⊃PEA-DA (88, 0.5) slurries with chloroform-*d* and **(b)** the chloroform-*d* solution of P(EA-DA) and PBA-CD PP(10, 2).

12. Determination of glass transition temperatures (T_g) by DSC measurements

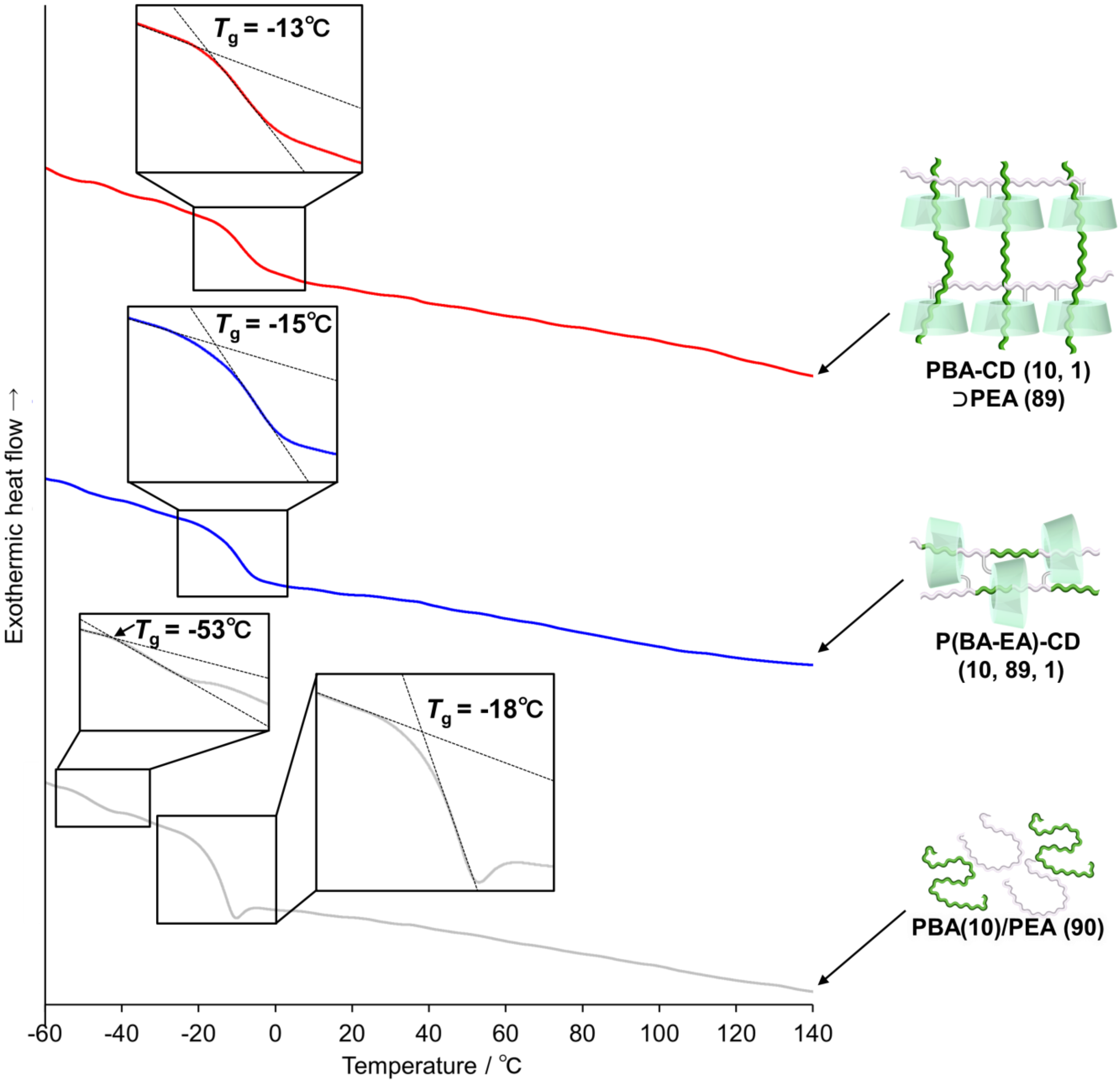


Fig. S41. DSC curves of PBA-CD (10, 1)⊃PEA (89) (red line), P(BA-EA)-CD (10, 89, 1) (blue line), and PBA(10)/PEA(90) (gray line).

