

Supporting Information

Thermally Healable and Reprocessable Bis(hindered amino)disulfide-Cross-Linked Polymethacrylate Networks

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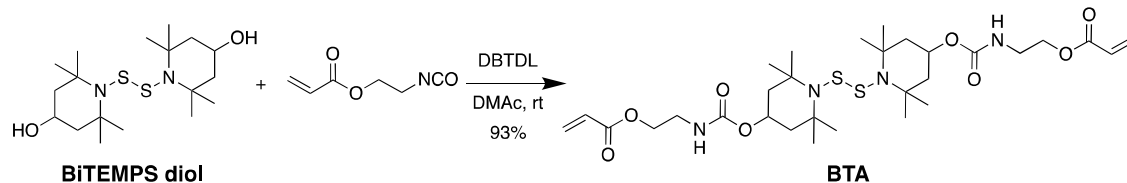
1. General Information

All reagents and solvents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, or Kanto Chemical and used as received, unless otherwise noted. Hexyl methacrylate (HMA) and 1,4-dioxane were purified by basic alumina column (Merck KGaA) to remove the stabilizer prior to use. Diol derivative of BiTEMPS was synthesized according to the previously reported procedure.¹ ¹H NMR spectra were measured at 25 °C using a 500 MHz Bruker spectrometer with tetramethylsilane (TMS) as an internal standard in chloroform-*d* (CDCl₃). IR spectra were obtained with a Perkin-Elmer Spectrum One infrared spectrometer as thin films with KBr. Gel permeation chromatography (GPC) measurements were carried out at 40 °C on TOSOH HLC-8320 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards ($M_n = 4430\text{--}3242000$; $M_w/M_n = 1.03\text{--}1.08$) were used to calibrate the GPC system. Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-60A differential scanning calorimeter at a heating rate of 10 °C/min under N₂ flow. Thermal gravimetric analysis (TGA) was performed on a Shimadzu DTG60/60 simultaneous thermogravimetry/differential thermal analyzer at a heating rate of 10 °C/min under N₂ flow. Stress relaxation measurements were carried out using Hitachi High-Tech Science TMA7100 under N₂ flow. Tensile tests were performed on SHIMADZU EZ-L instrument equipped with a 50 N load cell. Pulverization of the PHMAs was performed with a Retsch Mixer Mill MM 400.

2. Synthetic Procedure

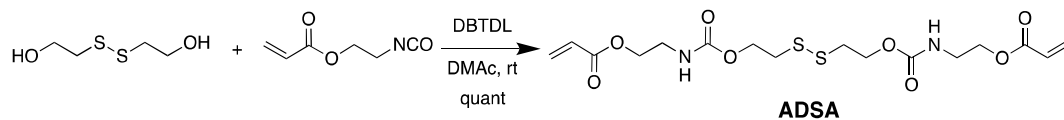
2.1. Synthesis of diacrylate crosslinkers

2.1.1. BiTEMPS-containing diacrylate (BTA)



2-Isocyanatoethyl acrylate (1.28 g, 9.10 mmol) was added dropwise to a solution of BiTEMPS diol (0.857 g, 2.28 mmol) and one drop of di-*n*-butyltin dilaurate (DBTDL) in dry DMAc (15 mL), and the solution was stirred overnight. The resulting solution was poured into water (80 mL) and extracted with diethyl ether for 4 times. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated to some extent under reduced pressure. Purification by neutral silica gel column chromatography (hexane/ethyl acetate, 2/1, v/v) afforded BTA as a white solid (1.40 g, 93%). ¹H NMR (500 MHz, CDCl₃) : δ/ppm 6.44 (dd, *J* = 17.3, 1.4 Hz, 2H, CH₂CHCOO–), 6.13 (dd, *J* = 17.3, 10.5 Hz, 2H, CH₂CHCOO–), 5.87 (dd, *J* = 10.5, 1.4 Hz, 2H, CH₂CHCOO–), 4.98 (br, 4H, –C(CH₃)₂CH₂CH< and –OCH₂CH₂NHCOO–), 4.25 (t, *J* = 4.9 Hz, 4H, –OCH₂CH₂NHCOO–), 3.49 (dd, *J* = 4.9, 4.7 Hz, 4H, –OCH₂CH₂NHCOO–), 1.98 (d, *J* = 9.5 Hz, 4H, –C(CH₃)₂CH₂CH<), 1.48 (t, *J* = 12.1 Hz, 4H, –C(CH₃)₂CH₂CH<), 1.43 (s, 12 H, –C(CH₃)₂CH₂CH<), 1.23 (s, 12H, –C(CH₃)₂CH₂CH<). ; ¹³C NMR (100 MHz, CDCl₃) : δ/ppm 166.14, 156.10, 131.50, 128.10, 67.82, 63.68, 59.67, 46.08, 40.19, 34.92, 26.84. FT-IR (KBr, cm^{–1}): 3372, 2975, 2933, 1724, 1703, 1685, 1637, 1523, 1459, 1409, 1380, 1271, 1239, 1195, 1175, 1074, 1018.

