

Supporting Information

Closed-loop chemically recyclable covalent adaptive networks derived from elementary sulfur

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General Information

Materials

All the chemicals and reagents, including Elemental Sulfur (S₈, 99.5%), (±)-α-thioctic acid (TA, 99%), tert-Butylimino-tri(pyrrilidino)phosphorane (tBu-P₁, 98%), Benzyl Mercaptan (BnSH, 98%), 4-Dimethylaminopyridine (DMAP, 99%), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI, > 97%), Didodecyldimethylammonium Bromide (DDAB, 98%), N, N'-disuccinimidyl carbonate (> 98%), Methyl Alcohol (99.9%), 1,4-Butanediol (> 99%), Pentaerythritol, Hydrazine hydrate (80% aqueous solutions), Propylamine (> 99%), 1,4-Dibromopentane (98%), 1,5-Dibromopentane (99%), were purchased from TCI, Adamas@beta and Sigma-Aldrich, and used without any further purification

Equipment and measurements

Nuclear magnetic resonance (NMR) spectrum was tested by Brüker AV-400 spectrometer using tetramethylsilane to be the internal standard. Gel Permeation Chromatography (GPC) (Waters Corporation; Waters1515) and Matrix-Assisted Laser Desorption/ Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) (Singapore ABS Corporation; 400 ~ 500000Da/4800plus) were used to determine the polymer molecular weight distribution. Raman spectra were recorded by using a Laser Micro-Raman Spectrometer (Renishaw, IO.2/cm/invia reflex) equipped with a high-performance grade Leica DMLM microscope and a 514 nm excitation wavelength. X-ray diffraction (XRD) patterns were obtained on a rotating anode X-ray powder diffractometer (18KW/D/max2550VB/PC) equipped with a copper target 18KW (450mA), a fully automated curved (plate) crystal graphite monochromator and a programmed variable slit system. Field emission scanning electron microscopy (FE-SEM) (Hitachi, S-4800, 15 kV) was used to detect the surface morphology and elements imaging of the copolymer samples. The thermal stability was measured by thermogravimetric analysis

(Mettler Toledo TGA/SDTA851, heating rate = $5^{\circ}\text{C min}^{-1}$). The thermal properties were measured by differential scanning calorimetry (TA instruments; modulated DSC2910, 1090B). The NIR transmittance spectra data were recorded by a Shimadzu UV-3600 UV-vis spectrophotometer. Attenuated Total Reflectance Infrared (ATR-IR) Spectroscopy was performed on a ThermoFisher instruments Nicolet iS50R FT-IR Spectrometer. Tensile tests of copolymers were measured by an Instron 34TM-5 universal testing system equipped with a 100 N sensor. The rheological experiments were performed by rotational rheometer (TA Instruments-Waters LLC; DHR-2).

Reprocessing procedure

The reprocessing of polysulfide CANs was conducted on the hot-press machine (Xin Nuo Instrument Co., Ltd., China; RYJ-600D1). The polymer samples were cut into pieces and hot pressed at $80\text{-}160^{\circ}\text{C}$ for 10 min under constant pressure of 2, 5, 10 MPa, respectively, to obtain smooth polymer films with different thickness for further measurements.

Methods for mechanical tensile tests

All stress-strain tests were performed on an Instron 34TM-5 universal testing system equipped with a 100 N sensor. The rectangular test samples ($30 \times 10 \times 0.5$ mm) were fixed on the jigs of the tension machine, with the initial length (10 mm) considered as the gap between the two edges of the jigs. The tensile stress was measured at a constant speed of 20 mm min^{-1} . Each group of samples was tested in parallel for at least three times. The data were recorded in real time by a connected computer.

Methods for rheological tests

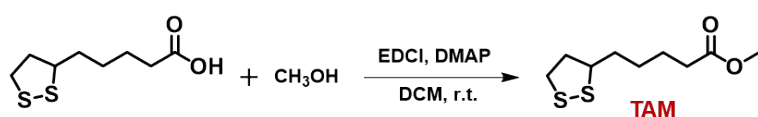
Rounded polymer samples were placed between a 20-mm-diameter parallel plate and a temperature-controlled plate with a gap of 0.5-1.0 mm. Temperature-dependent tests were

conducted in a range from -10°C to 150°C (5 °C/min) at a constant frequency of 1 Hz with an applied strain of 0.1%. Frequency sweep tests were conducted ranging from 100 Hz-0.01 Hz with an applied strain of 0.1% at specified temperature (-10°C~150°C). Stress relaxation tests were conducted under a constant prestrain of 1% at specified temperature (50°C~70°C).

IR transmissive applications

Poly(DTA₁-S₄) films (Thickness > 0.5 mm for meaningful IR transmission measurements) were fixed in front of the lens of the NIR camera and LWIR thermal camera as the optical window. The NIR camera was used to capture images under the illumination of a 980 nm laser. The wavelength of the LWIR thermal camera detector ranges from 7.5 μm to 13 μm.

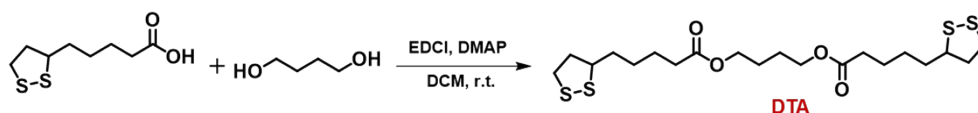
Synthetic procedures



Scheme S1. The synthesis routes to compound TAM.

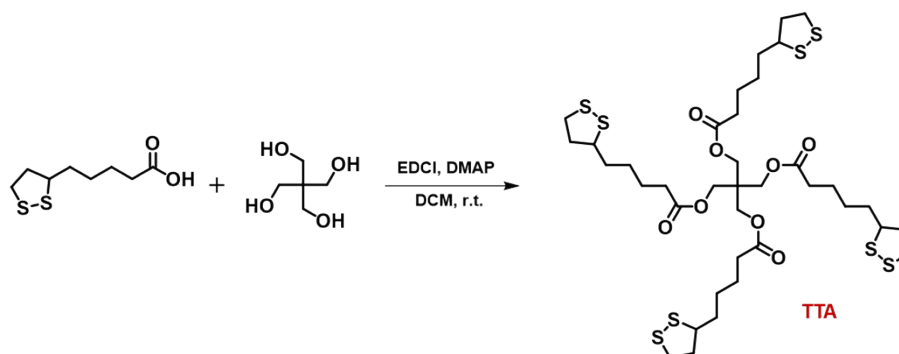
In a 500 mL round-bottom flask, thioctic acid (10.0 g, 48.6 mmol, 1.0 eq.) was dissolved in DCM (150 mL) to obtain yellow transparent solution. DMAP (6.0 g, 48.6 mmol, 1.0 eq.), EDCI (11.2 g, 60.4 mmol, 1.2 eq.) and methanol (19.6 mL, 486 mmol, 10.0 eq.) were added successively in the above solution under stirring. After stirred at room temperature for 5 h, the reaction mixture was washed by 1 M HCl aq. solution, deionized water, saturated NaHCO₃ aq. solution, and brine for three time, respectively. The extracted organic phase was dried over with Na₂SO₄, evaporated under vacuum, and purified by column chromatography to obtain yellow viscous compound TAM (9.6 g, 90% yield). ¹H NMR (400 MHz, CDCl₃) δ

(ppm):3.70-3.61 (m, 1H), 3.61-3.49 (m, 0H), 3.23-3.02 (m, 1H), 2.44 (td, J = 12.4, 6.5 Hz, 0H), 2.35-2.25 (m, 1H), 1.96-1.82 (m, 0H), 1.73-1.59 (m, 1H), 1.54-1.35 (m, 1H).



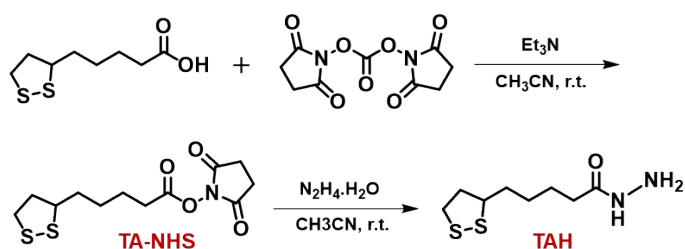
Scheme S2. The synthesis routes to compound DTA

In a 500 mL round-bottom flask, thioctic acid (7.2 g, 35.0 mmol, 1.0 eq.) was dissolved in DCM (150 mL) to obtain yellow transparent solution. DMAP (4.3 g, 35.0 mmol, 1.0 eq.), EDCI (8.0 g, 42.0 mmol, 1.2 eq.) and 1,4-butanediol (1.3 g, 14.6 mmol, 0.42 eq.) were added successively in the above solution under stirring. After stirred at room temperature for 5 h, the reaction mixture was washed by 1 M HCl aq. solution, deionized water, saturated NaHCO₃ aq. solution, and brine for three time, respectively. The extracted organic phase was dried over with Na₂SO₄, evaporated under vacuum, and purified by column chromatography to obtain yellow viscous compound DTA (5.8 g, 85% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm):4.12-4.00 (m, 1H), 3.55 (dq, J = 12.8, 6.4 Hz, 0H), 3.21-3.03 (m, 1H), 2.45 (td, J = 12.4, 6.5 Hz, 1H), 2.34-2.22 (m, 1H), 1.97-1.79 (m, 1H), 1.77-1.56 (m, 3H), 1.55-1.35 (m, 1H).



