Supplementary Information (SI) for Polymer Chemistry.

Supporting information

For

Elemental sulfur utilization: Construction of a reprocessable covalent crosslinked polydisulfide with enhanced mechanical properties

Ji-Yan Chao[†], *Tian-Jun Yue*[†], *Xiao-Bing Lu*[†] *and Wei-Min Ren**[†]

[†]State Key Laboratory of Fine Chemicals, Frontiers Science Center for Smart Materials, Dalian University of Technology, 2 Linggong Road, 116024 Dalian, China.

E-mail: wmren@dlut.edu.cn

Contents

1. Materials

Phenyl glycidyl ether (> 99%), 4-hydroxybenzaldehyde (98%), 2-(bromomethyl) oxirane (> 98%), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDCI, 98%), 4-dimethylaminopyridine (> 99%), 1,8-diamino-3,6-dioxaoctane (> 98%), 1,6-hexanediamine (99%), 1, 4-cyclohexanediamine (> 97%), 4,4'-oxydianiline (98%), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, 97%) and pentaerythritol tetra(3-mercaptopropionate) (PTMP, 98%) were purchased from Beijing Innochem Technology Co. LTD and used without further purification. Elemental sulfur (S_8, 99%), potassium carbonate (K_2CO_3, 98%), sodium hydroxide (NaOH, 98%), sodium chloride (NaCl, 98%), aluminium oxide (Al_2O_3, 99%) and thiourea (98%) were purchased from Tianjin Damao Chemical Reagent Factory and used without further purification. N,N-Dimethylformamide (DMF, 99.9%, extra dry), dichloromethane (CH_2Cl_2, AR), ethyl acetate (AR), acetonitrile (CH_3CN, AR), n-hexane (AR), ethanol (EtOH, AR) and methanol (MeOH, AR) were purchased from Anhui Zesheng Technology Co. LTD and used without further purification.

2. Synthesis of episulfide monomers

2.1 Synthesis of 2-(phenoxymethyl) thiirane (POMT)

Thiourea (0.12 mol) added to a round-bottomed flask, followed by the addition of water (300 mL) and Al_2O_3 (0.01 mol) was added as catalyst. Then the phenyl glycidyl ether (0.1 mol) was added dropwise to the solution at 25 °C. Then the system was heated to 40 °C for 12 h. The progress of the reaction was monitored by thin-layer chromatography (hexane/ethyl acetate = 5:1). After the reaction was complete, the mixture was extracted three times with CH_2Cl_2, and the organic phase was retained. The solvent was removed under vacuum to obtain a colorless oily liquid 2-(phenoxymethyl) thiirane and dried with CaH_2 for twice before copolymerization. The yield was 96%.

<u>^{1}H NMR</u> (400 MHz, Chloroform-*d*) δ (ppm) 7.37 – 7.18 (m, 2H), 7.02 – 6.84 (m, 3H), 4.20 (dd, J = 10.2, 5.5 Hz, 1H), 3.91 (ddd, J = 17.3, 10.7, 6.3 Hz, 1H), 3.34 – 3.15 (m, 1H), 2.59 (d, J = 6.1 Hz, 1H), 2.31 (d, J = 5.2 Hz, 1H).

<u>^{13}C NMR</u> (101 MHz, Chloroform-*d*) δ (ppm) 159.4, 129.5, 129.3, 120.3, 114.5, 114.3, 83.7, 31.6, 23.8.

2.2 Synthesis of 4-(2-thiiranylmethoxy) benzaldehyde (BAOMT)

4-Hydroxybenzaldehyde (0.1 mol) and K_2CO_3 (0.15 mol) were added to a round-bottomed flask, followed by the addition of CH_3CN (200 mL). The mixture was stirred for 2 hours. Subsequently, 2-(bromomethyl) oxirane (0.2 mol) was added, and the mixture was heated to reflux for 12 hours. The progress of the reaction was monitored by thin-layer chromatography (hexane/ethyl acetate = 1:1). After the reaction was complete, the reaction mixture was diluted with ethyl acetate (200 mL) and washed three times with 2 mol/L NaOH and saturated NaCl solution, respectively. The progress of the extraction was monitored by thin-layer chromatography, and the organic phase was retained. The product was purified by column chromatography (hexane/ethyl acetate = 3:1), and the second product spot was collected. The solvent was removed under vacuum, and the residue was dried to obtain a white powder 4-(2-oxiranylmethoxy) benzaldehyde. The yield was 86%.

4-(2-Oxiranylmethoxy) benzaldehyde (0.1 mol) and thiourea (0.12 mol) were added to a round-bottomed flask, followed by the addition of a mixed solution of EtOH and deionized water ($EtOH/H_2O$ = 1:1, 300 mL). The mixture was stirred for 4 hours, and the progress of the reaction was monitored by thin-layer chromatography (hexane/ethyl acetate = 1:1). After the reaction was complete, the solution was diluted with water and extracted three times with ethyl acetate, with the organic phase being retained. The product was purified by column chromatography (hexane/ethyl acetate = 5:1), and the first product spot was collected. The solvent was removed under vacuum, and the residue was dried to obtain a white powder 4-(2-thiiranylmethoxy) benzaldehyde. The yield was 53%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 9.89 (s, 1H), 7.91–7.75 (m, 2H), 7.07–6.96 (m, 2H), 4.26 (dd, J = 0.2, 5.7 Hz, 1H), 4.03 (dd, J = 10.2, 6.9 Hz, 1H), 3.39–3.21 (m, 1H), 2.71–2.57 (m, 1H), 2.35 (dd, J = 5.2, 1.5 Hz, 1H).

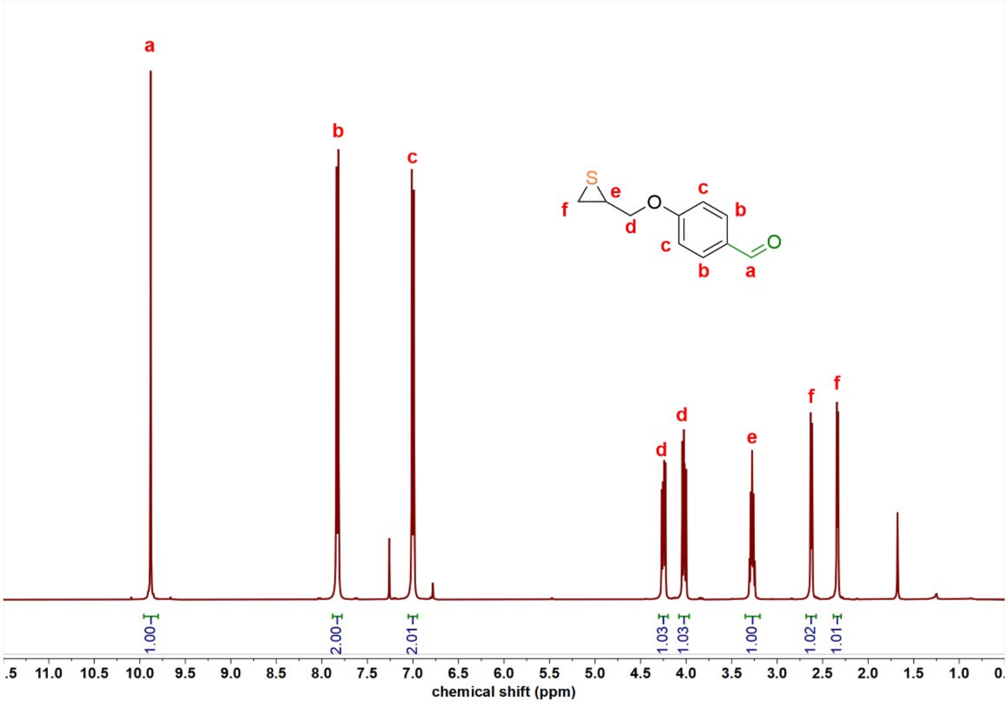


Figure S1 ^{1}H NMR spectra of BAOMT

^{13}C NMR (101 MHz, Chloroform-*d*) *δ* (ppm) 190.7, 163.3, 132.0, 130.3, 130.3, 114.8, 114.8, 114.8, 72.7, 30.9, 23.7.