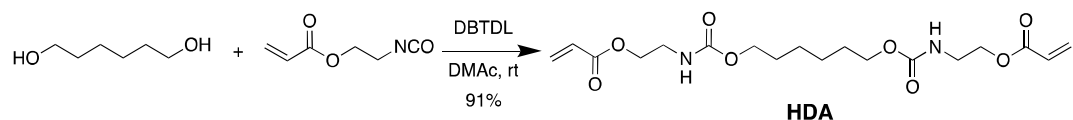
2.1.2. Dialkyl disulfide-containing diacrylate (ADSA)



The sample was synthesized in a similar manner to **2.1.1** using bis(2-hydroxyethyl) disulfide (0.385 g, 2.50 mmol), 2-isocyanatoethyl acrylate (1.42 g, 10.0 mmol), dry DMAc (25 mL), and one drop of DBTDL. ADSA was obtained as a white solid (0.997 g, quant). ¹H NMR (500 MHz, CDCl₃) : δ/ppm 6.44 (dd, *J* = 17.3, 1.4 Hz, 2H, CH₂CHCOO–), 6.14 (dd, *J* = 17.3, 10.5 Hz, 2H, CH₂CHCOO–), 5.87 (dd, *J* = 10.5, 1.4 Hz, 2H,

CH_2CHCOO^-), 5.28 (br, 2H, $-OCH_2CH_2NHCOO^-$), 4.33 (t, $J = 6.3$ Hz, 4H, $-OCH_2CH_2SS^-$), 4.25 (t, $J = 4.9$ Hz, 4H, $-OCH_2CH_2NHCOO^-$), 3.50 (dd, $J = 5.1, 4.8$ Hz, 4H, $-OCH_2CH_2NHCOO^-$), 2.93 (t, $J = 6.3$ Hz, 4H, $-OCH_2CH_2SS^-$).

2.1.3. Hexylene-containing diacrylate (HDA)



The sample was synthesized in a similar manner to **2.1.1** using 1,6-hexanediol (0.295 g, 2.50 mmol), 2-isocyanatoethyl acrylate (1.42 g, 10.0 mmol), dry DMAc (24 mL), and one drop of DBTDL. HDA was obtained as a white solid (0.907 g, 91%). 1H NMR (500 MHz, $CDCl_3$) : δ /ppm 6.44 (dd, $J = 17.3, 1.4$ Hz, 2H, CH_2CHCOO^-), 6.14 (dd, $J = 17.3, 10.5$ Hz, 2H, CH_2CHCOO^-), 5.87 (dd, $J = 10.5, 1.4$ Hz, 2H, CH_2CHCOO^-), 4.98 (br, 2H, $-OCH_2CH_2NHCOO^-$), 4.25 (t, $J = 5.0$ Hz, 4H, $-OCH_2CH_2NHCOO^-$), 4.06 (t, $J = 6.3$ Hz, 4H, $-OCH_2CH_2CH_2-$), 3.49 (dd, $J = 5.0, 4.6$ Hz, 4H, $-OCH_2CH_2NHCOO^-$), 1.62 (br, 4H, $-OCH_2CH_2CH_2-$), 1.38 (br, 4H, $-OCH_2CH_2CH_2-$).