Scheme S3. The synthesis routes to compound TTA

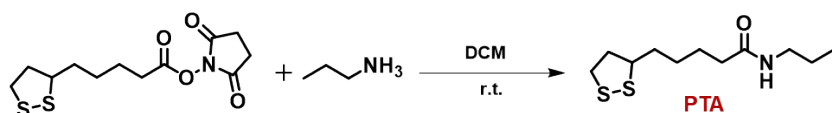
In a 500 mL round-bottom flask, thioctic acid (10.8 g, 52.5 mmol, 1.0 eq.) was dissolved in DCM (250 mL) to obtain yellow transparent solution. DMAP (6.4 g, 52.5 mmol, 1.0 eq.), EDCI (12.0 g, 63.0 mmol, 1.2 eq.) and pentaerythritol (1.5 g, 11.0 mmol, 0.21 eq.) were added successively in the above solution under stirring. After stirred at room temperature for 5 h, the reaction mixture was washed by 1 M HCl aq. solution, deionized water, saturated NaHCO₃ aq. solution, and brine for three time, respectively. The extracted organic phase was dried over with Na₂SO₄, evaporated under vacuum, and purified by column chromatography to obtain yellow viscous compound TTA (7.8 g, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.10 (d, J = 8.9, 1H), 3.57 (dq, J = 12.7, 6.4, 1H), 3.25-3.06 (m, 1H), 2.47 (td, J = 12.4, 6.5, 1H), 2.34 (t, J = 7.4, 1H), 1.91 (dq, J = 13.7, 6.9, 1H), 1.78-1.57 (m, 2H), 1.54-1.35 (m, 1H).



Scheme S4. The synthesis routes to compound TAH

In a 500 mL round-bottom flask, thioctic acid (10.0 g, 48.6 mmol, 1.0 eq.) and N, N'-disuccinimidyl carbonate (15.0 g, 58.3 mmol, 1.2 eq.) were dissolved in CH₃CN (300 mL) to obtain yellow homogeneous solution. After the addition of Et₃N (20.3 mL, 145.8 mmol, 3.0 eq.), the mixture was stirred at room temperature for 5 h. The reaction solution was concentrated under vacuum and then dropwise added into 5% NaHCO₃ aq. solution (600 mL) under stirring to precipitate TA-NHS as pale yellow powder. TA-NHS was separated by

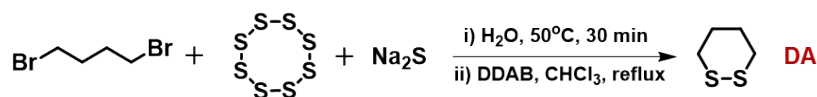
filtration, washed by water, and then dissolved in CH₃CN (300 mL). 80% hydrazine monohydroxide (13.0 eq., 32.4 mL) was dropwise added into the above solution, and the mixture was stirred at room temperature for 5 h. The reaction mixture was filtered and concentrated under vacuum. The concentrated solution was diluted with DCM (300 mL) and washed by 5% NaHCO₃ aq. solution for three times. The extracted organic phase was dried over with Na₂SO₄, and evaporated under vacuum to obtain compound TAH as yellow solid (8.6 g, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 6.75 (s, 0H), 3.90 (s, 1H), 3.56 (dq, J = 12.7, 6.4, 0H), 3.24-3.01 (m, 1H), 2.46 (dt, J = 12.2, 6.6, 0H), 2.24-2.05 (m, 1H), 1.90 (tt, J = 13.1, 6.6, 1H), 1.79-1.56 (m, 2H), 1.57-1.34 (m, 1H).



Scheme S5. The synthesis routes to compound PTA.

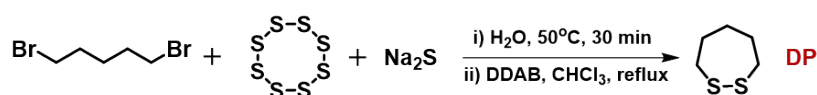
In a 500 mL round-bottom flask, TA-NHS (10.0 g, 33.0 mmol, 1.0 eq.) was dissolved in DCM (200 mL). 4.1 mL Propylamine (2.9 g, 49.4 mmol, 1.5 eq.) was dropwise added into the above solution, and the mixture was stirred at room temperature for 5 h. The reaction mixture was washed by brine (80 mL × 3), dried over with Na₂SO₄, and evaporated under vacuum to obtain yellow viscous compound PTA (6.5 g, 80% yield).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 5.42 (s, 1H), 3.50 (dq, J = 12.9, 6.4, 1H), 3.20-2.95 (m, 4H), 2.39 (td, J = 12.5, 6.5, 1H), 2.17-2.01 (m, 3H), 1.93-1.77 (m, 1H), 1.73-1.53 (m, 4H), 1.52-1.29 (m, 4H), 0.87 (dt, J = 14.8, 7.4, 3H).



Scheme S6. The synthesis routes to compound DA

In a 500 mL round-bottom flask, sulfur (6.7 g, 30.0 mmol, 1.0 eq.) and Na₂S (2.3 g, 30.0 mmol, 1.0 eq.) were added into H₂O (75 mL). The mixture was stirred at 50°C for 30 min, and then cooled down. Catalytic amount of DDAB and 150 mL CHCl₃ solution of 1,4-dibromobutane (3.2 g, 15.0 mmol, 0.5 eq.) were added in the above solution, and the mixture was stirred under reflux (30°C) for 4 h. The product was extracted by ether (50 mL × 2), and the combined organic phase was washed by water, dried over with Na₂SO₄, and evaporated under vacuum to obtain colorless liquid. The crude product was purified by chromatography on a short silica gel column (PE), and recrystallized from ethanol to obtain the compound DA (1.3 g, 72%yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.85 (s, 1H), 1.97 (s, 1H).



Scheme S7. The synthesis routes to compound DP

In a 500 mL round-bottom flask, sulfur (6.7 g, 30.0 mmol, 1.0 eq.) and Na₂S (2.3 g, 30.0 mmol, 1.0 eq.) were added into H₂O (75 mL). The mixture was stirred at 50°C for 30 min, and then cooled down. Catalytic amount of DDAB and 150 mL CHCl₃ solution of 1,5-dibromopentane (3.4 g, 15.0 mmol, 0.5 eq.) were added in the above solution, and the mixture was stirred under reflux (30°C) for 4 h. The product was extracted by ether (50 mL × 2), and the combined organic phase was washed by water, dried over with Na₂SO₄, and evaporated

under vacuum to obtain colorless liquid. The crude product was purified by chromatography on a short silica gel column (PE), and recrystallized from ethanol to obtain the compound DP (1.5 g, 75%yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 2.88 -2.77 (m, 2H), 2.09-1.97 (m, 2H), 1.82-1.72 (m, 1H).

Polymerization procedure

General polymerization conditions: The molar ratio [Disulfides]: [S]: [Initiator]: [Quencher] = 100: 100~400: 1: 10 / CHCl₃ / r.t. / N₂ / [Disulfides] = 1.8 M.

Typical procedure for linear polysulfide copolymers:

For poly(TAM₁-S₂), 500 mg TAM (2.27 mmol, 100 eq.) dissolved in 1.26 mL CHCl₃ ([TAM]₀ = 1.8 M) and 145 mg S₈ (0.57 mmol, 25 eq.) were added in a 10-mL reaction vial equipped with a screw cap, a PTFE/silicon septum, and a small-sized magnetic stir bar. The resulting sealed vial was vacuumized and backfilled with nitrogen three times to provide oxygen-free environment. Then initiator mixture (0.023 mmol, 1 eq.) consisting of 1.66 μL BnSH and 5.78 μL ^tBu-P₁ diluted with 100 μL CHCl₃ was deoxidized and immediately injected into the above sealed vial under stirring to initiate the polymerization reaction. The mixture turned red rapidly and S₈ powder gradually dissolved. The reaction continued at room temperature for 8 h until quenched by 17.6 μL TFA (0.23 mmol, 10 eq.). 20 μL quenched reaction mixture was withdrawn and dissolved in 600 μL CDCl₃ directly for ¹H NMR analysis. The resulting reaction mixture was diluted in a small amount of CHCl₃ and then precipitated into 100 mL cyclohexane for three times and dried under high vacuum to obtain pure poly(TAM₁-S₂) as buff gum for further characterization.

When [Disulfides]: [S] < 1: 2, the resulting reaction mixture containing excess unreacted S₈ powder was firstly diluted with acetone and then filtrated to remove insoluble S₈ solid. The filtrate was further purified according to the above steps.

Typical procedure for crosslinked polysulfide CANs:

For poly(DTA₁-S₄), the reaction mixture containing DTA (100 eq.), S₈ (50 eq.) and initiator (2 eq.) was stirred in CHCl₃ to obtain homogeneity according to the above steps, and was quickly poured into a polytetrafluoroethylene mold for curing overnight. The resulting crosslinked copolymer was immersed in 50 mL CHCl₃ containing excess TFA (20 eq.) to

quench the reaction and remove unreacted monomers. The purified copolymer was dried under high vacuum and hot-press molded at 80°C for further tests.

The preparation process of the poly(TTA₁-S₈) copolymer was the same as the above method [n (TTA: S₈: initiator: quencher) = 100: 100: 4: 40].

The preparation process of the poly(DTA₄-TAH₁-S₁₈) copolymer was the same as the above method [n (DTA: TAH: S₈: initiator: quencher) = 400: 100: 225: 9: 90].

The preparation process of the poly(TTA₂-TAH₁-S₁₈) copolymer was the same as the above method [n (TTA: TAH: S₈: initiator: quencher) = 200: 100: 225: 9: 90].