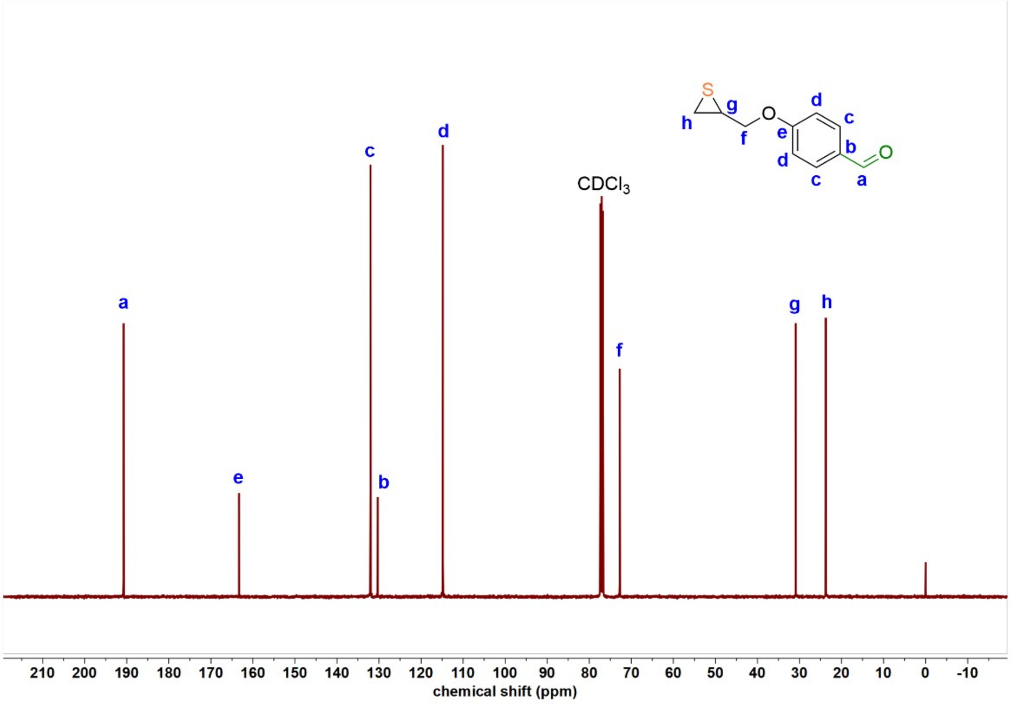


Figure S2 ^{13}C NMR spectra of BAOMT

FT-IR: The FT-IR spectrum of BAOMT is shown in Figure S3.

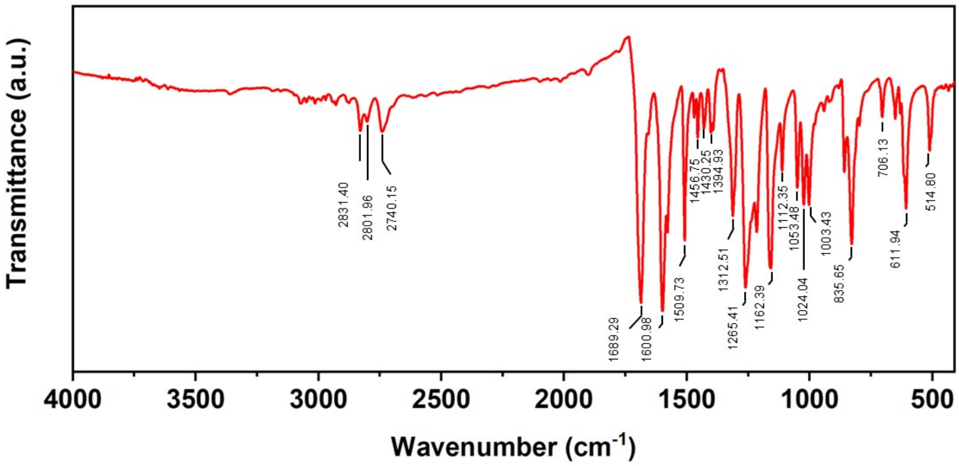


Figure S3 FT-IR spectra of BAOMT

ESI-MS *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{11}O_2S^+$ 195.05; Found 195.03.

Melting temperature: 40.3 ± 1.0 °C

Elemental analysis: $C_{10}H_{10}O_2S$. Theoretical content: C, 61.83%; H, 5.19%; O, 16.47; S, 16.50. Test content: C, 61.79%; H, 5.22%; O, 16.53; S, 16.46.

3. Synthesis of shape memory dynamic covalent network

The shape memory dynamic covalent network was prepared by a one-pot two-step method. The overall reaction route is shown in Figure 1. S_8, bis(triphenylphosphine) hexafluoroantimonate ammonium ($[PPN]SbF_6$), MTBD, PTMP and extra dry DMF were successively added to a round-bottomed flask, followed by POMT and BAOMT in a certain proportion. The mixture was stirred at 25 °C for 4 h and the color gradually faded from red to light yellow during the reaction. A small amount of stock solution was taken for molecular weight determination. Then diamine and the same volume of extra dry DMF were added to the reaction solution, and stirring was continued for another 4 hours at room temperature. The viscosity of the system gradually increased to the gel state. At this time, the maximum crosslinking density is basically reached (Figure 1). Then the solvent in the system was removed by distillation under vacuum, and 200 mL of methanol (for 3 times) was added to remove the catalyst and the unfinished monomer in the system. Finally, the product was dried to give a light-yellow powder solid.

4. Characterization

Nuclear Magnetic Resonance Spectrometer: ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 MHz type (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer and Bruker Avance NEO-600 MHz type (^{1}H, 600 MHz; ^{13}C, 125 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shift at 0 ppm for ^{1}H NMR and against the solvent, $CDCl_3$ at 77.4 ppm for ^{13}C NMR, respectively.

Gel Permeation Chromatography (GPC): Molecular weights and molecular weight distributions of copolymers were measured by GPC analysis at 30 °C and a flow rate of 1.0 mL/min, with THF as the eluent, on an Agilent 1260 instrument coupled with Agilent triple detectors (refractive index, intrinsic viscosity, and two light scattering detectors (15° and 90°, laser wavelength, $\lambda = 660$ nm)). The sample concentration was about 0.1%, and the injection volume was 100 μL.