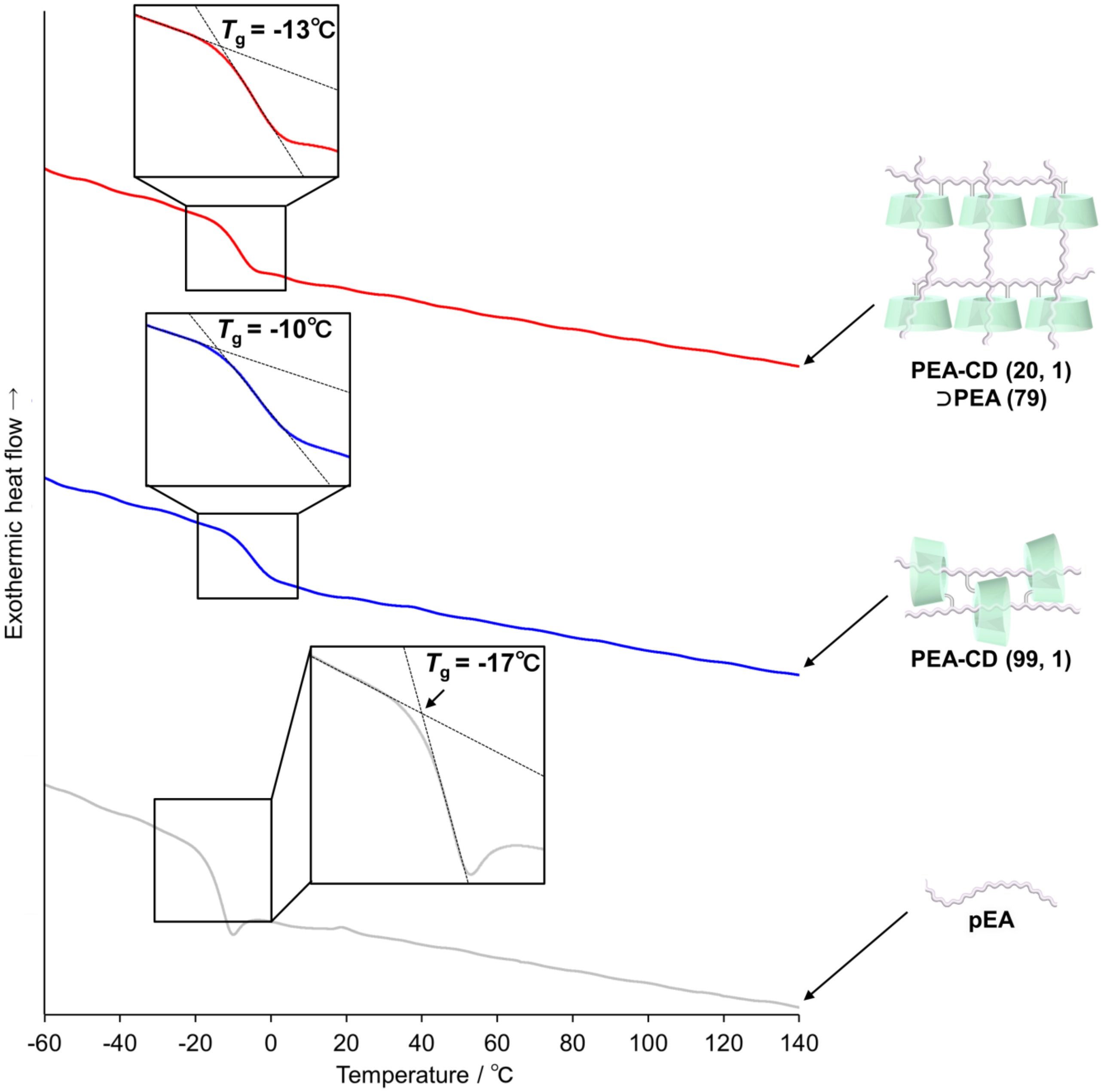


Fig. S42. DSC curves of PEA-CD (20, 1)⊃PEA (79) (red line), PEA-CD (99, 1) (blue line), and PEA (gray line).

13. Investigation of thermal stabilities by TGA measurements.

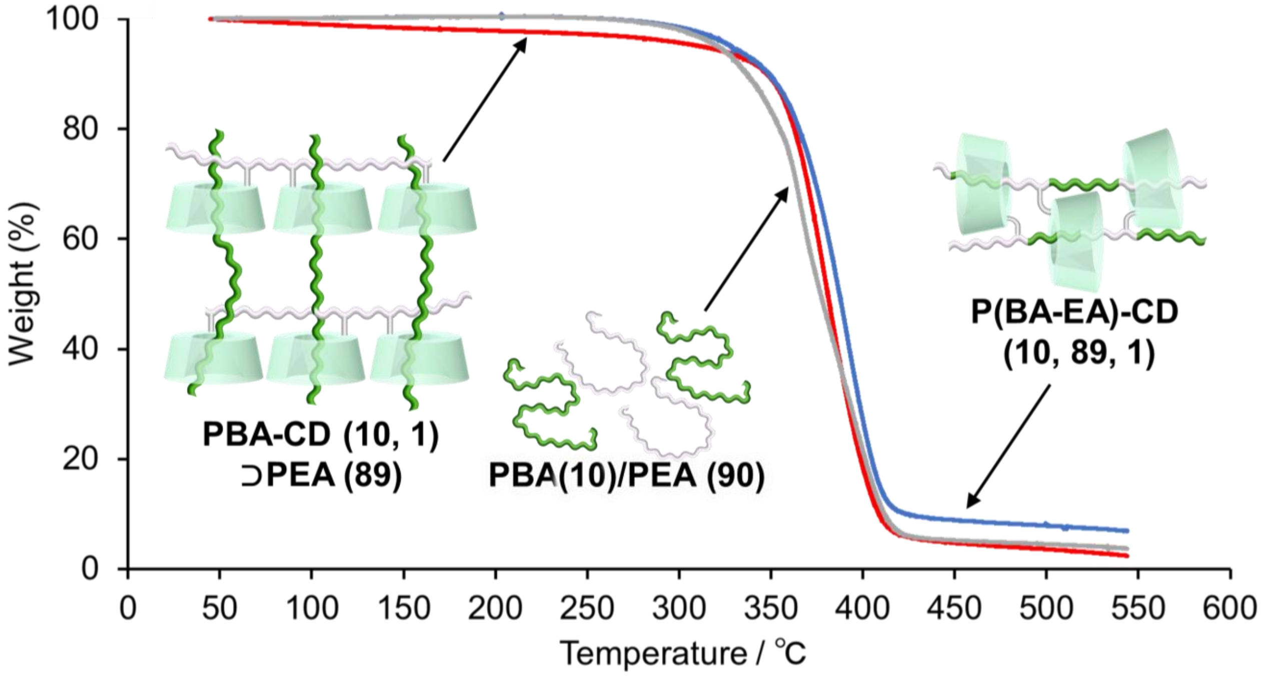


Fig. S43. Thermal degradation behaviors of PBA-CD (10, 1)⊃PEA (89), P(BA-EA)-CD (10, 89, 1), and PBA(10)/PEA(90).