Depolymerization procedure

General depolymerization conditions: Purified poly (TAM₁-S₂) was used for monomer regeneration. The molar ratio [Polymer]: [BnSH]: [Base] = 100: 10: 1 / THF / 60°C / N₂ / [Polymer] = 0.5 M. ([Polymer] was calculated as [TAM])

Typical procedure: 328 mg purified poly(TAM₁-S₂) (1.49 mmol, 100 eq.) dissolved in 3 mL dry THF ([Polymer] = 0.5 M) was added in 50 mL round-bottom flask. The resulting sealed flask was vacuumized and backfilled with nitrogen three times to provide oxygen-free environment. Then initiator mixture consisting of 11 μL BnSH (0.15 mmol, 10 eq.) and 3.8 μL ^tBu-P₁ (0.015 mmol, 1 eq.) diluted with 100 μL THF was deoxidized and immediately injected into the above sealed flask under stirring to initiate the depolymerization reaction. The nearly colorless solution gradually turned yellow and the reaction continued under reflux at 60°C for 12 h until quenched by 11.5 μL TFA (0.15 mmol, 10 eq.). After cooling to room temperature, the mixture was dried under reduced pressure and diluted with DCM, then washed with saturated Na₂CO₃ solution for three times to remove catalyst and quencher, and then distilled under reduced pressure to remove solvent. 61 mg S₈ monomer was precipitated as yellow crystal (82% yield). The resulting oil was washed with PE to remove white flocculent oligomer. The filtrate was dried under high vacuum to obtain 198 mg

recycled TAM monomer as yellow oil (95% purity, 78% yield).

The depolymerization of 500 mg poly(DTA₁-S₄) CANs followed the same procedure, and the transformation from insoluble gel to yellow solution proved the monomer regeneration. Recycled DTA and S₈ monomers could be efficiently purified and separated via simple extraction operation (see the depolymerization procedure of poly(TAM₁-S₂)), yielding 335 mg DTA monomer (85% yield, 95% purity) and 88 mg crystalline S₈ solid (82% yield).

Supporting Figures

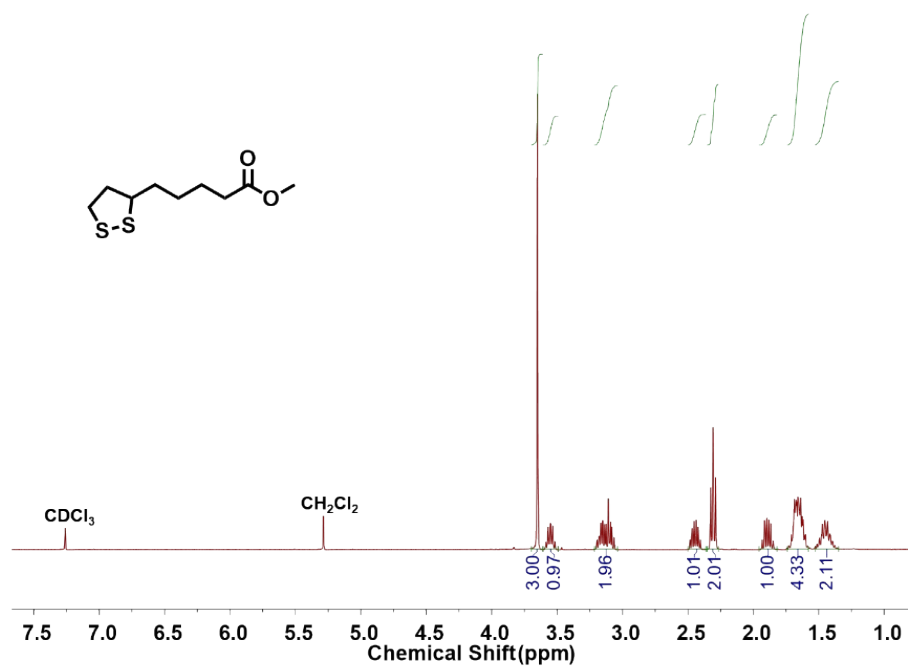


Figure S1. ^1H NMR spectrum of TAM (CDCl_3 , 400 MHz, 298 K).

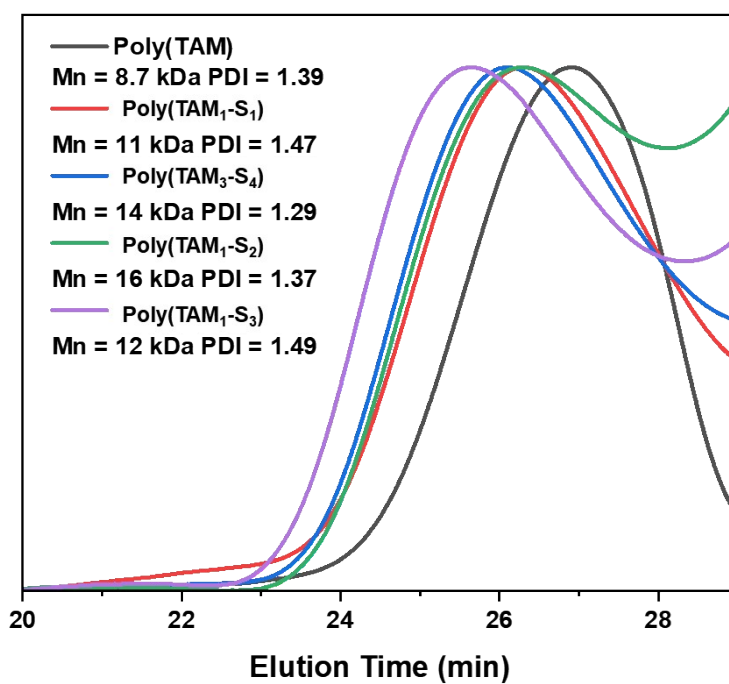


Figure S2. GPC of copolymers with different feed molar ratio of TAM and S.

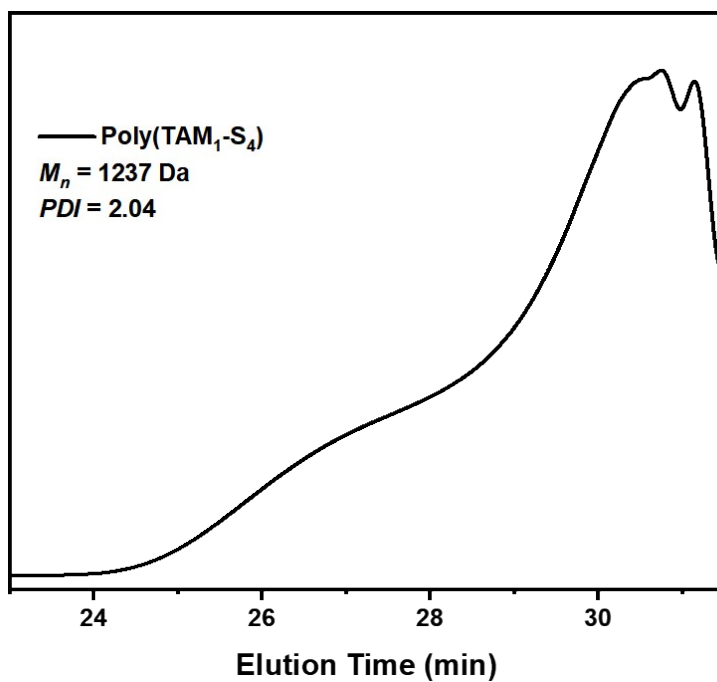


Figure S3. GPC of poly(TAM1-S4) copolymer.

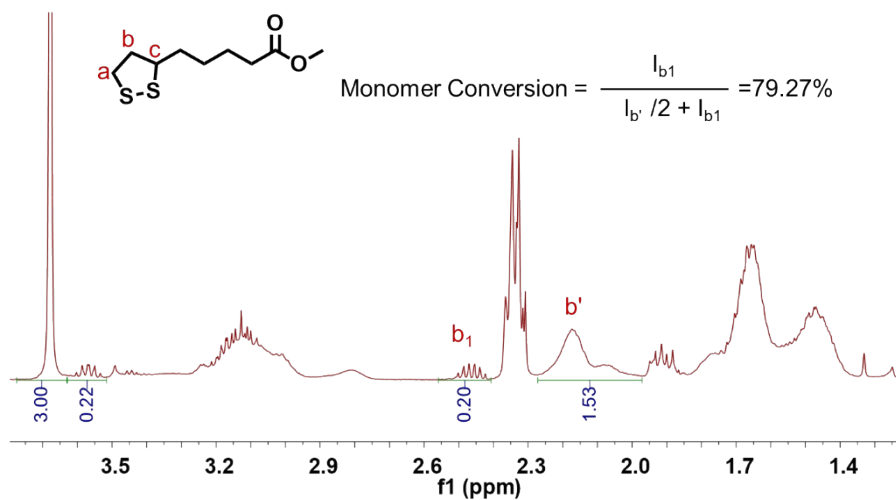


Figure S4. ^1H NMR spectrum of poly(TAM₁-S₂) (CDCl₃, 400 MHz, 298 K). The monomer conversion is calculated by the b proton peaks of polymers and unreacted monomers.

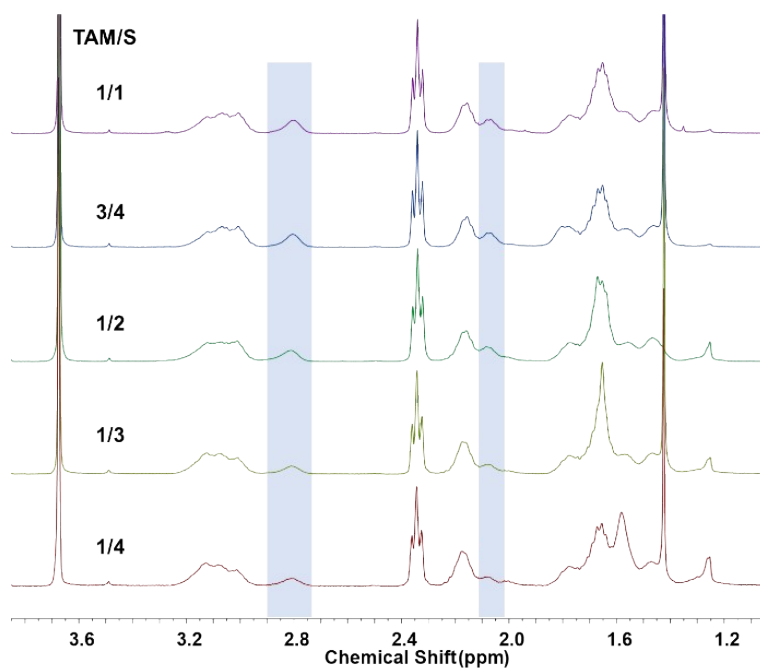


Figure S5. ^1H NMR spectra of purified copolymer with different feed molar ratio of TAM and S (CDCl_3 , 400 MHz, 298 K).