Differential Scanning Calorimeter (DSC): The analysis of DSC was carried out with a Mettler-Toledo DSC 3 thermal analyzer. N_2 with the flow of 50 mL/min was used as protective gas, and the sample was annealed at 110 °C for 10 min and cooled to –20°C at a rate of –10 K /min, then heated to 150 °C at a rate of 10 K/min. The DSC curve shows the second heating section of thermodynamic process.

Thermo-Gravimetric Analyses (TGA): TGA of the resulted polymers were measured on a Mettler-Toledo TGA/SDTA851e. N_2 with the flow of 50 mL/min was used as protective gas and the heating rate during whole test was 10 K/min.

Plate Vulcanization Instrument: Hefei Kexing YLJ-HP300. The processing temperatures of the upper and lower plates range from 70 °C to 130 °C. The solid polymer is placed in a square mold (with a length of 4.0 ± 0.1 cm and a width of 4.0 ± 0.1 cm), and is hot-pressed at a pressure of 15.0 MPa for 10 minutes. It is then slowly cooled to room temperature to obtain a square sample.

Micro-mixing Rheometer and Micro-injection Molding Combined System: Thermo Fisher MiniLab 3 & Minijet Pro, barrel temperature 70 °C to 130 °C, mold temperature 60 °C to 120 °C, injection pressure 500 bar, maintained for 300 seconds. Mold dimensions: length 30.0 ± 0.1 mm, width 4.0 ± 0.1 mm, thickness 2.0 ± 0.1 mm.

Dynamic Thermal Mechanical Analyzer (DMA): TA Q800 dynamic thermal mechanical analyzer, using the stress relaxation mode to measure the stress relaxation characteristics of polymers, with test temperatures ranging from 25 °C to 100 °C, isothermal accuracy of 0.1 °C, and maximum deformation under static force of 5%. It also uses the stress-strain mode to measure the shape memory characteristics of polymers, with test temperatures ranging from 40 °C to 60 °C, isothermal accuracy of 0.1 °C.

Universal Tensile Testing Machine: Instron 68TM-10, with a tensile temperature of 25 °C. The prepared polymer films were cut into dumbbell-shaped strips with a standard cutter, each with a length of 14.0 ± 0.1 mm, a width of 2.0 ± 0.1 mm, and a thickness of 0.5 ± 0.1 mm. Each sample was tested 5 times in parallel, with a tensile speed of 20 mm/min, and the average value of the results was taken.

Stress-Birefringence Instrument: The stress distribution of the material is measured using the WPA-200 birefringence thin film stress distribution tester (Photonic Lattice, Japan). The measurement wavelengths are 523, 543, and 575 nm, with a measurement range of 0-3500 nm and a measurement accuracy of 1 nm. The stress distribution is represented by the phase difference σ.

5. ^{1}H NMR spectrum of S_8/BAOMT/POMT copolymers

In the ^{1}H NMR spectrum of S_8/BAOMT/POMT copolymers, ***a*** is the characteristic peak of proton in the aldehyde group of the polymer (–CHO, δ 7.81), and ***d*** and ***i*** are the characteristic peaks of proton in the methylene group connected to the oxygen atom of the polymer (–CH_2, δ 4.55–5.55). Therefore, the proportion of pBA segments in the polymer can be calculated based on the peak area ratio of the above characteristic peaks. The calculation formula is:

$$c_{\mathrm{pBA}} = \frac{A_{(7.81)}}{A_{(4.55\ -\ 5.55)}/2} \times 100\%$$

The specific ^{1}H NMR spectra of each copolymer are as follows:

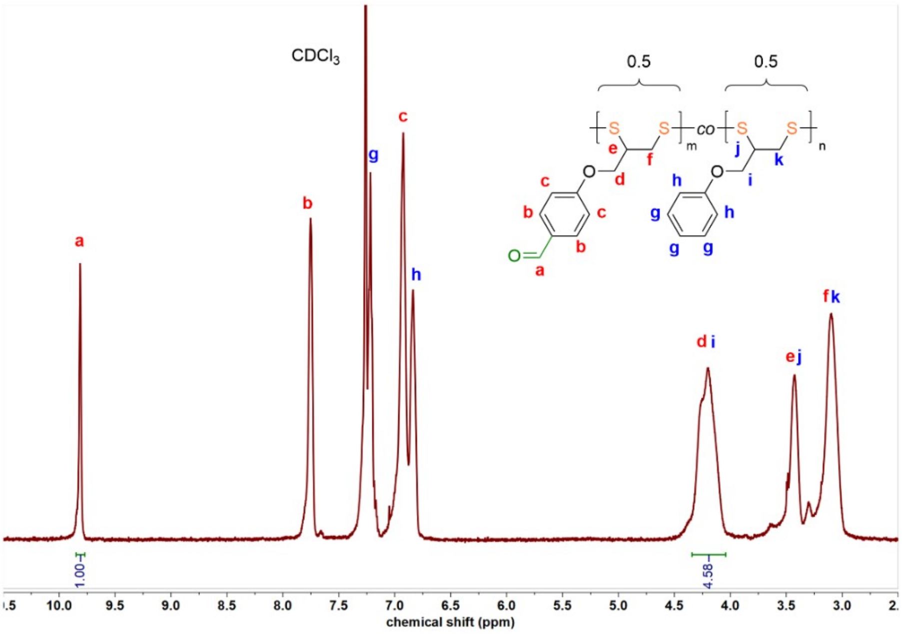


Figure S4 ^{1}H NMR spectra of $pBA_{0.5}P_{0.5}$

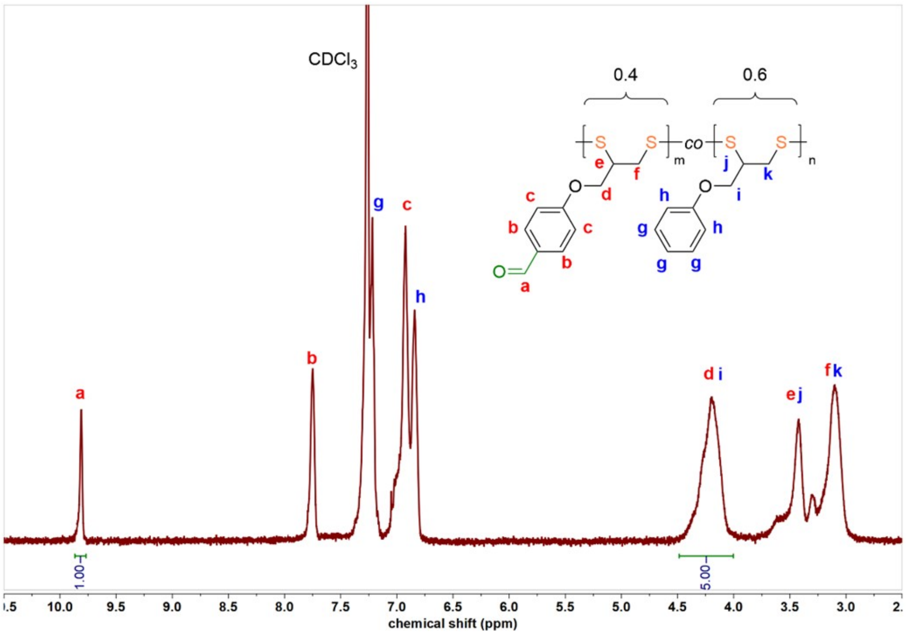


Figure S5 ^{1}H NMR spectra of pBA$_{0.4}$P$_{0.6}$

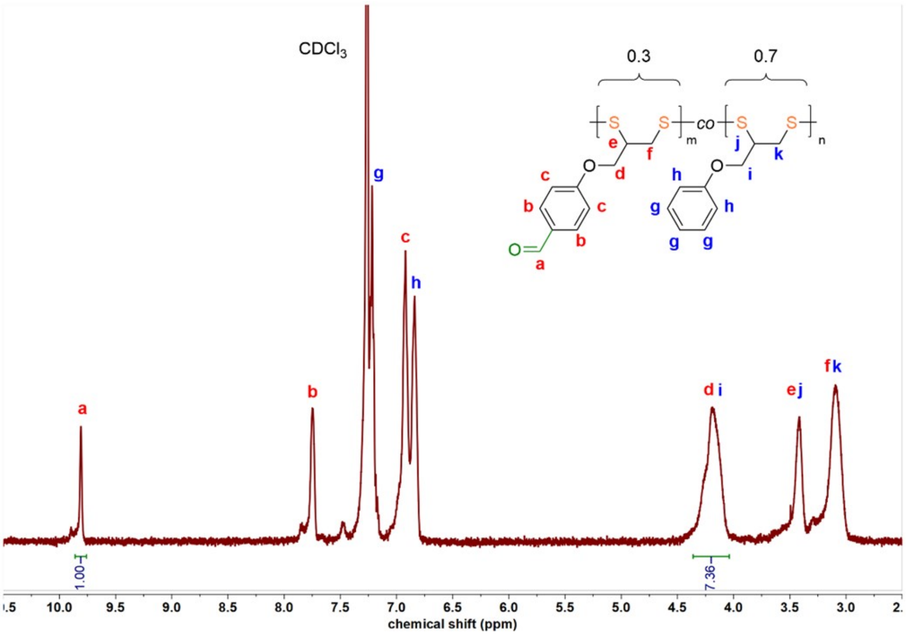


Figure S6 ^{1}H NMR spectra of pBA$_{0.3}$P$_{0.7}$

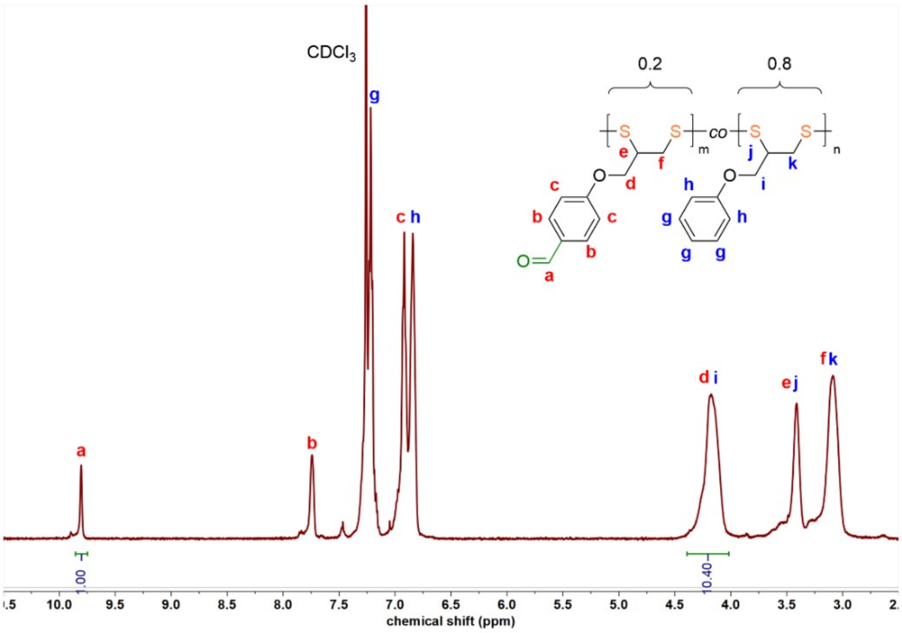


Figure S7 ^{1}H NMR spectra of $pBA_{0.2}P_{0.8}$

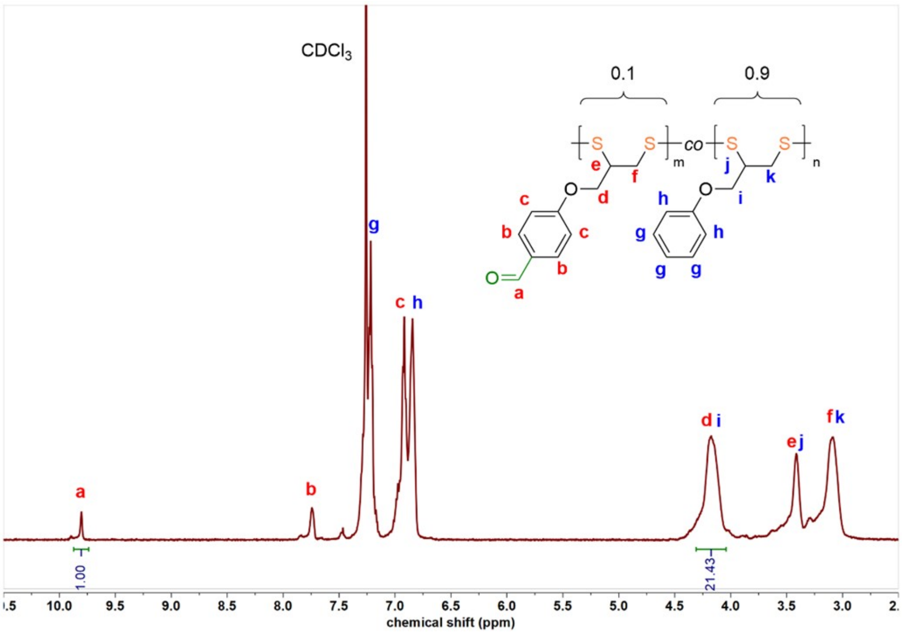
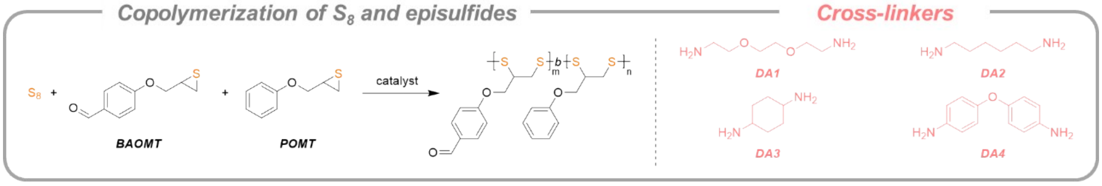