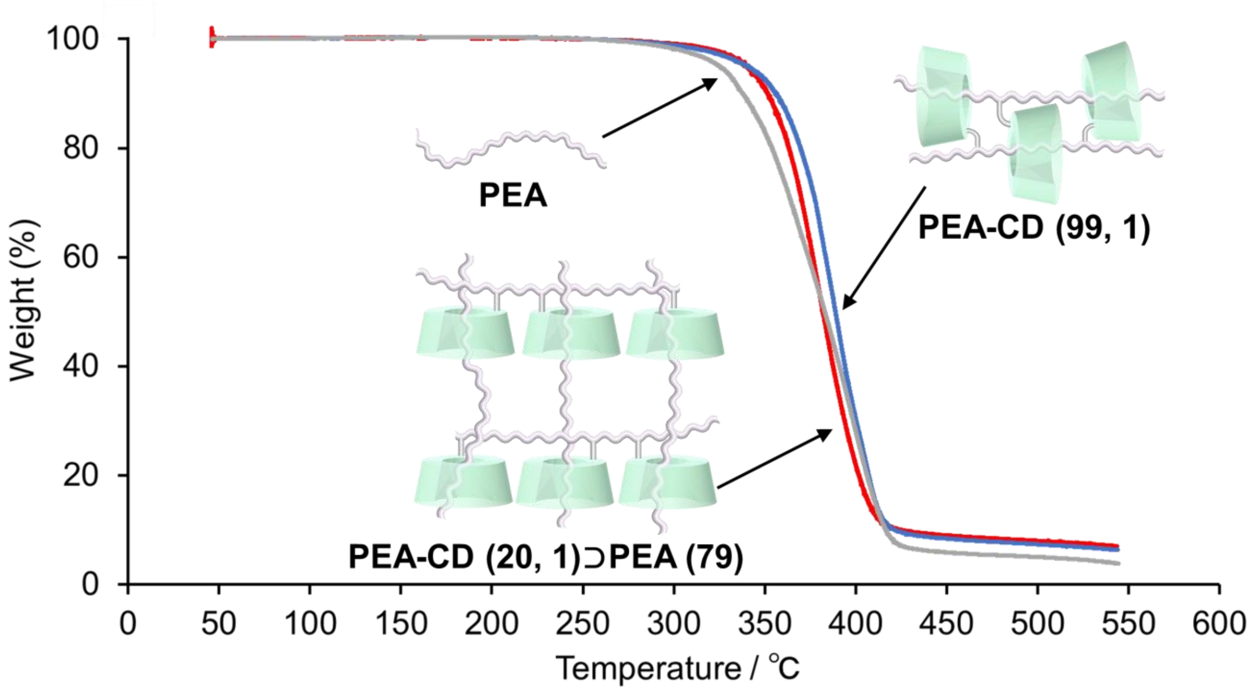


Fig. S44. Thermal degradation behaviors of PEA-CD (20, 1)⊃PEA (79), PEA-CD (99, 1), and PEA.

14. Investigation of deformation behaviors in cyclic tensile test.

We investigated the effect of the movable cross-links with cyclic tensile tests of P(BA-EA)-CD (10, 89, 1), PBA(10)/PEA(90), and PBA-CD (10, 1)⊃PEA (89). Test pieces were continuously stretched and recovered without interval, where the maximum strains were set to 100%, 200%, 300%, 400%, 500%, 600%, 700%, 800%, 900%, and 1000% with a deformation rate of 1 mm/s (**Fig. S45**). W_{in} and W_{out} were determined from the stress-strain curve in the cyclic tensile tests. As a results, the maximum stress of P(BA-EA)-CD (10, 89, 1) increased as the number of cycles increased, indicating the mechanically interlocked cross-links lead to elastic behavior. However, the maximum stress of PBA-CD (10, 1)⊃pEA (89) decreased after 4 cycles, indicating that larger deformation increased the contribution by dethreading of secondary polymers.

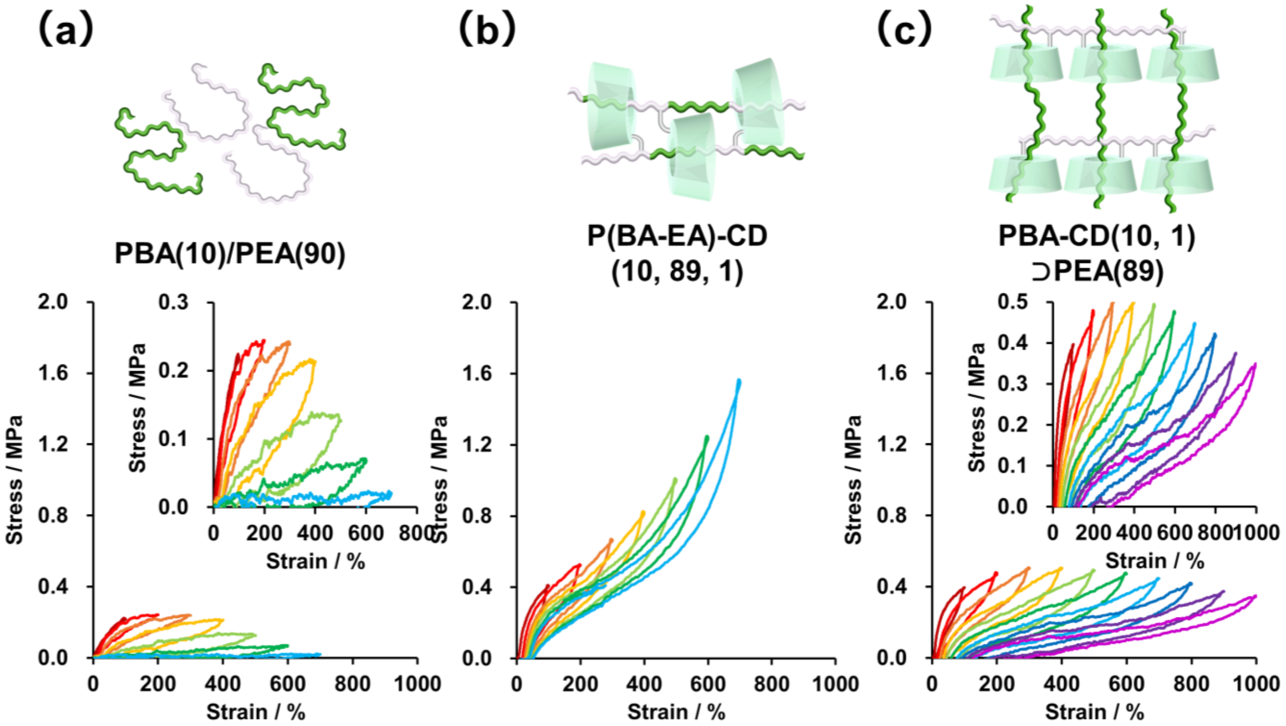


Fig. S45. Cyclic tensile tests for **(a)** PBA(10)/PEA(90), **(b)** P(BA-EA)-CD (10, 89, 1), and **(c)** PBA-CD (10, 1)⊃PEA(89).