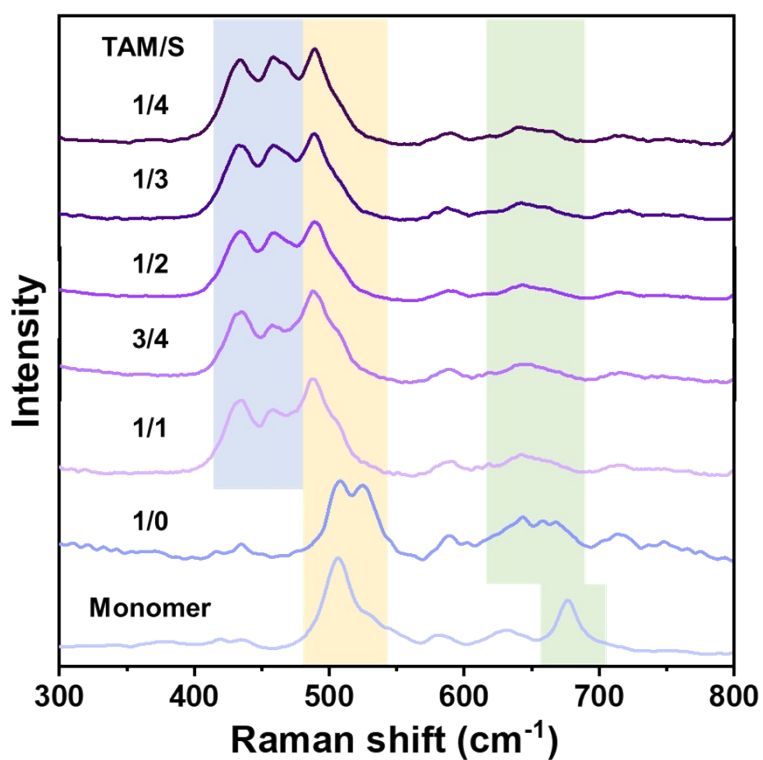


Figure S6. Raman spectra of TAM monomer and purified copolymer with different feed molar ratio of TAM and S.

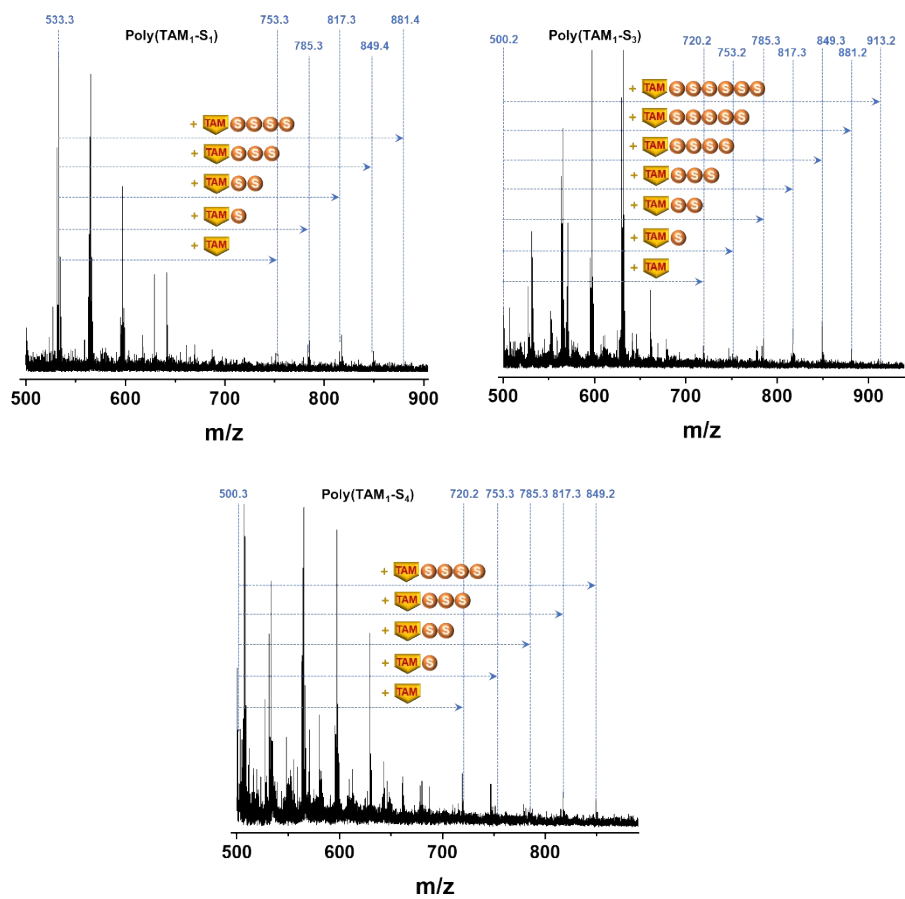


Figure S7. MALDI-TOF-MS spectra of copolymer with different molar ratio of TAM and S.

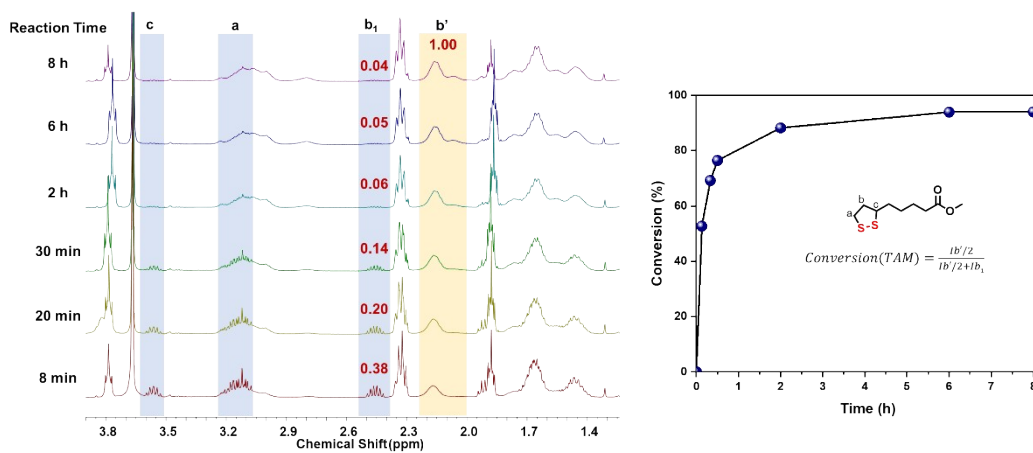


Figure S8. Time-dependent ¹H NMR spectra of the copolymerization, and the corresponding conversion rate of TAM monomer.

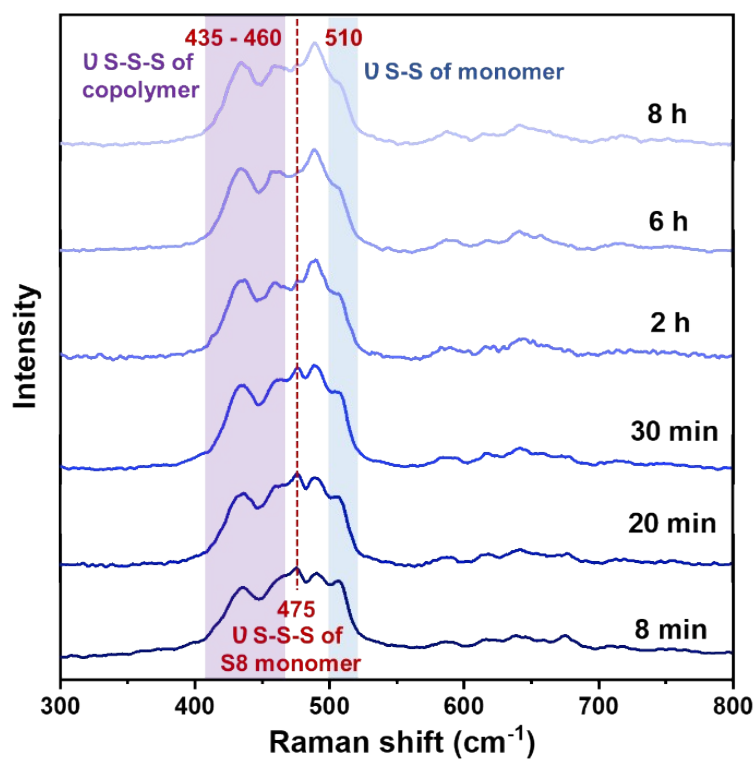


Figure S9. Time-dependent Raman spectra of the copolymerization.