Figure S8 ^{1}H NMR spectra of $pBA_{0.1}P_{0.9}$

6. Outcomes of the synthesis of dynamic covalent network

Table S1 Outcomes of the synthesis of dynamic covalent network



entry[a]	Sample	Molar ratio [BAOMT/POMT]	Diamine	M_{n1} [b] [kg/mol]	$Đ_1$ [b]	T_{g1} [c] [°C]	T_{d1} [c] [°C]	T_{g2} [d] [°C]	T_{d2} [d] [°C]
1	PBA$_{1.0}$	10/0	-	77.1	1.31	23.6	264.4	-	-
2	PP$_{1.0}$	0/10	-	58.6	1.08	33.4	263.5	-	-
3	PBA$_{0.1}$P$_{0.9}$-DA1	1/9	DA1	77.9	1.47	15.7	202.5	17.8	217.5
4	PBA$_{0.2}$P$_{0.8}$-DA1	2/8	DA1	70.8	1.31	20.4	204.0	22.0	191.7
5	PBA$_{0.3}$P$_{0.7}$-DA1	3/7	DA1	73.9	1.76	28.2	225.2	29.5	181.7
6	PBA$_{0.1}$P$_{0.9}$-DA2	1/9	DA2	77.9	1.47	15.7	202.5	19.1	213.2
7	PBA$_{0.2}$P$_{0.8}$-DA2	2/8	DA2	70.8	1.31	20.4	204.0	21.1	192.3
8	PBA$_{0.3}$P$_{0.7}$-DA2	3/7	DA2	73.9	1.76	28.2	225.2	33.9	180.7
9	PBA$_{0.1}$P$_{0.9}$-DA3	1/9	DA3	77.9	1.47	15.7	202.5	26.3	221.5
10	PBA$_{0.2}$P$_{0.8}$-DA3	2/8	DA3	70.8	1.31	20.4	204.0	31.6	219.5
11	PBA$_{0.3}$P$_{0.7}$-DA3	3/7	DA3	73.9	1.76	28.2	225.2	40.8	202.7
12	PBA$_{0.1}$P$_{0.9}$-DA4	1/9	DA4	77.9	1.47	15.7	202.5	25.2	203.7
13	PBA$_{0.2}$P$_{0.8}$-DA4	2/8	DA4	70.8	1.31	20.4	204.0	32.9	193.2
14	PBA$_{0.3}$P$_{0.7}$-DA4	3/7	DA4	73.9	1.76	28.2	225.2	36.4	145.0

[a] Reactions were performed with the molar ratio of [S_8/episulfides/PTMP/[PPN]SbF_6] = 50/400/1/1 in the presence of extra dry DMSO (V_{DMF}:$V_{episulfide}$ = 1:1) under 25 °C. The molar ratio of [BAOMT/diamine] was 1:1.2 during the crosslinking reaction. [b] Determined as absolute molecular weight by gel permeation chromatography with triple detectors (refractive index, intrinsic viscosity, and two light scattering detectors (15° and 90°, laser wavelength = 660 nm)). [c] Before crosslinking reaction. [d] After crosslinking reaction.

7. FT-IR spectra of covalent polydisulfide network before and after crosslinking

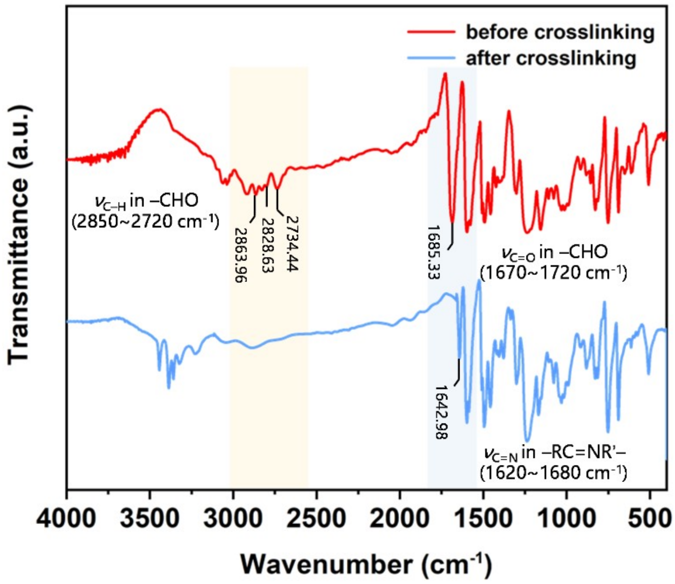


Figure S9 FT-IR spectra of covalent polydisulfide network before and after crosslinking

8. DSC curves of the polymers before and after crosslinking

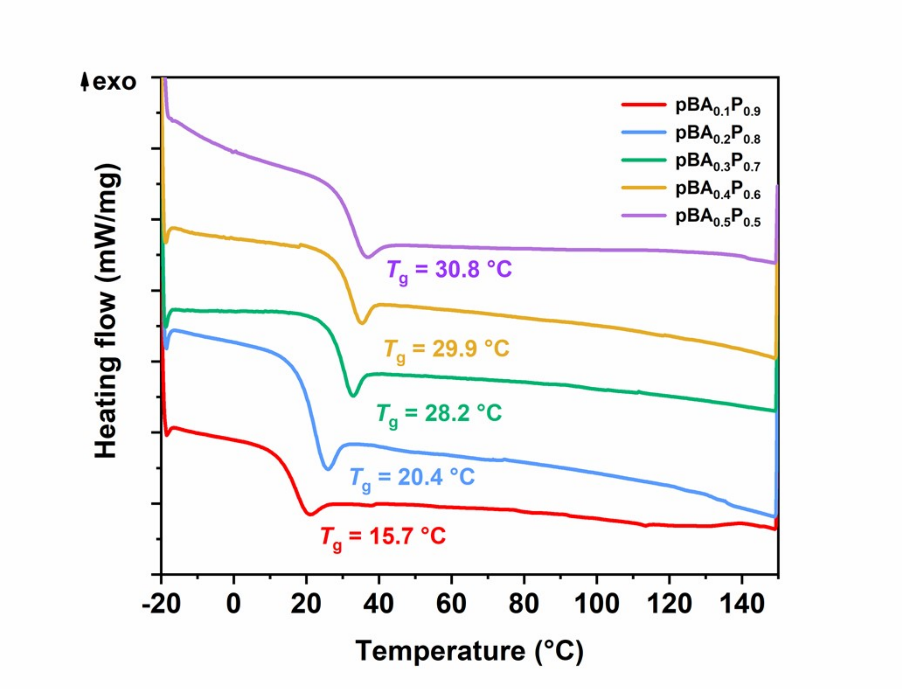


Figure S10 DSC curves of $PBA_{0.1}P_{0.9}$, $PBA_{0.2}P_{0.8}$, $PBA_{0.3}P_{0.7}$, $PBA_{0.4}P_{0.6}$ and $PBA_{0.5}P_{0.5}$ before crosslinking