2.2. Synthesis of the PHMA films via free radical polymerization

2.2.1. P(HMA-co-BTA)

A solution of HMA (2.00 g, 11.8 mmol) and BTA (0.408 g, 0.619 mmol) in dry DMAc (2.4 mL, *ca.* 50 wt%) was degassed by bubbling with N_2 for 20 minutes. V-70 (38.1 mg, 0.124 mmol) was then added, and the solution was again bubbled with N_2 for 20 minutes. After 30 minutes stirring at 25 ± 5 °C, the solution was transferred via syringe onto a petri dish inside of a N_2 -filled separable flask, which was left for 48 hours. The reaction was quenched by exposure to air, and the obtained polymer film was washed with the mixture of dichloromethane/methanol (gradient from 3/1 to 1/3) for several times. The washed film was dried at room temperature for 12 h and then in vacuo at elevated temperatures (gradually from 40 °C to 100 °C) to afford a colorless film of P(HMA-co-BTA) (2.14 g, 86% yield, Figure S1). FT-IR (KBr, cm^{-1}): 3376, 2933, 2859, 1728, 1525, 1468, 1379, 1365, 1241, 1152, 1066, 987, 967, 912.

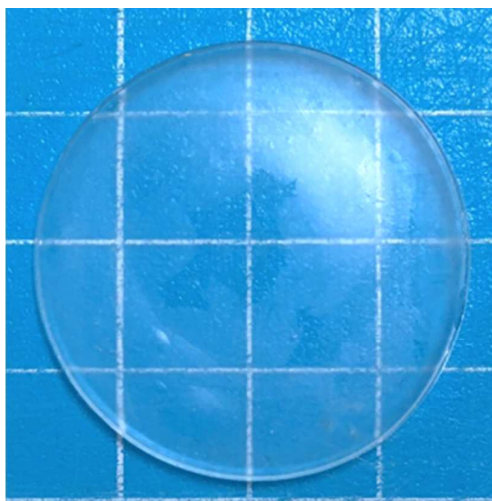


Figure S1. Photograph of the obtained network P(HMA-*co*-BTA) film.

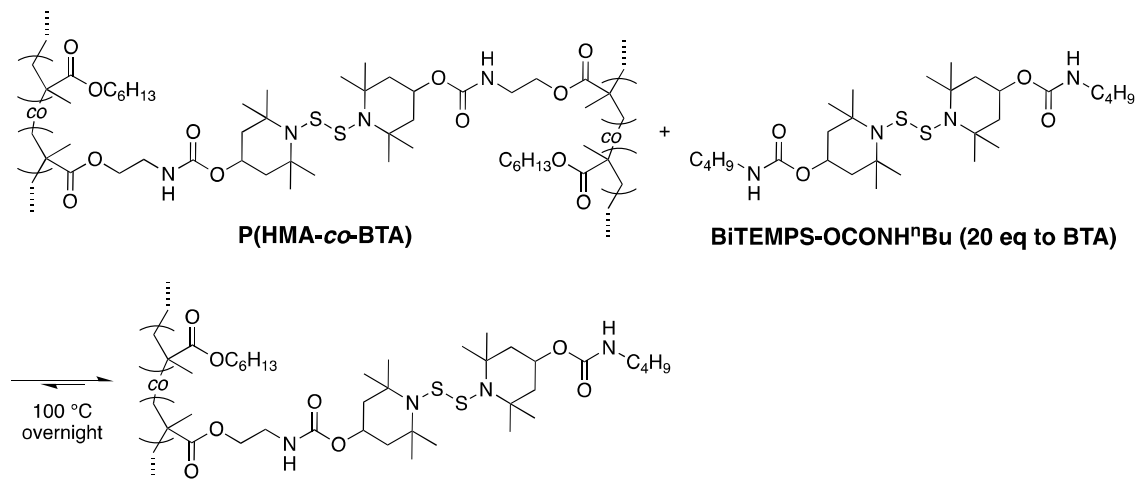
2.2.2. P(HMA-*co*-ADSA)

The sample was synthesized in a similar manner to **2.2.1** using HMA (1.80 g, 10.6 mmol) and BTA (0.243 g, 0.557 mmol), V-70 (16.3 mg, 0.0529 mmol), and dry DMAc (2.0 mL). P(HMA-*co*-ADSA) was obtained as a colorless film (1.95 g, 92%). FT-IR (KBr, cm^{-1}): 3377, 2956, 2931, 2859, 1729, 1527, 1468, 1389, 1269, 1242, 1151, 1067, 990, 970, 911, 749, 726.

2.2.3. P(HMA-*co*-HDA)

The sample was synthesized in a similar manner to **2.2.1** using HMA (1.80 g, 10.6 mmol) and BTA (0.223 g, 0.557 mmol), V-70 (16.3 mg, 0.0529 mmol), and dry DMAc (2.0 mL). P(HMA-*co*-ADSA) was obtained as a colorless film (1.84 g, 88%). FT-IR (KBr, cm^{-1}): 3569, 3399, 2956, 2931, 2859, 1729, 1542, 1525, 1509, 1468, 1389, 1270, 1242, 1151, 1067, 990, 968, 909.