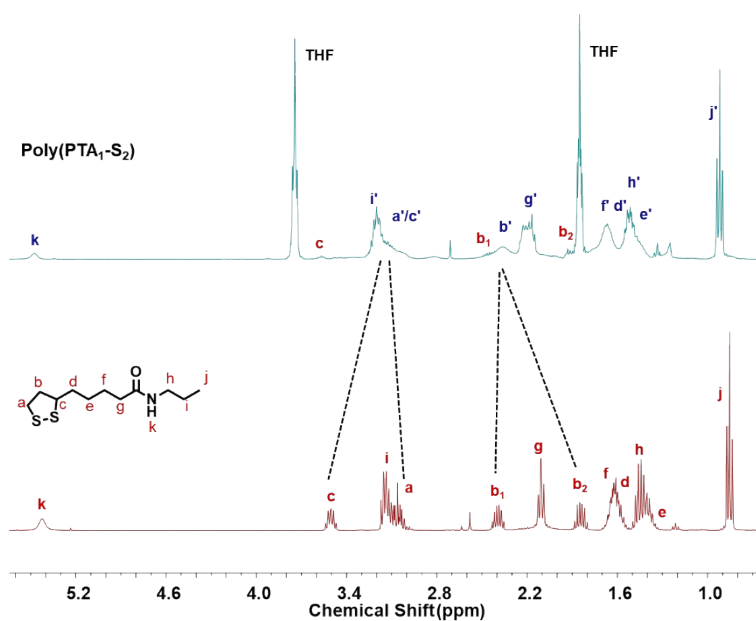


Figure S10. ^1H NMR spectra of poly($\text{PTA}_1\text{-S}_2$) and PTA monomer (CDCl_3 , 400 MHz, 298 K).

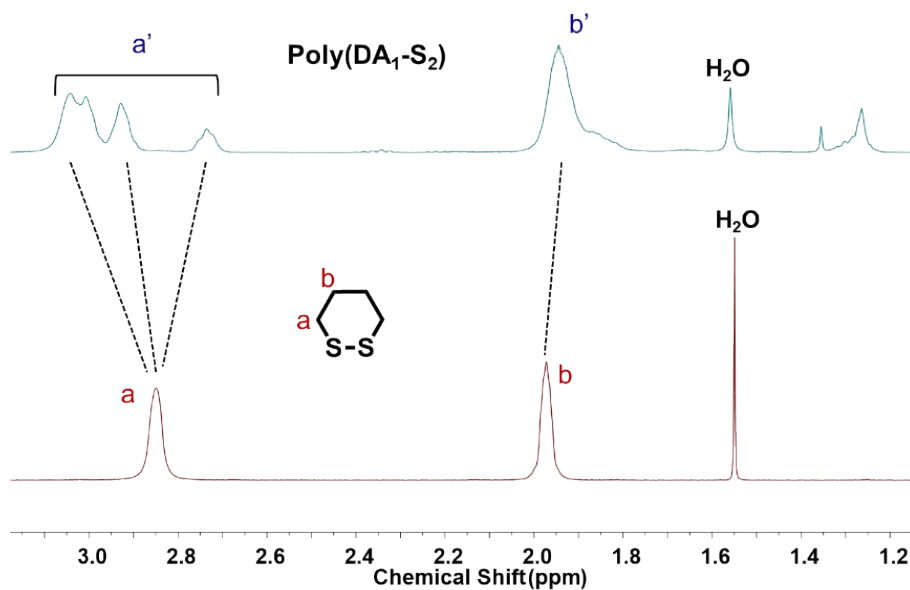


Figure S11. ^1H NMR spectra of poly($\text{DA}_1\text{-S}_2$) and DA monomer (CDCl_3 , 400 MHz, 298 K).

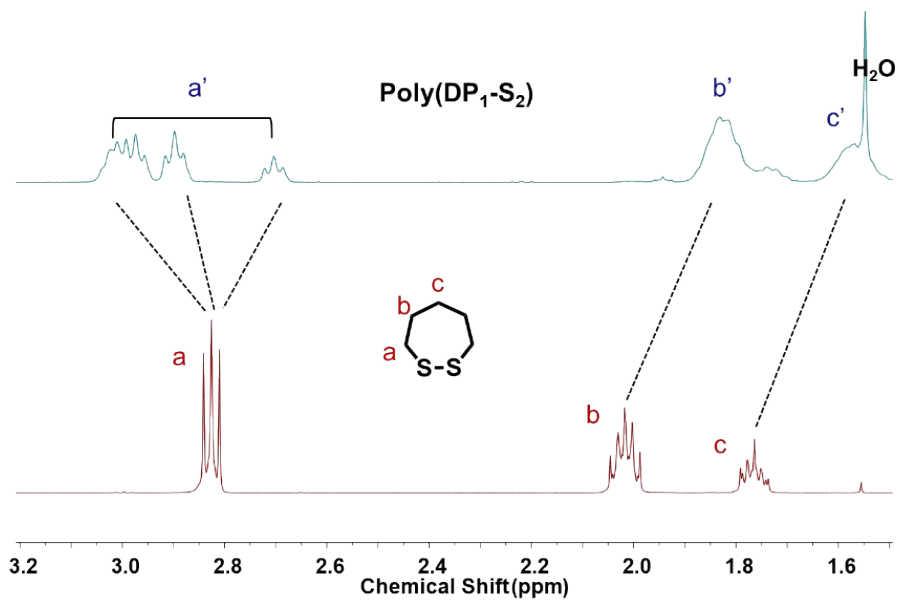


Figure S12. ^1H NMR spectra of poly($\text{DP}_1\text{-S}_2$) and DP monomer (CDCl_3 , 400 MHz, 298 K).

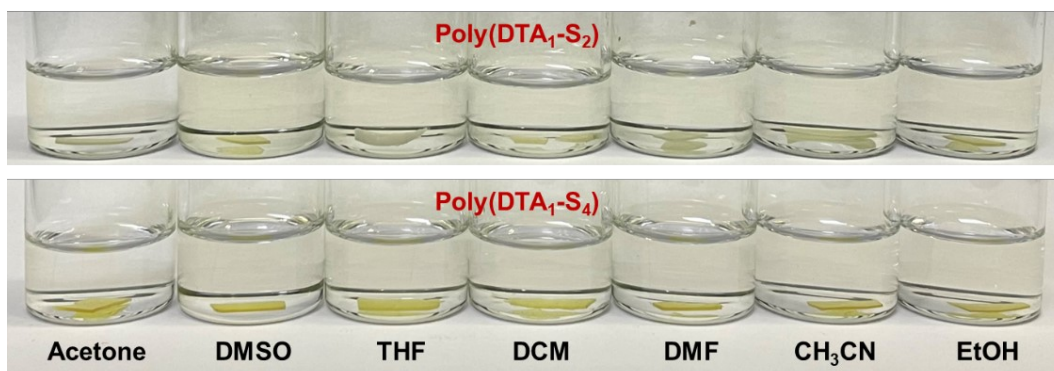


Figure S15. Photographs of the copolymer samples immersed in different organic solvents (including acetone, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dichloromethane (DCM), N,N-dimethylformamide (DMF), acetonitrile (CH₃CN), ethyl alcohol (EtOH)) for 24 h.

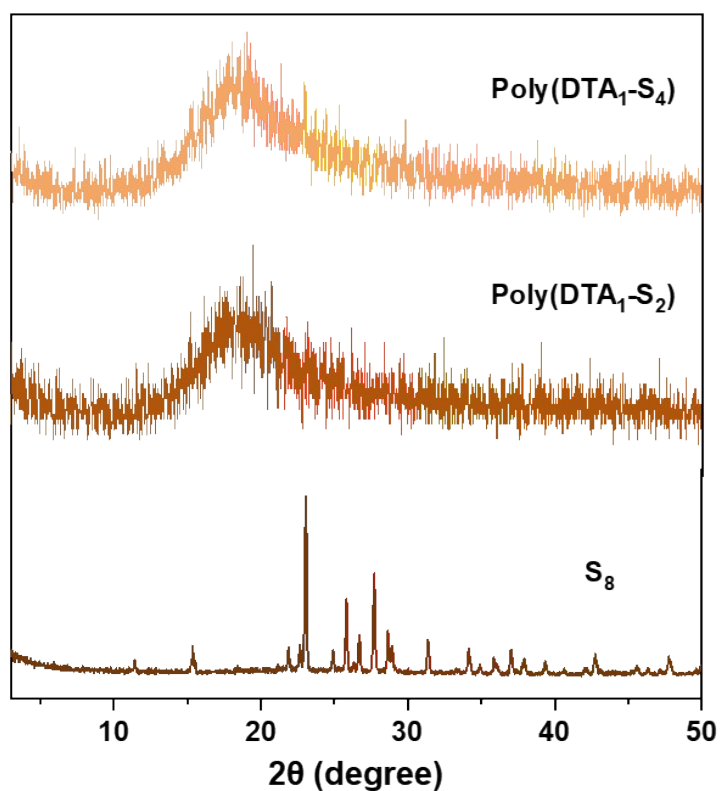


Figure S16. XRD pattern of S₈, poly(DTA₁-S₂) and poly(DTA₁-S₄).

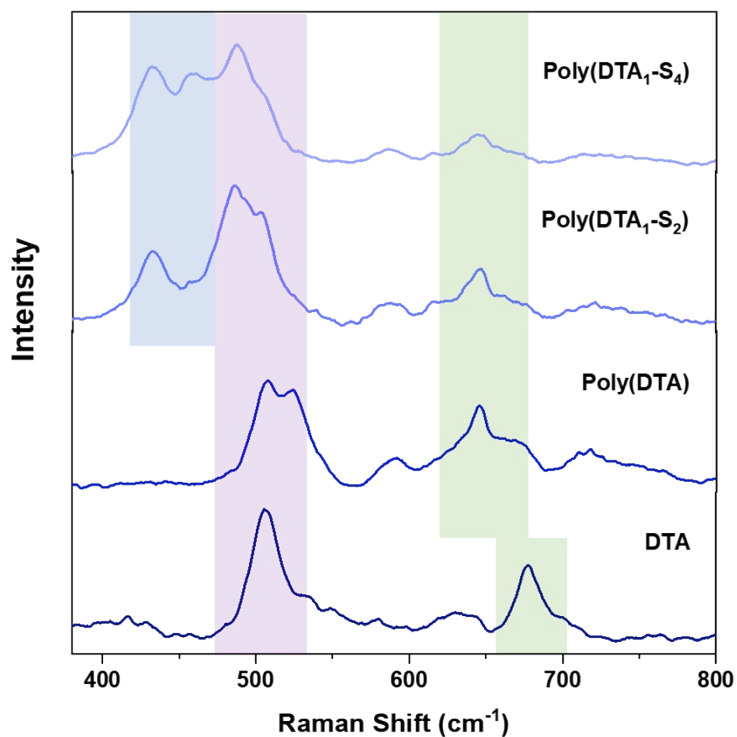


Figure S17. Raman spectra of DTA monomer, crosslinked poly(DTA) homopolymer and poly(DTA-S) copolymers.