15. Stress relaxation tests.

The curve fitting of stress-relaxation behaviors of P(BA-EA)-CD (10, 89, 1) and PBA-CD (10, 1)⊃PEA (89) were carried out by non-linear least square curve fitting method using Kohlrausch-Williams-Watts models. The stress σ versus relaxation time t curves were well fitted ($R^2 > 0.99$) (**Fig. S46**).

$$\sigma = \sigma_{\mathrm{r}} \exp\left\{-\left(\frac{t}{\tau}\right)^{\beta}\right\} + \sigma_{\infty}$$

σ_{r} (relaxable stress), σ_{∞} (residual stress), τ (time constant), and β (stretching exponent) are fitting parameter.

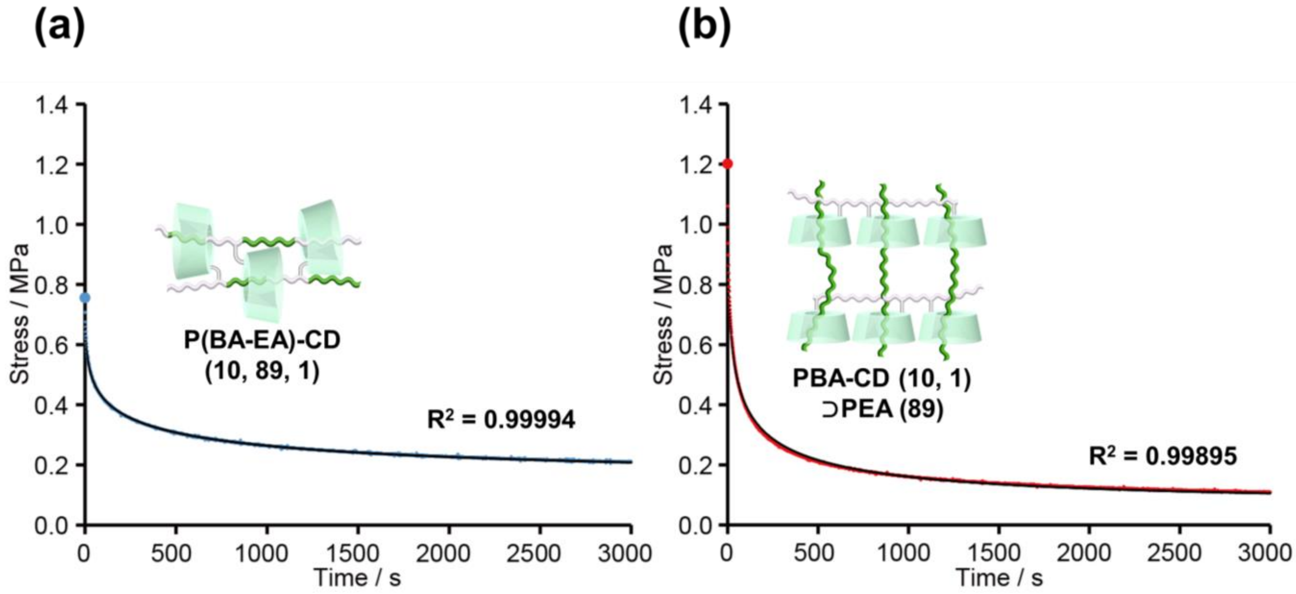


Fig. S46. Stress relaxation of **(a)** PBA-CD (10, 1)⊃PEA (89) (blue line) and **(b)** P(BA-EA)-CD (10, 89, 1) (red line) at 400% strain and fitting curves (black line).

16. Evaluation of viscoelastic properties by DMA measurements

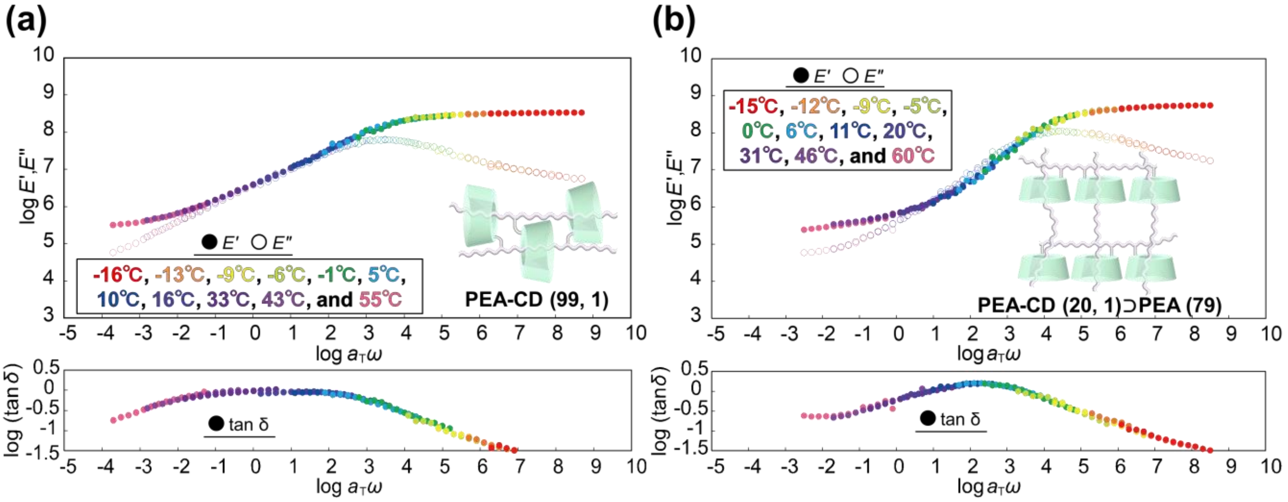


Fig. S47. Composite curves of logarithmic moduli (logE' and logE'') and log(tanδ) of **(a)** PEA-CD (99, 1) and **(b)** PEA-CD (20, 1)⊃PEA (79).