3. De-cross-linking Experiment of P(HMA-co-BTA)



P(HMA-co-BTA) (49.1 mg, *ca.* 12.6 μmol of BTA) was immersed in a 2.0 mL 1,4-dioxane solution of BiTEMPS-OCONHⁿBu¹ (9.3 mg, 16 μmol) and stirred at 100 °C in air for 12 h. The resulting solution was concentrated, and the obtained polymer ($M_{\text{peak top}}$: 55 300 g/mol) was purified by reprecipitation into cold methanol for 4 times. The precipitates were collected by filtration and dried under reduced pressure (13.0 mg).

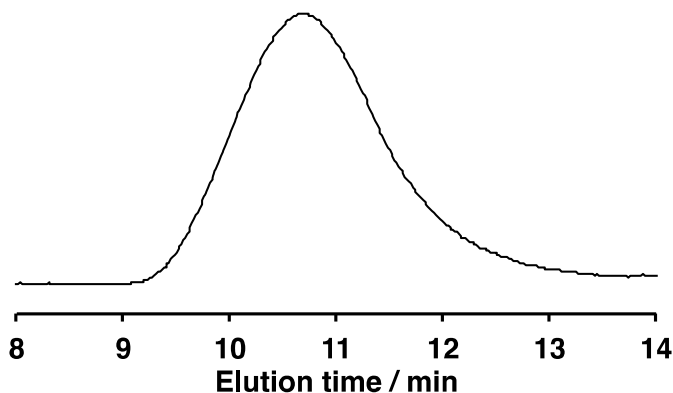


Figure S2. GPC curve of the de-cross-linked product of P(HMA-co-BTA).

The BTA content was calculated from ^1H NMR spectrum with the integral ratio of the peak n for BTA and c+k for the sum of HMA and BTA as follows:

$$\text{BTA content (mol\%)} = (\text{Peak area of n} / \text{Peak area of c+k}) \times 100$$

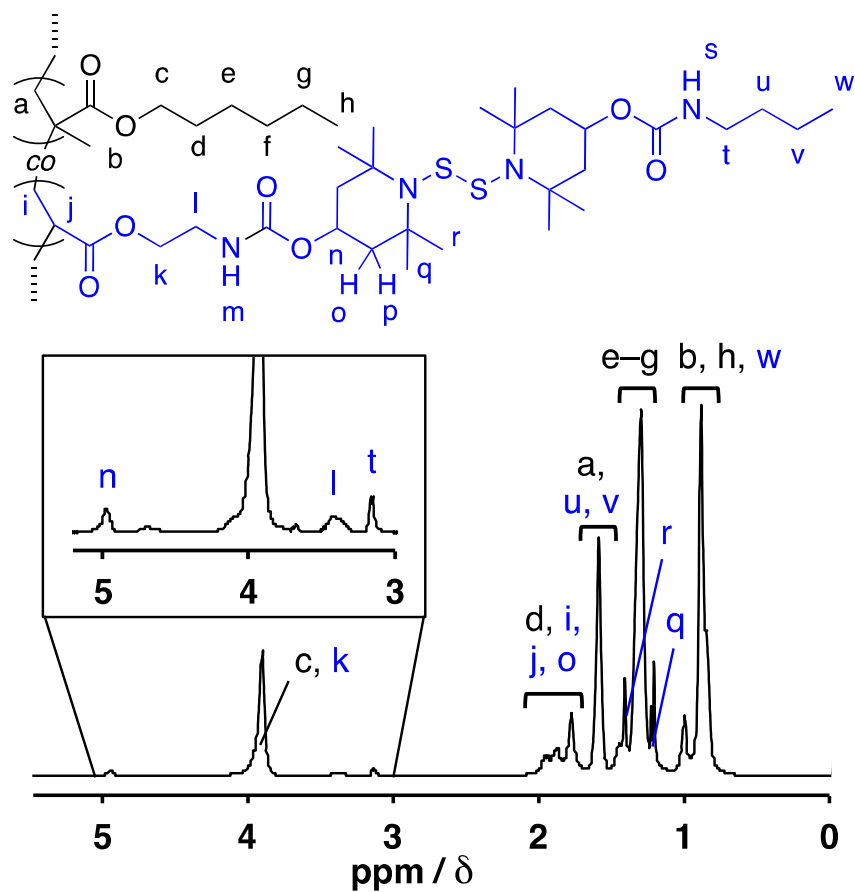


Figure S3. ^1H NMR spectrum of the de-cross-linked product of P(HMA-co-BTA).