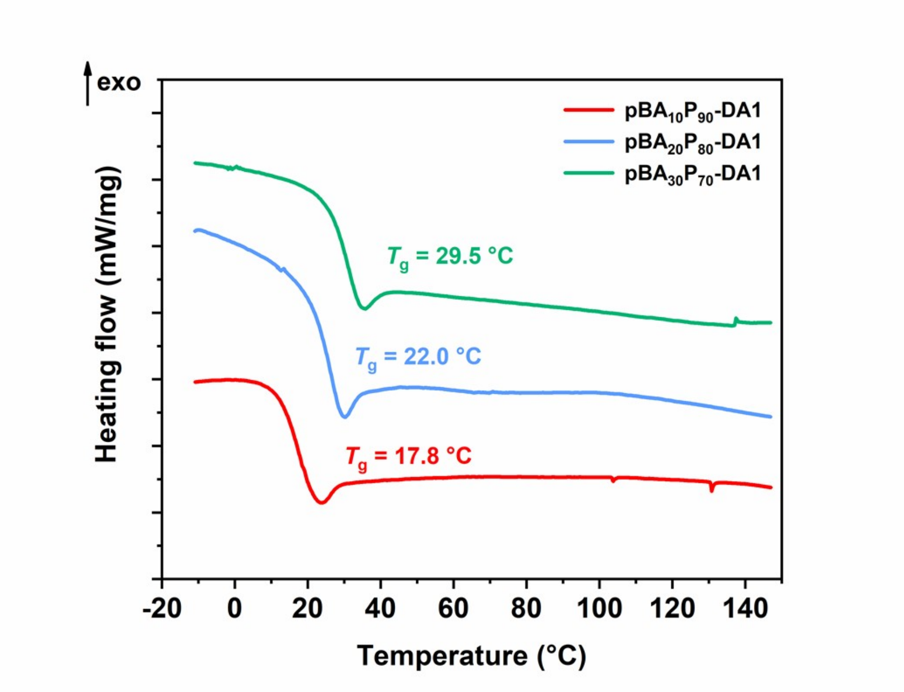


Figure S11 DSC curves of $PBA_{0.1}P_{0.9}$-DA1, $PBA_{0.2}P_{0.8}$-DA1 and $PBA_{0.3}P_{0.7}$-DA1

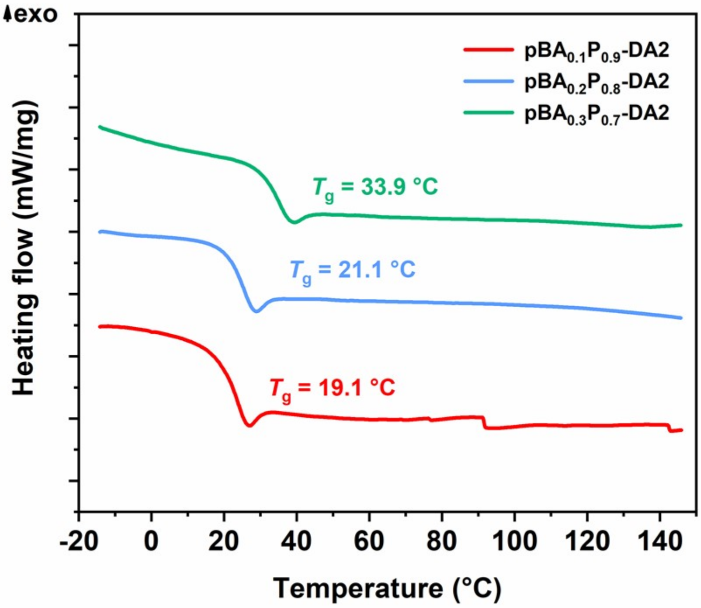


Figure S12 DSC curves of $PBA_{0.1}P_{0.9}$-DA2, $PBA_{0.2}P_{0.8}$-DA2 and $PBA_{0.3}P_{0.7}$-DA2

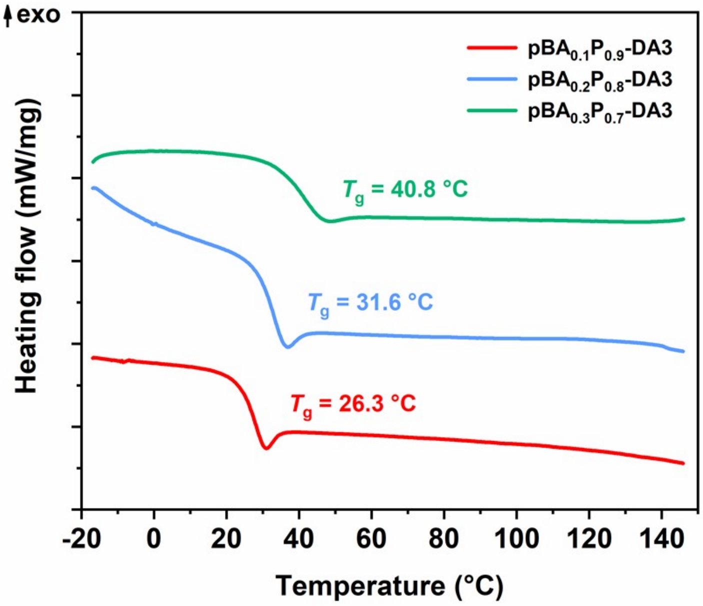


Figure S13 DSC curves of $PBA_{0.1}P_{0.9}$-DA3, $PBA_{0.2}P_{0.8}$-DA3 and $PBA_{0.3}P_{0.7}$-DA3

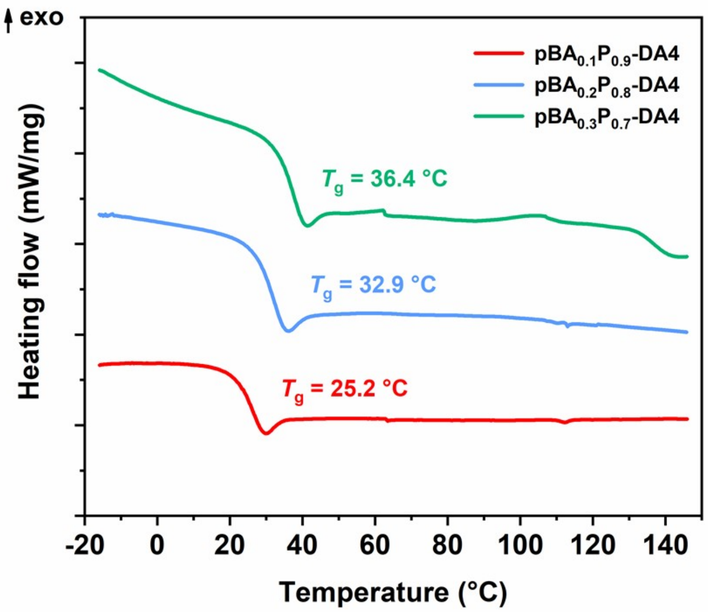


Figure S14 DSC curves of PBA$_{0.1}$P$_{0.9}$-DA4, PBA$_{0.2}$P$_{0.8}$-DA4 and PBA$_{0.3}$P$_{0.7}$-DA4