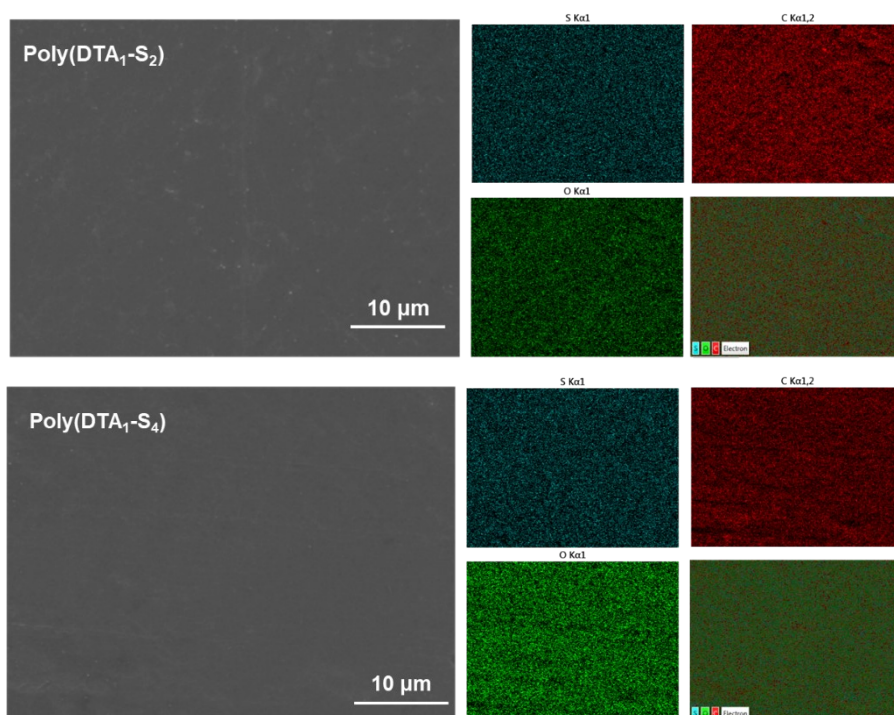


Figure S18. SEM analysis and element mapping images of poly(DTA₁-S₂) and poly(DTA₁-S₄) films.

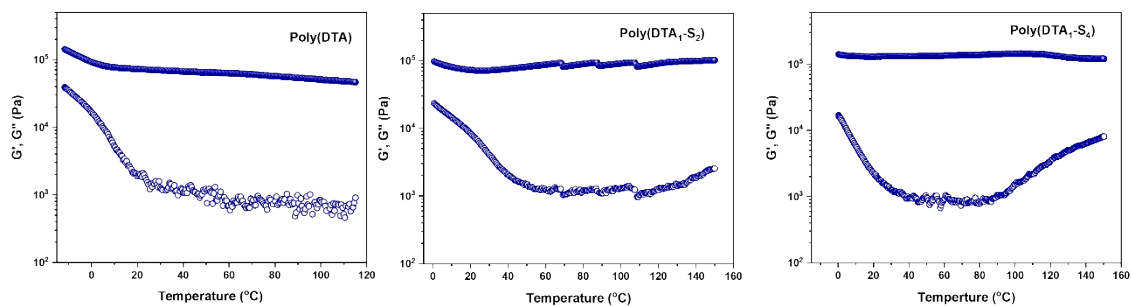


Figure S19. Temperature-dependent rheology curves of poly(DTA), poly(DTA₁-S₂) and poly(DTA₁-S₄).

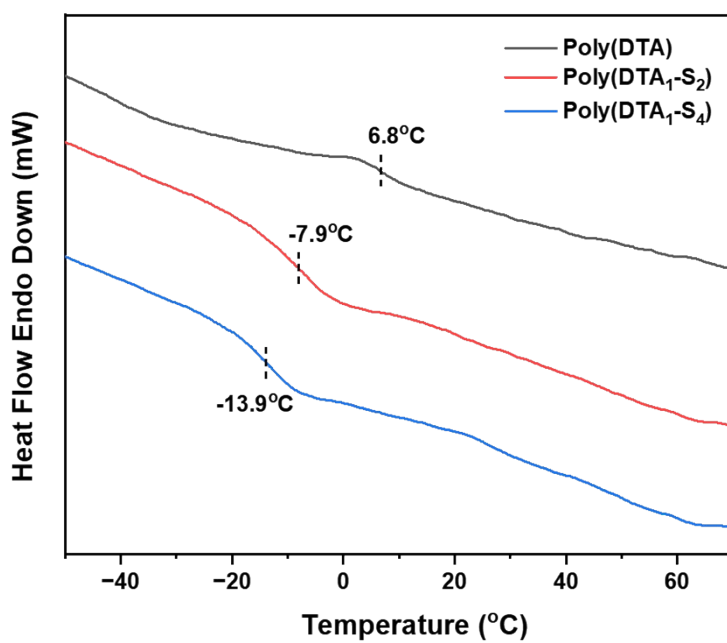


Figure S20. DSC curves of poly(DTA), poly(DTA₁-S₂) and poly(DTA₁-S₄).

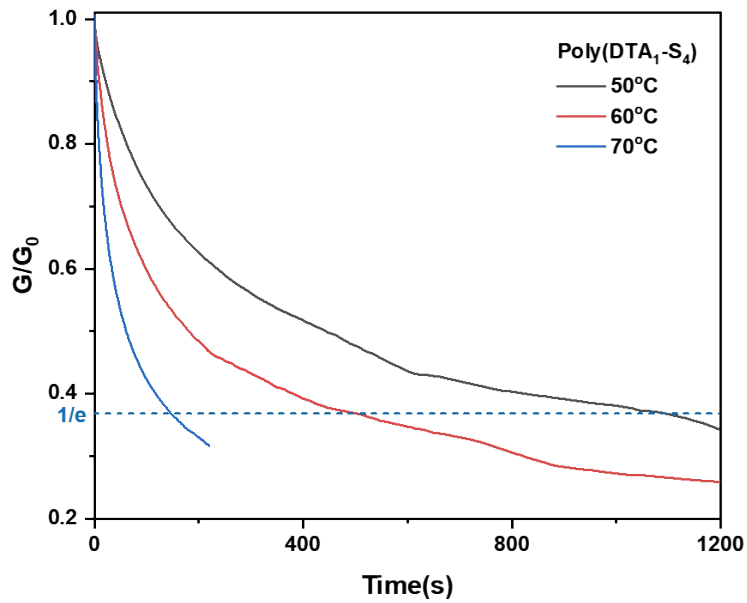


Figure S21. Stress relaxation curves of poly(DTA1-S4) at different temperature.

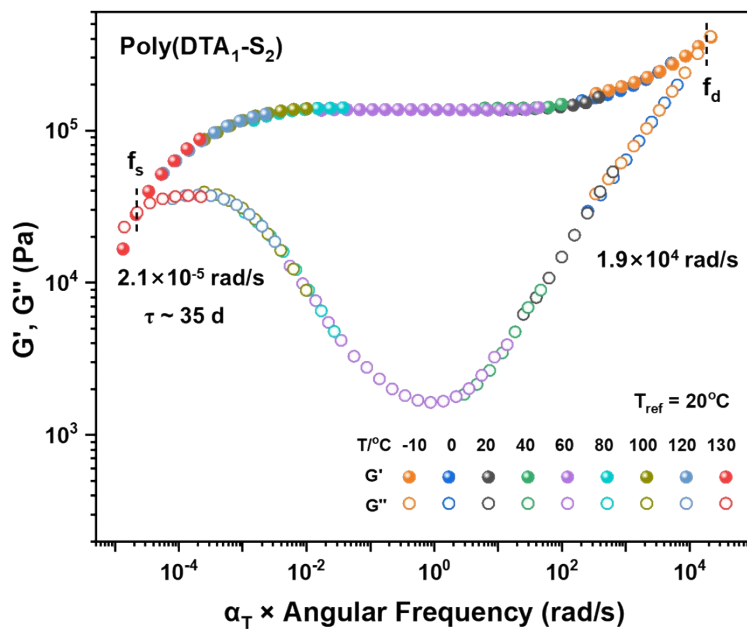


Figure S22. Time-temperature superposition for the frequency sweep plot of G' and G'' for poly(DTA₁-S₂) at 20°C.