The apparent activation energy ΔE_a was calculated from Arrhenius equation, where α_T was the shift factor, R was the ideal gas constant, and A was a constant.

$$\sigma_T = A \exp\left(\frac{\Delta E_a}{RT}\right)$$

The activation energy values were obtained from slopes in the ln α_T versus $1/T$ (T = 0~60°C) plots, where the ln α_T versus $1/T$ plots obey the Arrhenius equation in following style. T_0 is reference temperature (T_0 = 293K).

$$\ln \sigma_T = \frac{\Delta E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

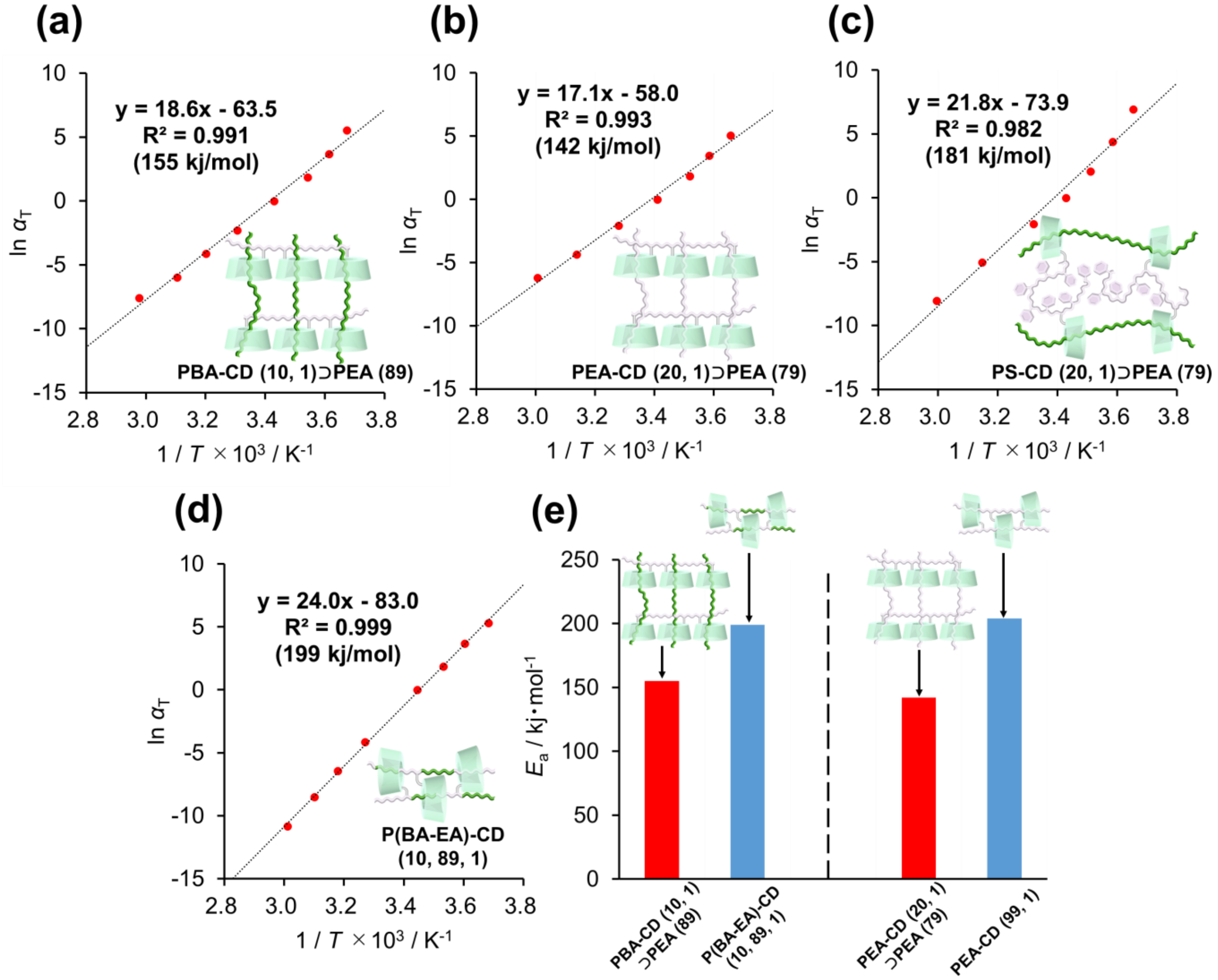


Fig. S48 The Arrhenius plots (α_T versus 1/*T*; T = 0-60°C) of **(a)** PBA-CD (10, 1)⊃PEA (89), **(b)** PEA-CD (20, 1)⊃PEA (79), **(c)** PS-CD (20, 1)⊃PEA (79), and **(d)** P(BA-EA)-CD (10, 89, 1). **(e)** Arrhenius activation energies (E_a) for the network relaxation calculated from the temperature dependence of a_T for. PBA-CD (10, 1)⊃PEA (89), P(BA-EA)-CD (10, 89, 1), PEA-CD (20, 1)⊃PEA (79), and PEA-CD (99, 1).

17. Properties of PS(20)/PEA(80) and PS-CD (20, 1)⊃PEA (79)

PS-CD (20, 1)⊃PEA (79) show highest tough in PS-CD (20, *y*) ⊃PEA (80-*y*) (*y* = 0.5. 1, and 2) (**Fig. S49**). PS-CD (20, 0.5)⊃PEA (79) showed lower toughness and higher Young's modulus than PS-CD (20, 1)⊃PEA (79). These results suggested that the small mol% contents of the TAcγCD units bring low miscibility and much aggregation of PS domain. Low fracture strain of PS-CD (20, 2)⊃PEA (78) could be contributed by too high Young's modulus based on dense cross-links and hard PS domain.