9. The tensile curves of PBA$_{0.1}$P$_{0.9}$-DA1, PBA$_{0.2}$P$_{0.8}$-DA1 and PBA$_{0.3}$P$_{0.7}$-DA1by reprocessing

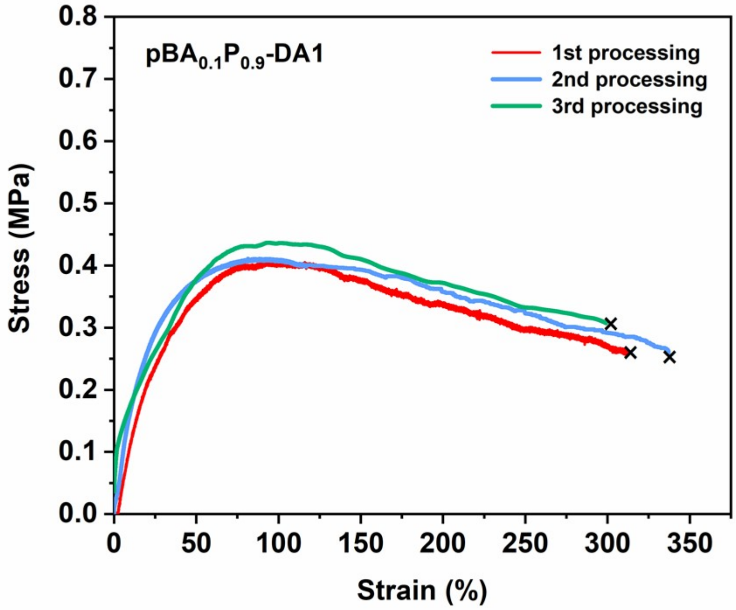


Figure S15 The tensile curves of PBA$_{0.1}$P$_{0.9}$-DA1 by reprocessing

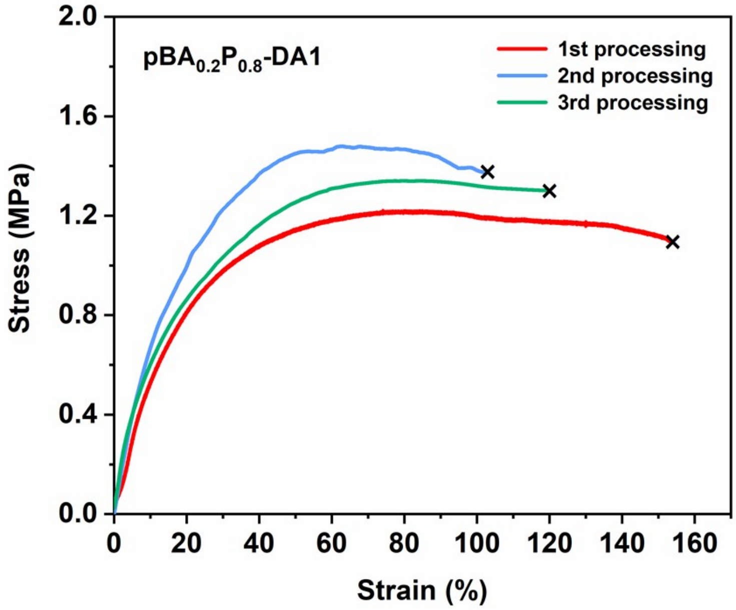


Figure S16 The tensile curves of PBA$_{0.2}$P$_{0.8}$-DA1 by reprocessing

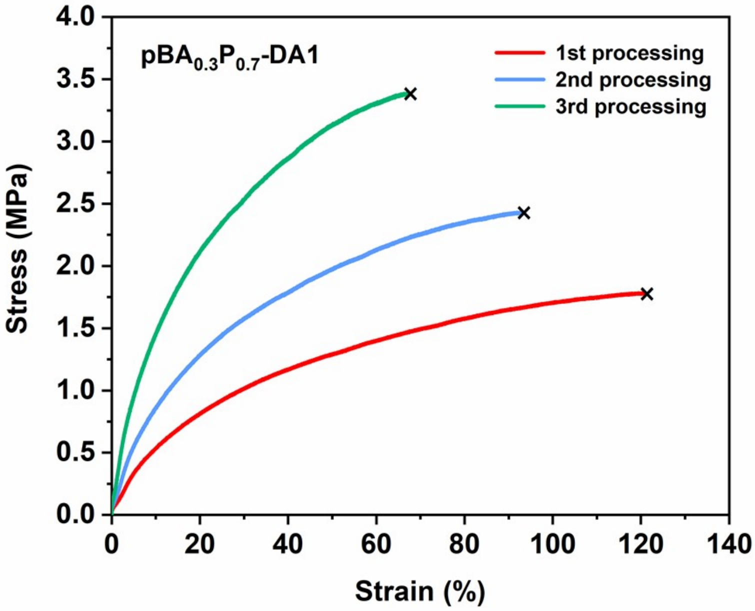


Figure S17 The tensile curves of PBA$_{0.3}$P$_{0.7}$-DA1 by reprocessing

10. The stress relaxation curves of PBA$_{0.2}$P$_{0.8}$-DA1 and PBA$_{0.3}$P$_{0.7}$-DA1 under different temperature

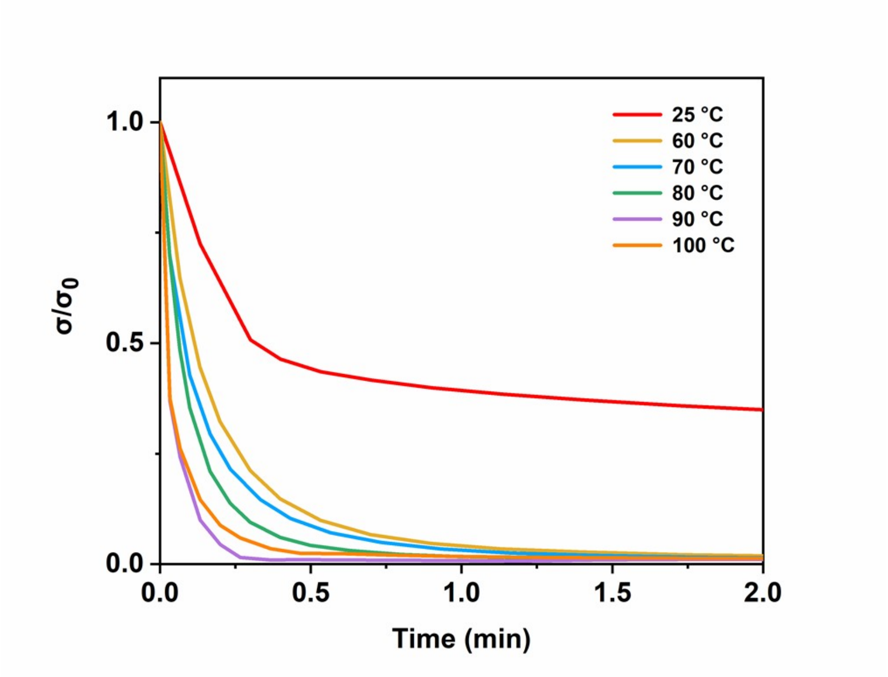


Figure S18 The stress relaxation curves of PBA$_{0.2}$P$_{0.8}$-DA1 under different temperature.