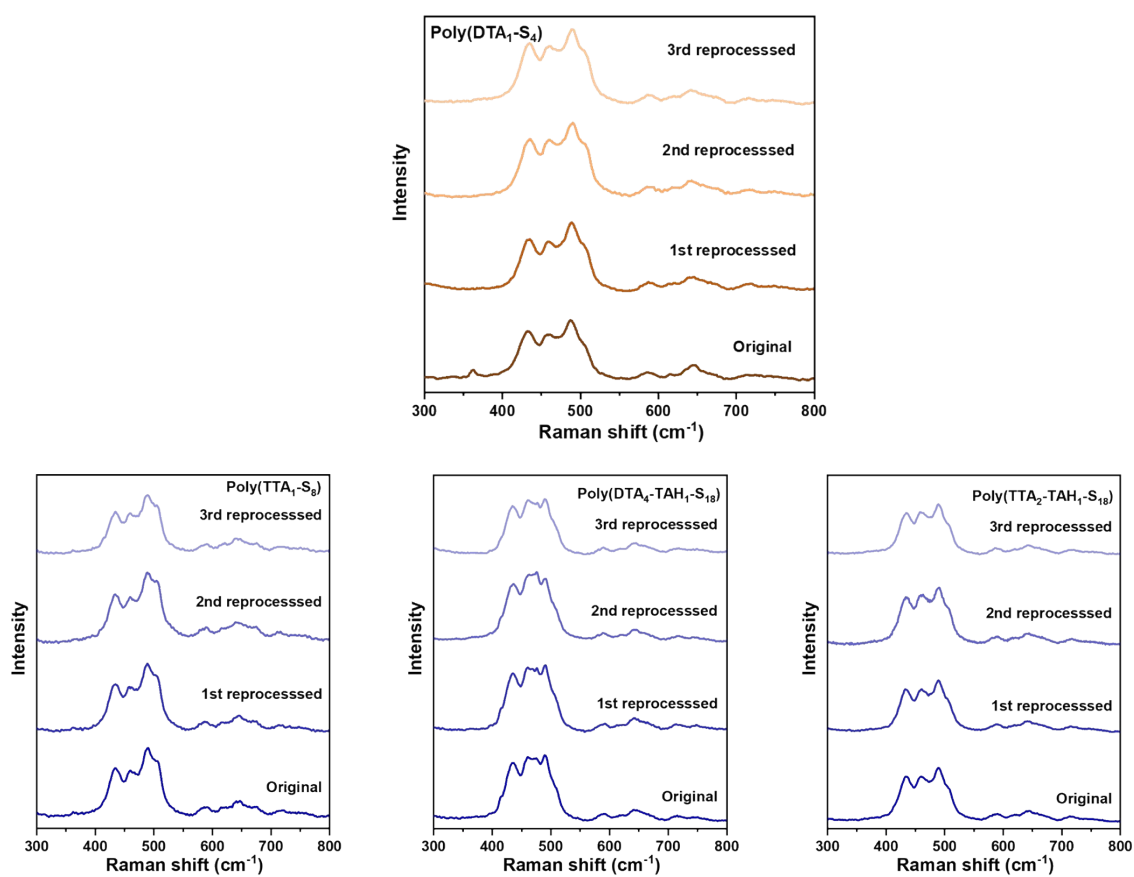


Figure S23. Raman spectra of original and reprocessed polysulfide copolymers.

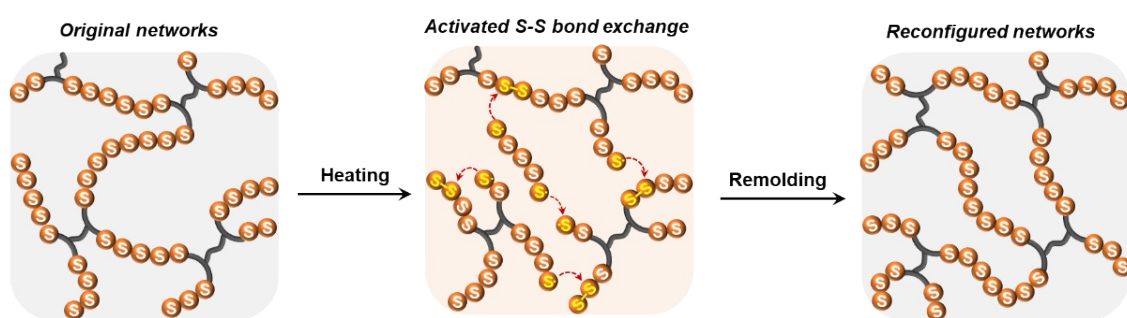


Figure S24. Schematic representation of the heat activated S-S bond exchange and network rearrangement.

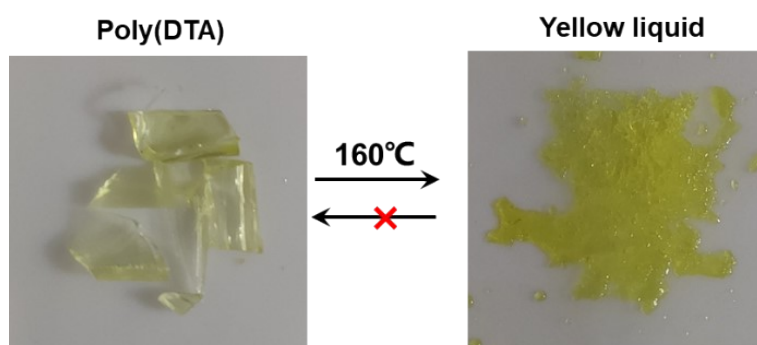


Figure S25. Photographs of original and hot-pressed poly(DTA) at 160°C.

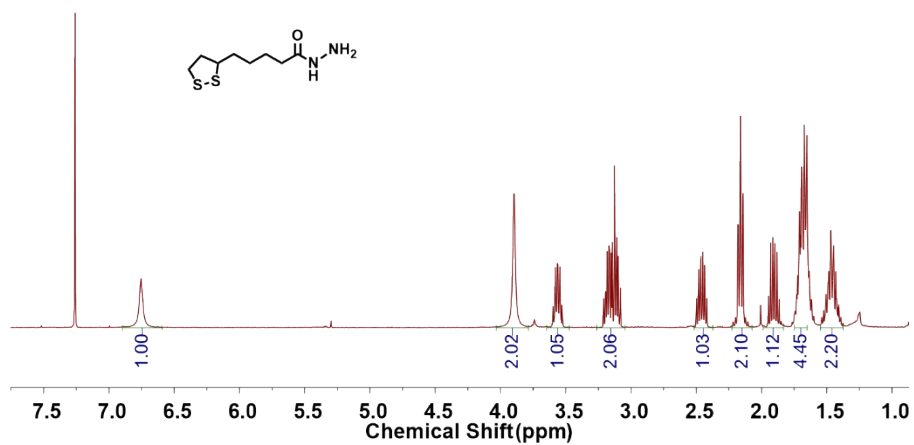


Figure S26. ¹H NMR spectrum of TAH (CDCl₃, 400 MHz, 298 K).

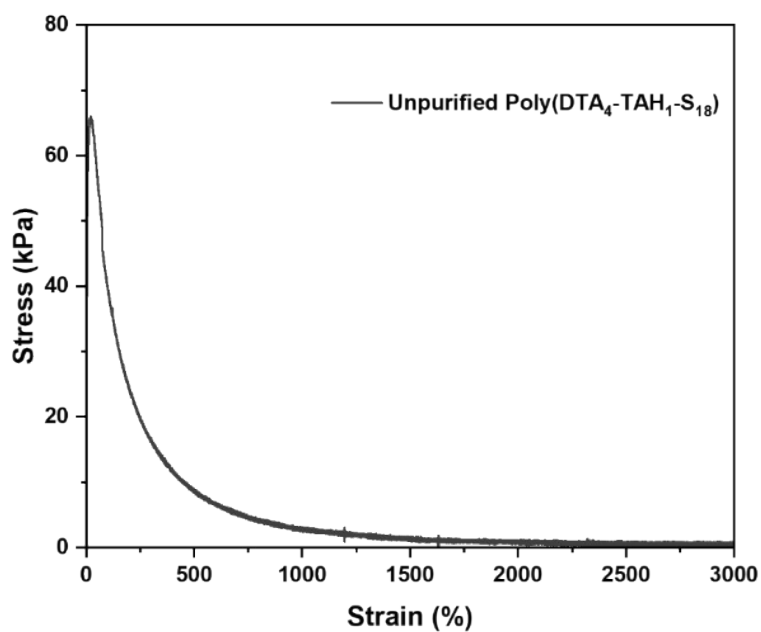


Figure S27. The stress-strain curve of unpurified poly(DTA₄-TAH₁-S₁₈).

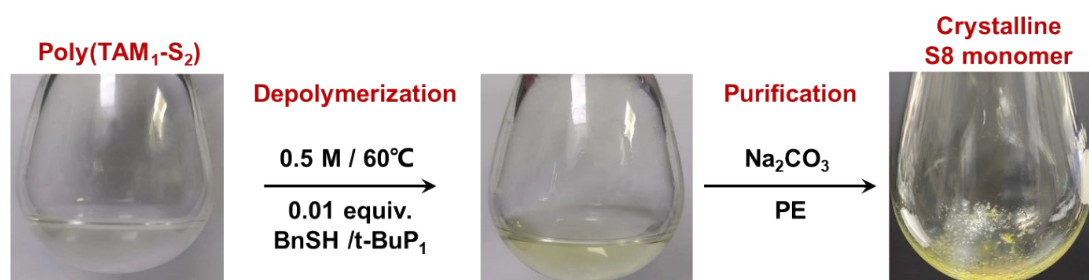


Figure S28. Photographs of the depolymerization and purification process of poly(TAM₁-S₂).