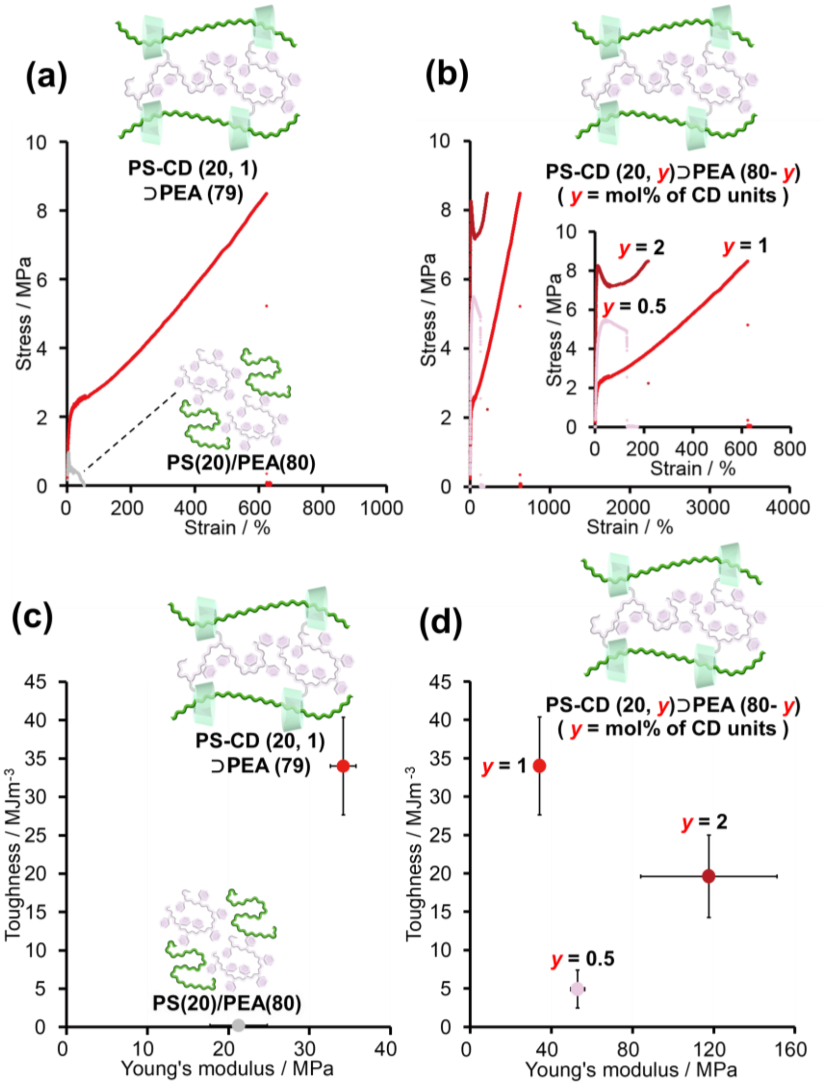


Fig. S49. Stress-strain curves for **(a)** PS-CD (20, 1)⊃PEA (79) (red line), PS(20)/PEA(80) (gray line), and **(b)** PS-CD (20, *y*)⊃PEA (80-*y*) (*y* = 0.5 : pale red filled line, *y* = 1 : red filled line, and *y* =2 : dark red filled line). Plots of toughness and Young's modulus for **(c)** PS-CD (20, 1)⊃PEA (79) (red filled circle), PS(20)/PEA(80) (gray filled circle), and **(d)** PS-CD (20, *y*)⊃PEA (80-*y*) (*y* = 0.5 : pale red filled circle, *y* = 1 : red filled circle, and *y* =2 : dark red filled circle).

Table S11. Mechanical properties of PS-CD (20, *y*)⊃PEA (80-*y*) (*y* = 0.5, 1, and 2), PS(20)/PEA(80), and PS-CD (20, 1)⊃PEA (79).

Name	Maximum stress	Maximum strain	Toughness	Young's modulus
	/MPa	/%	$/\mathrm{MJm}^{-3}$	/MPa
PS-CD(20, 0.5)⊃PEA(79)	5.3±0.2	103±46	4.9±2.5	53±4
PS-CD(20, 1)⊃PEA(79)	8.7±0.6	671±72	34±6	34±2
PS-CD(20, 2)⊃PEA(78)	8.1±0.7	451±28	20±5	120±30
PS(20)/PEA(80)	5.3±0.2	40±13	0.20±0.06	21±4
PEA-CD(20, 1)⊃PEA(79)	3.7±0.1	1016±80	22±2	4.1±1.6