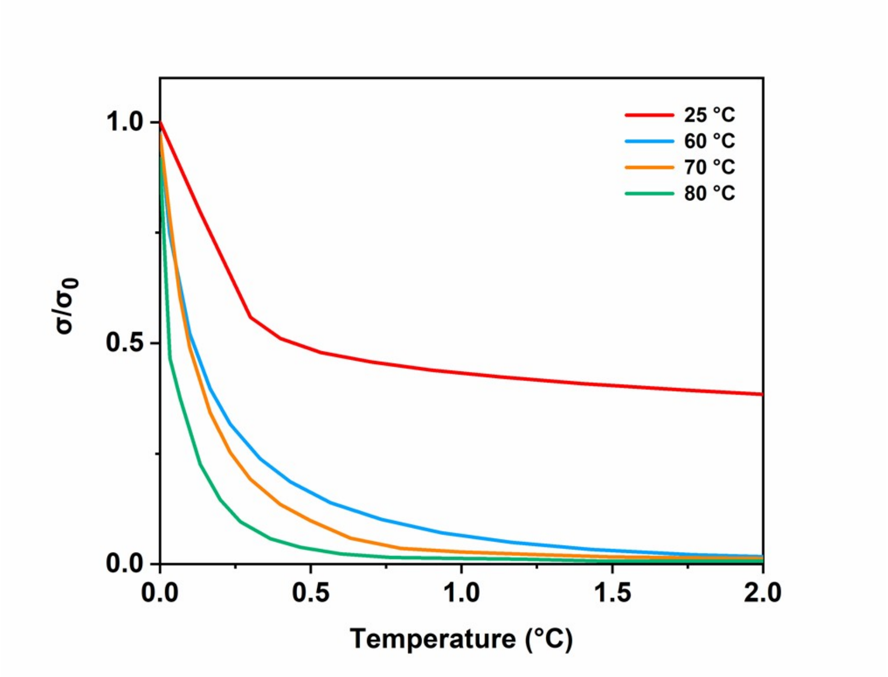


Figure S19 The stress relaxation curves of PBA$_{0.3}$P$_{0.7}$-DA1 under different temperature.

11. The stress relaxation curves of polymers under 60 °C, 70 °C, 80 °C and Arrhenius model

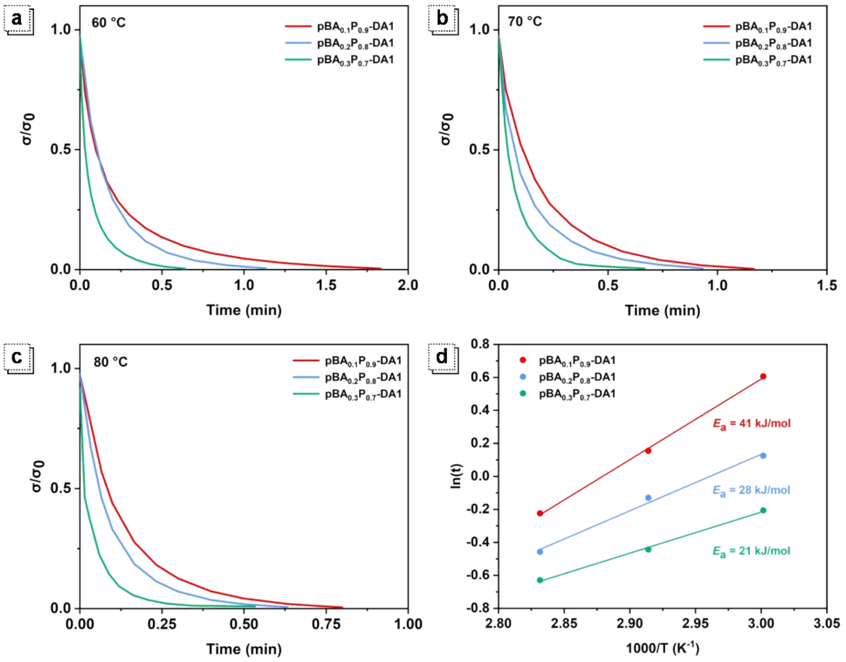


Figure S20 The stress relaxation curves of polymers under 60 °C, 70 °C, 80 °C and Arrhenius model

12. The elastic shape memory cycle of PBA$_{0.2}$P$_{0.8}$-DA1

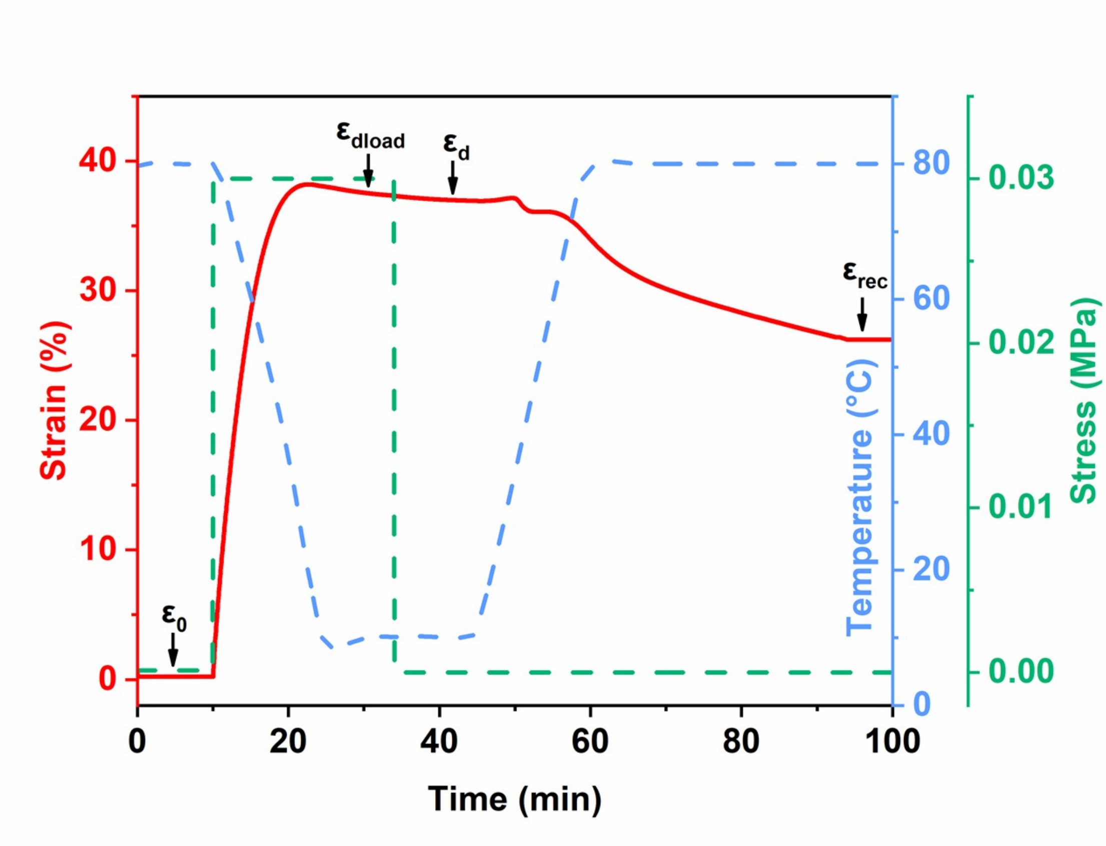


Figure S21 The elastic shape memory cycle of PBA$_{0.2}$P$_{0.8}$-DA1. $R_f=\varepsilon_d/\varepsilon_{dload}\times100\%$ and $R_r=(\varepsilon_d-\varepsilon_{rec})/\ \varepsilon_d$, with ε_0, ε_{dload}, ε_d, and ε_{rec} being the original strain, the maximum strain under load, the fixed strain, and the recovered strain, respectively.