4. Thermal Analysis Data

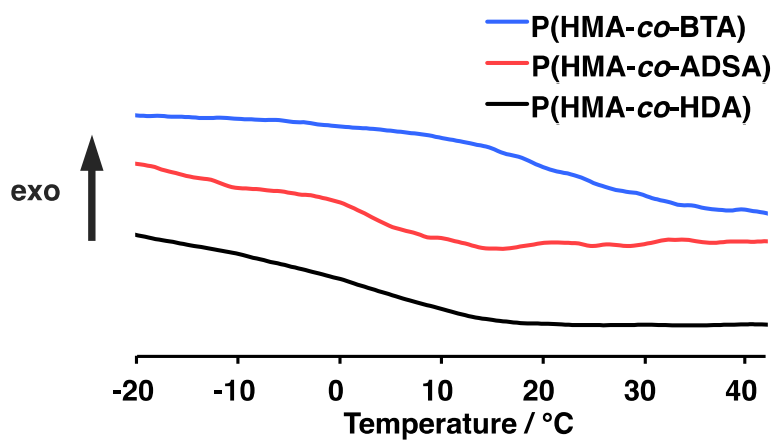


Figure S4. DSC curves of the network PHMAs (2nd heating).

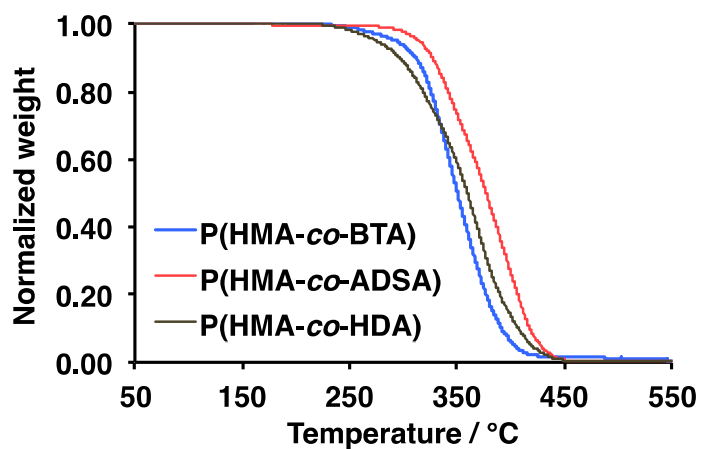


Figure S5. Thermal decomposition behavior of the network PHMAs.

Table S1. Thermal properties of the network PHMAs.

Sample	T_g (°C)	T_{ds} (°C)
P(HMA- <i>co</i> -BTA)	20	295
P(HMA- <i>co</i> -ADSA)	3	315
P(HMA- <i>co</i> -HDA)	6	275

5. Swelling Tests

In a screw-capped vial in the dark, a piece of each PHMA (approx. 3 mm x 3 mm x 0.6 mm) was immersed in 1,4-dioxane at room temperature for 5 h, and then the solution was heated at 80 °C. The ratio of weight increase was calculated by the weights of swollen gel and the original pieces. The weight of the gels was measured at out of the solution after removing excess solution from the surface. The plots were made from the average value obtained in three different measurements.

6. Tensile, Healing, and Reprocessing Tests

6.1. General procedure of tensile tests

The tests performed with ISO 37-4 specimens (12 mm × 2 mm × 1.5–2 mm) punched out from the films of the network PHMAs, which were stretched at strain rate of 100 mm/min. The measurements were performed three times for each test, and the average values with standard error were calculated.

6.2. Healing tests

The specimens were cut with a razor blade in half and the pieces were pressed together tightly at the cut surface. The specimens were set in a stainless mold, and sandwiched by two stainless plates. The plates were then pressed by a paper clip at *ca.* 70 kPa, and the whole instruments were heated at 120 °C in air over 24 h.