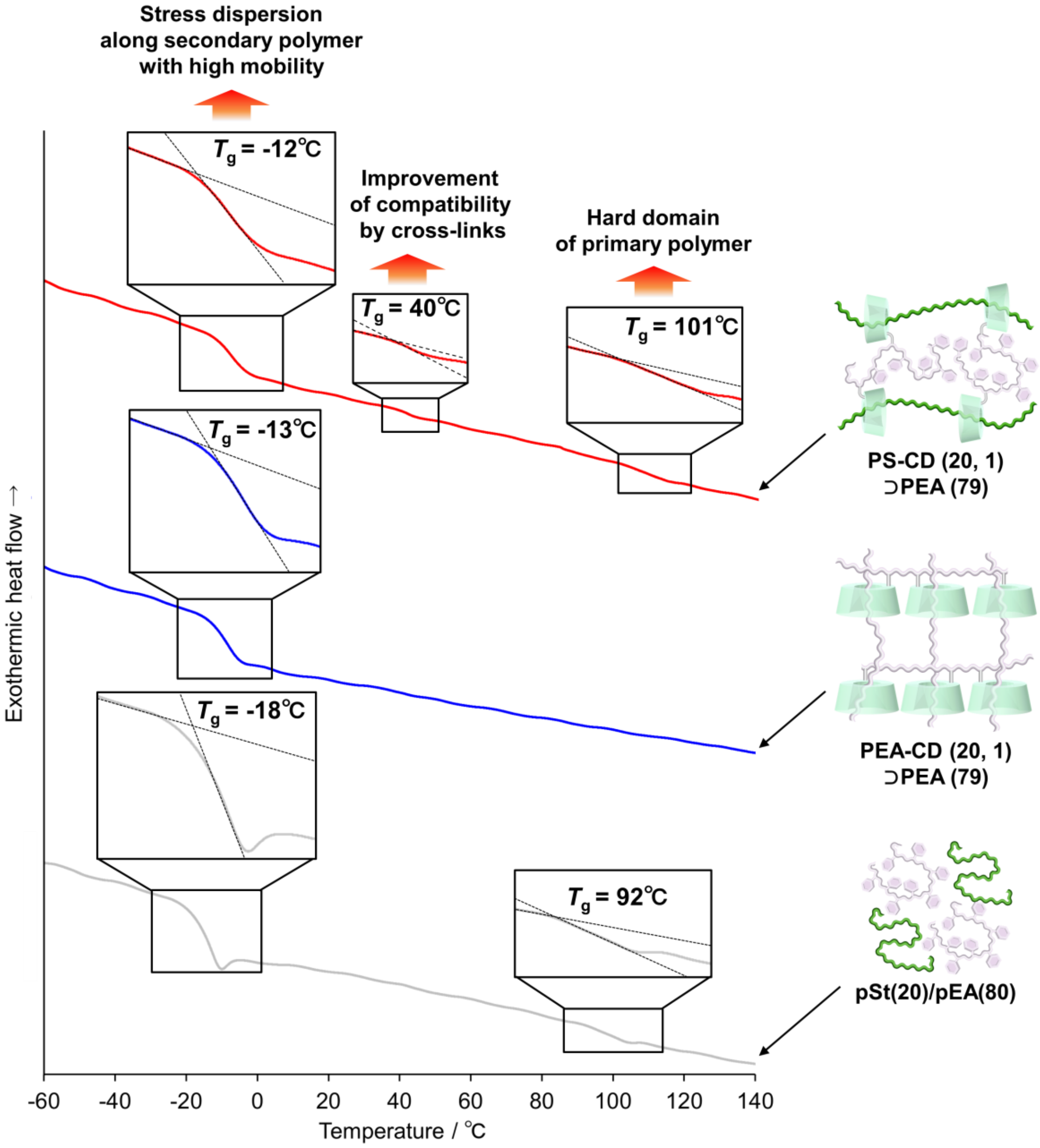


Fig. S50. DSC curves of PS-CD (20, 1)⊃PEA (79) (red line), PEA-CD (20, 1)⊃PEA (79) (blue line), and PS(20)/PEA(80) (gray line).

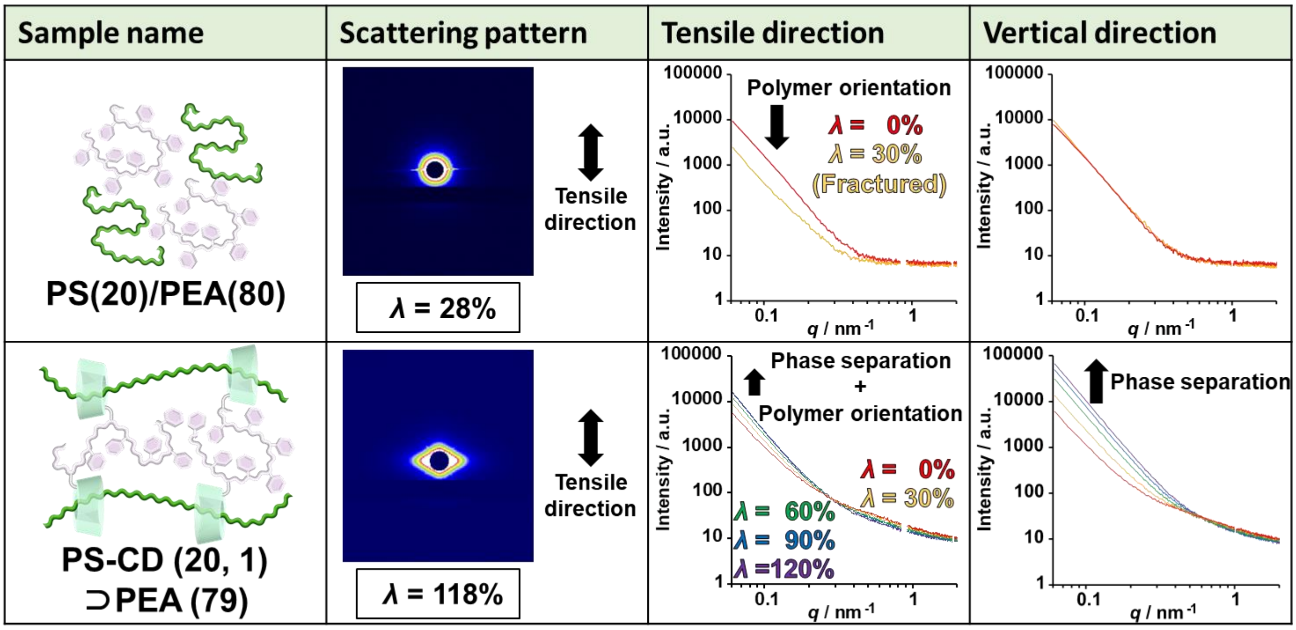


Fig. S51. Scattering patterns of PS(20)/PEA(80) with 28% strain and PS-CD (20, 1)⊃PEA (79) with 118% strain. SAXS profiles of PS(20)/PEA(80) and PS-CD (20, 1)⊃PEA (79) with λ strains (λ = 0% : red line, λ = 30% : yellow line, λ = 60% : green line, λ = 90% : blue line, and λ = 120% : purple line) in tensile and vertical direction.