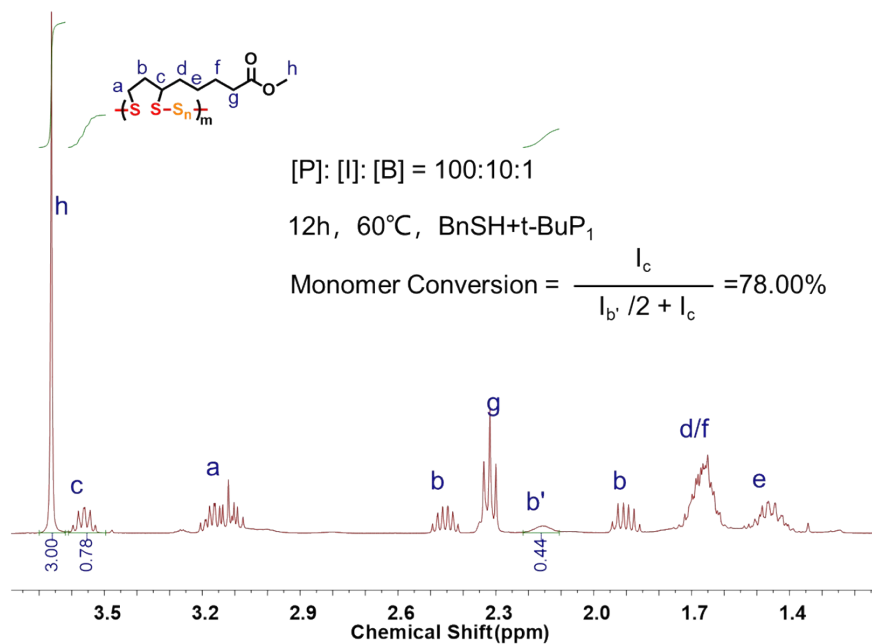


Figure S29. ¹H NMR spectrum of the depolymerization mixture of poly(TAM₁-S₂) (CDCl₃, 400 MHz, 298 K).

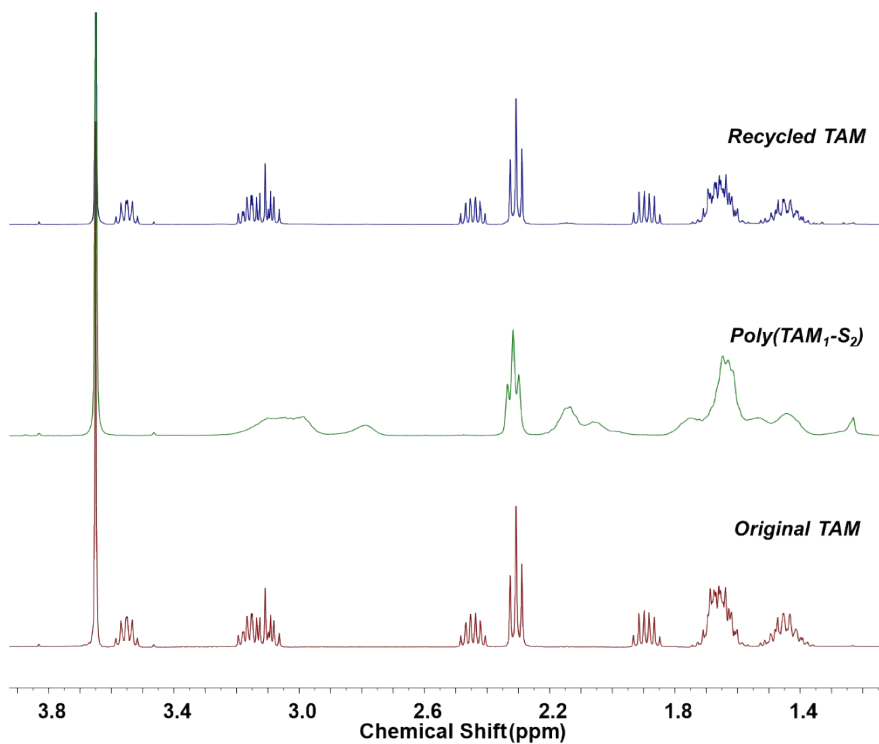


Figure S30. ¹H NMR spectra of the original, copolymerized, and recycled TAM (CDCl₃, 400 MHz, 298 K).

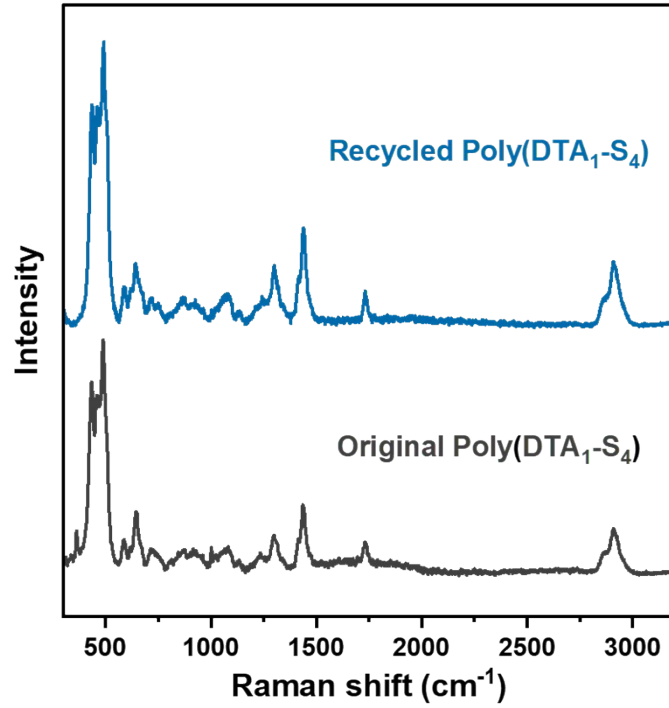


Figure S31. Raman spectra of the original and recycled poly(DTA₁-S₄).

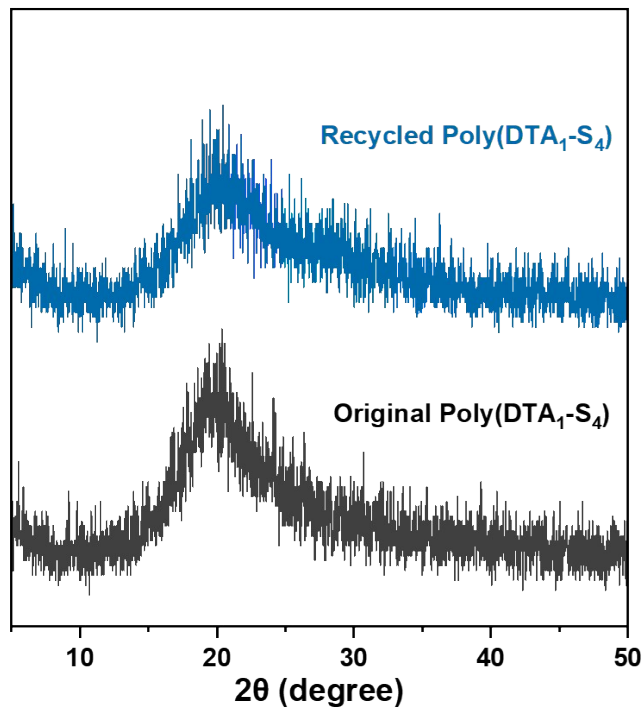


Figure S32. XRD spectra of the original and recycled poly(DTA₁-S₄).

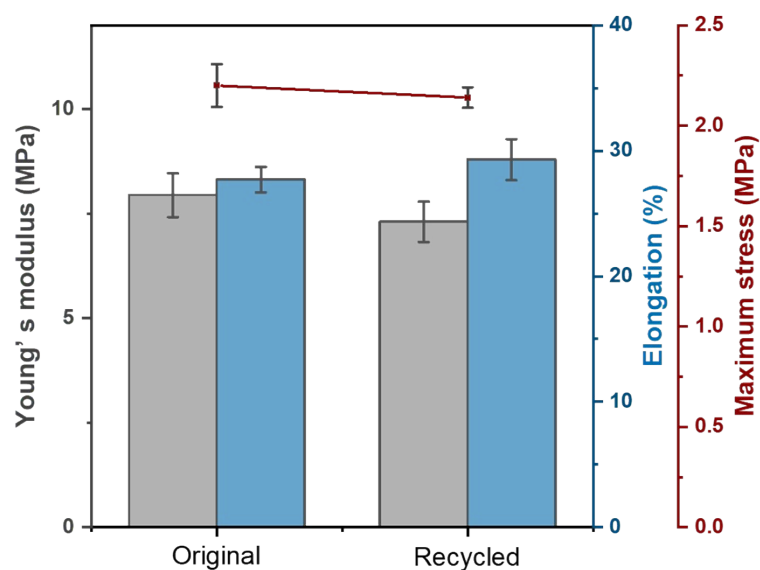


Figure S33. Comparison of mechanical performance of original and recycled poly(DTA₁-S₄) polymer films.

Entry	Disulfide Monomer	[M] ₀ ^a	Monomer [D]:[S]	Conv.S ^b (%)	Conv.D ^c (%)	Polymer [D]:[S]	M _n (Da)	PDI	Solvent	Content S (wt%)
1	TAM	1.8M	1:4	53.54%	80.43%	1:2.34	1237	2.04	CHCl ₃	47.09
2	TAM	1.8M	1:3	53.21%	78.68%	1:2.03	16466	1.37	CHCl ₃	45.24
3	TAM	1.8M	1:2	100%	77.66%	1:2.56	14010	1.29	CHCl ₃	48.32
4	TAM	1.8M	3:4	100%	73.68%	1:1.80	11889	1.45	CHCl ₃	43.79
5	TAM	1.8M	1:1	100%	66.30%	1:1.49	10580	1.46	CHCl ₃	41.71
6	TAM	3M	1:0	-	58.92%	-	15555	1.55	CHCl ₃	-
7	TAM	1.8M	1:0	-	24.09%	-	-	-	CHCl ₃	-
8	1,2-Dithiane	1.8M	1:2	32.34%	43.58%	1:1.48	2078	1.71	CHCl ₃	66.54
9	1,2-Dithiepane	1.8M	1:2	100%	61.97%	1:3.20	5092	3.5	CHCl ₃	70.38

Table S1. The anionic copolymerization of S₈ of cyclic disulfides. ^a[M]₀ was determined by the monomer concentration of disulfides. ^bS₈ monomer conversion (conv.S) was calculated by the solid mass of residual S₈ monomer. ^cDisulfide monomer conversion (conv.D) was calculated by the ¹H NMR spectra.