Table S2. Tensile data of before and after the cut-and-healed procedure

Sample	State	Stress (MPa)	Strain (%)
P(HMA- <i>co</i> -BTA)	Pristine	7.57 ± 0.82	276 ± 17
	Healed	6.47 ± 0.16 (85% of the pristine)	254 ± 10 (92% of the pristine)
P(HMA- <i>co</i> -ADSA)	Pristine	4.48 ± 0.36	321 ± 12
	Healed	1.64 ± 0.08 (37% of the pristine)	218 ± 7 (68% of the pristine)
P(HMA- <i>co</i> -HDA)	Pristine	2.48 ± 0.27	254 ± 10
	Healed	1.21 ± 0.02 (49% of the pristine)	160 ± 5 (63% of the pristine)

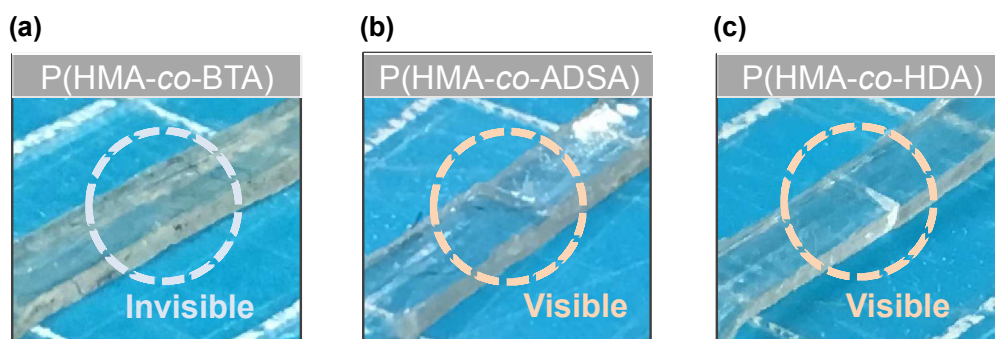


Figure S6. Photographs of the cut and hot-pressed specimen of (a) P(HMA-co-BTA), (b) P(HMA-co-ADSA), and (c) P(HMA-co-HDA).

6.3. Reprocessing test

Pieces of the film sample of the each PHMA were placed in the grinding jar, and cooled at *ca.* -20°C in a refrigerator to be vitrified. The samples were then ground with the milling machine for several minutes at 25–30 kHz. Powder of the ground samples was then transferred to the dumbbell-shaped stainless mold, and sandwiched by two stainless plates. The plates were then pressed by a paper clip at *ca.* 70 kPa, and the whole instruments were heated at 120°C in air over 48 h.



Figure S7. Photographs of (a) P(HMA-co-ADSA) and (b) P(HMA-co-HDA) after the reprocessing procedure for 48 h.

Table S3. Tensile data before and after the cut-and-healed procedure

Sample	Stress (MPa)	Strain (%)
Pristine	7.57 ± 0.82	276 ± 17
Reprocessed x1	5.99 ± 0.15 (79% of the pristine)	197 ± 8 (71% of the pristine)
Reprocessed x2	5.85 ± 0.09 (77% of the pristine)	230 ± 6 (86% of the pristine)
Reprocessed x3	5.18 ± 0.65 (68% of the pristine)	282 ± 43 (102% of the pristine)

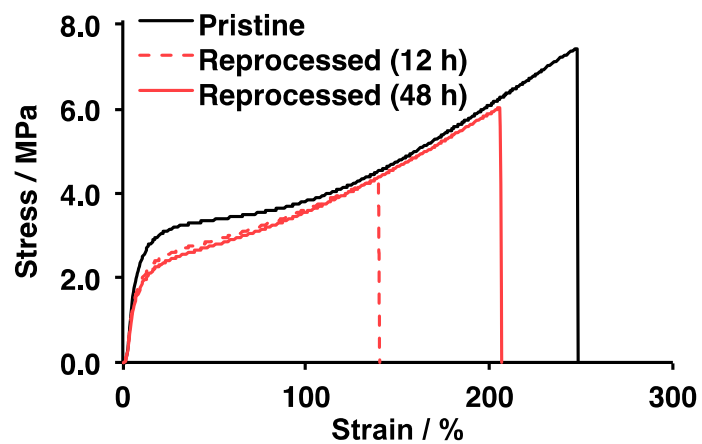


Figure S8. Stress–strain curves of the pristine and molded samples of P(HMA-*co*-BTA) at different processing hours.

7. Reference

1. Takahashi, A.; Goseki, R.; Otsuka, H. *Angew. Chem. Int. Ed.* **2017**, *56* (8), 2016–2021.