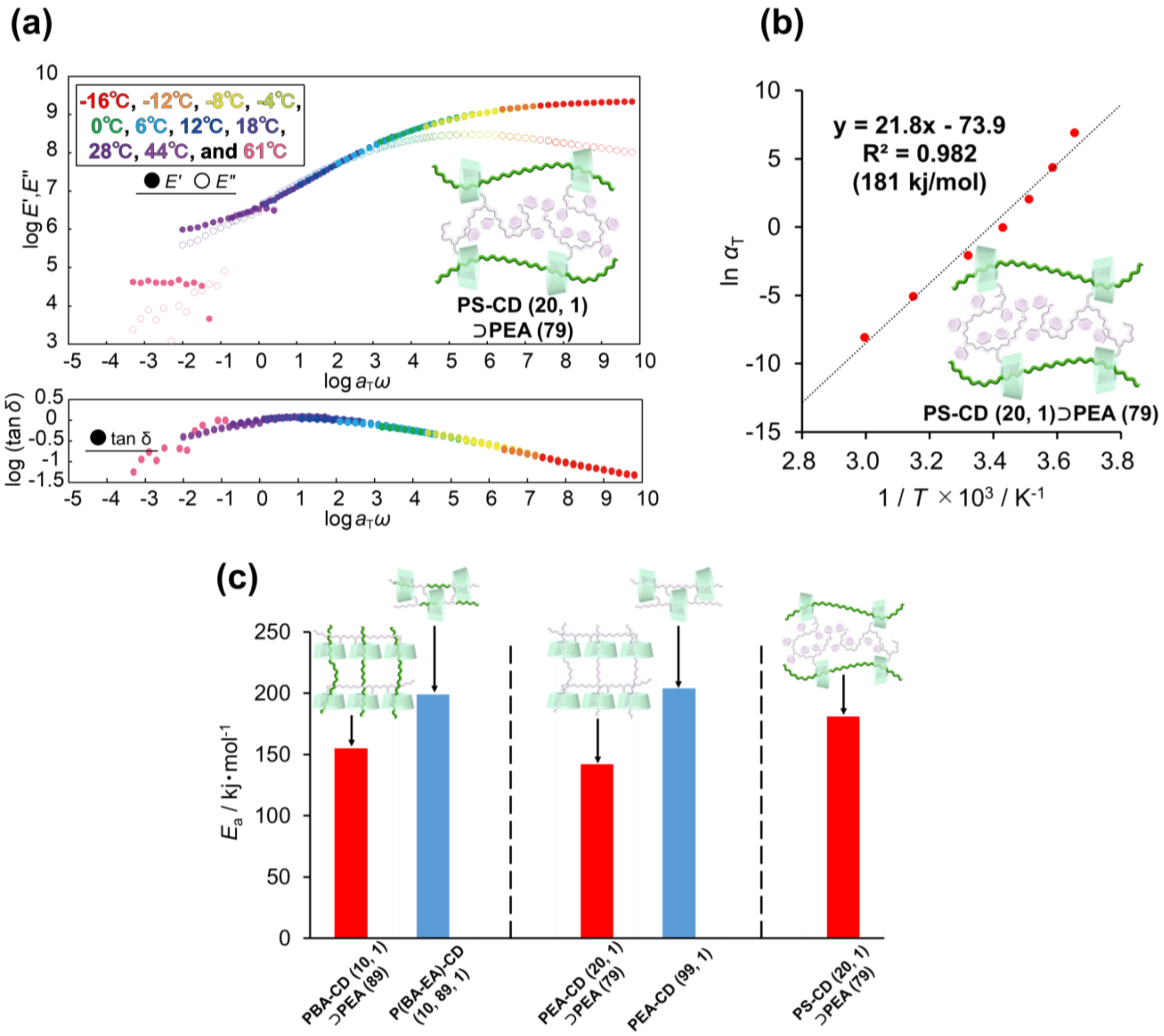


Fig. S52. Composite curves of logarithmic moduli (logE' and logE'') and log(tanδ) of **(a)** PS-CD (20, 1)⊃PEA (79). The Arrhenius plots (α_T versus 1/T; T = 0-60°C) of **(b)** PS-CD (20, 1)⊃PEA (79). **(c)** Arrhenius activation energies (E_a) for the network relaxation calculated from the temperature dependence of a_T for. PBA-CD (10, 1)⊃PEA (89), P(BA-EA)-CD (10, 89, 1), PEA-CD (20, 1)⊃PEA (79), PEA-CD (99, 1), PS-CD (20, 1)⊃PEA (79).

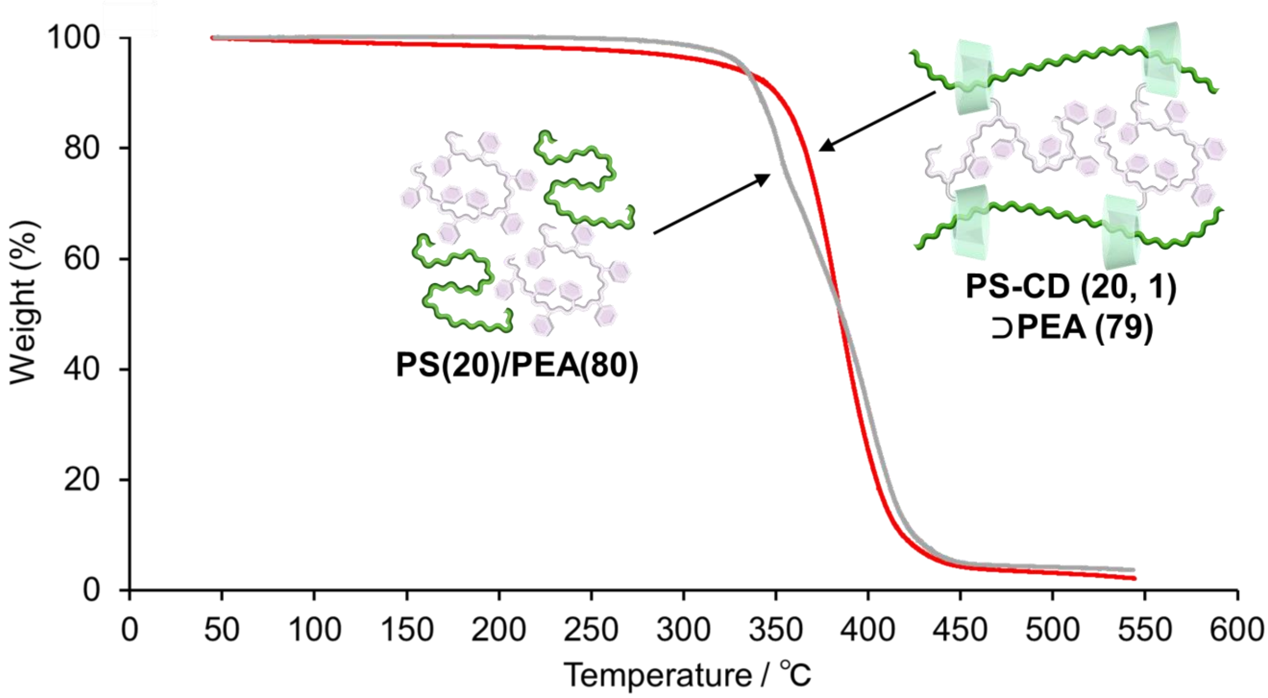


Fig. S53. Thermal degradation behaviors of PS-CD (20, 1)⊃PEA (79) and PS(20)/PEA(80).

Reference

1. S. Nomimura, M. Osaki, J. Park, R. Ikura, Y. Takashima, H. Yamaguchi and A. Harada, *Macromolecules*, 2019, **52**, 2659–2668.
2. R. Ikura, J. Park, M. Osaki, H. Yamaguchi, A. Harada and Y. Takashima, *Macromolecules*, 2019, **52**, 6953–6962.