Supplementary Information (SI) for ChemComm.

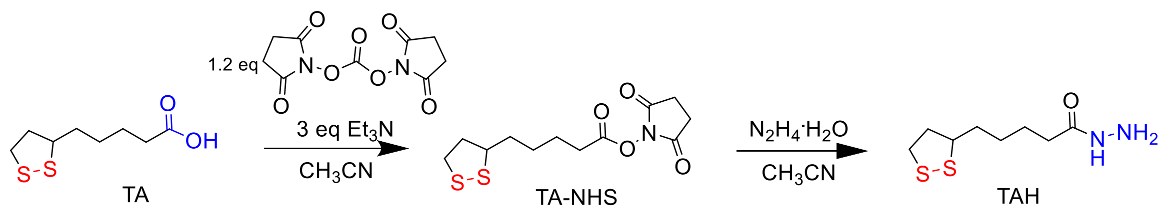
Content:

1. Materials and Methods

Commercial reagents and solvents: The key raw material (±) -alpha-lipoic acid (TA) is a reagent grade (99%) obtained from Aladdin. N, N' -diaminoacyl carbonate (NHS), triethylamine (>99%), hydrazine monohydrate (85%), m-tetramethylxylenediisocyanate (TMXDI), 1,6-diisocyanatohexane (HDI), Isophorone diisocyanate (IPDI), (2,4,6-trioxotriazine-1,3,5(2H,4H,6H)-triyl)tris(hexamethylene) isocyanate (THDI), 1,4-Phenylene diisocyanate (PDI), these substances are derived from commercial sources (Adamas®beta, TCI, Thermo Fisher, Aladdin, and Macklin) and are used directly as reactants without further purification. The solvents used for reaction and spectroscopy are AR grade or HPLC grade. The solvent used for NMR spectroscopy was the solvent received from Adamas®beta.

General Methods: NMR spectra were recorded a Bruker AV-400 spectrometer at room temperature (400 MHz, 298 K) (^{1}H: 400 MHz). Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ^{1}H NMR [DMSO-d_6: ^{1}H(δ) = 2.50 ppm]. All the spectra were recorded at room temperature. The UV/Vis absorption spectra data were documented by a Shimadzu UV-2600 UV-Vis spectrophotometer and all the fluorescent spectra were acquired by a FLS1000-stm Photoluminescence Spectrometer. Fourier transform infrared spectrometer (FT-IR) (Thermo Nicolet Corporation; 7800-350/cm 0.01/cm/6700) was used to analyze the monomer and polymer samples at room temperature (25°C). Tensile strength tests, adhesion tests were measured with an Instron 34TM-5 universal testing system equipped with a 100 N sensor.

2. Synthetic methods:

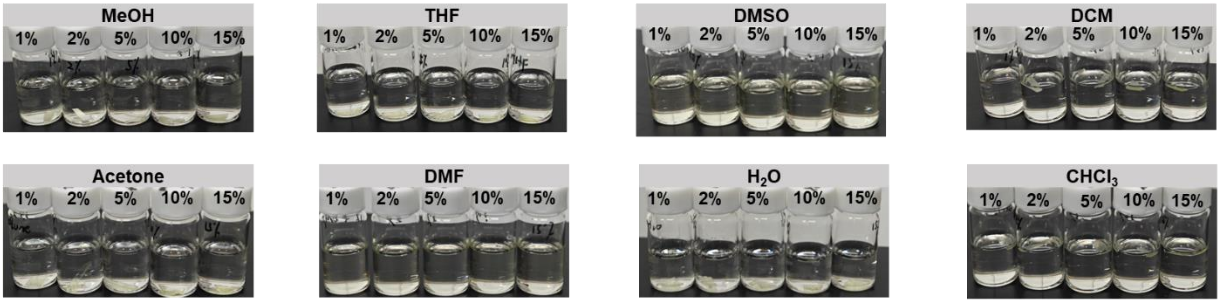


To a round-bottom flask, thioctic acid (9.6 g, 46.6 mmol, 1.0 eq) and N, N'-Disuccinimidyl carbonate (14.3 g, 55.9 mmol, 1.2 eq) was dissolved in the acetonitrile (400 mL) to obtain yellow homogeneous solution, which was then protected from light. After addition of triethylamine (20.0 mL, 139.8 mmol, 3.0 eq), the reaction mixture was stirred at room temperature for 2 h. Then, 2/3 of the solvent was evaporated, and the mixture was poured into 600 mL of 5% $NaHCO_3$ solution to form pale yellow precipitates, which was dissolved in acetonitrile (400 mL). Next 85% hydrazine monohydroxide (13.0 eq, 30 mL) was dropwise added into the solution and the mixture was stirred at room temperature for 3 h. The reaction mixture was stirred at room temperature for 3 h. The mixture was filtered and the filtrate was concentrated under reduced pressure. The concentrated solution was diluted with CH_2Cl_2 (200 mL) and washed by aqueous 5% $NaHCO_3$ solution three times. After drying over Na_2SO_4, the solvent was evaporated under reduced pressure to yield yellow solid TAH monomers (8.5 g, 86% yield).

Preparation of poly(TAH-TMXDI), poly(TAH-HDI), poly(TAH-THDI), poly(TAH-IPDI) and poly(TAH-PDI): In a typical procedure, 1 g (0.023 mol) TAH monomer and various molar ratio of crosslinkers (1%, 2%, 5%, 10%, 15%, 20% and 50%) were added into a 15 mL Teflon vial. The mixture was then heated by a metal heating block with a constant temperature of 145°C for 2 h to obtain homogeneity and the resulting liquid was quickly transferred into a

Teflon mold and cooled to room temperature to form free-standing polymer samples, and then the film was formed by hot pressing at 80°C under 2 MPa.

3. Supporting Figures



Sample	MeOH	THF	DMSO	DCM	Acetone	DMF	H_2O	$CHCl_3$
PolyTAH-1% TMXDI	▲	×	√	×	×	√	×	×
PolyTAH-2% TMXDI	▲	×	√	×	×	√	×	×
PolyTAH-5% TMXDI	▲	×	√	×	×	√	×	×
PolyTAH-10% TMXDI	▲	×	√	×	×	√	×	×
PolyTAH-15% TMXDI	▲	×	√	×	×	√	×	×

Figure S1. Solubility test of the resulting poly(TAH-TMXDI) with various amount of crosslinkers. The polymer samples soaked in different solvents for 24 h ("√" means totally soluble; "▲" means swelling; "×" means insoluble).

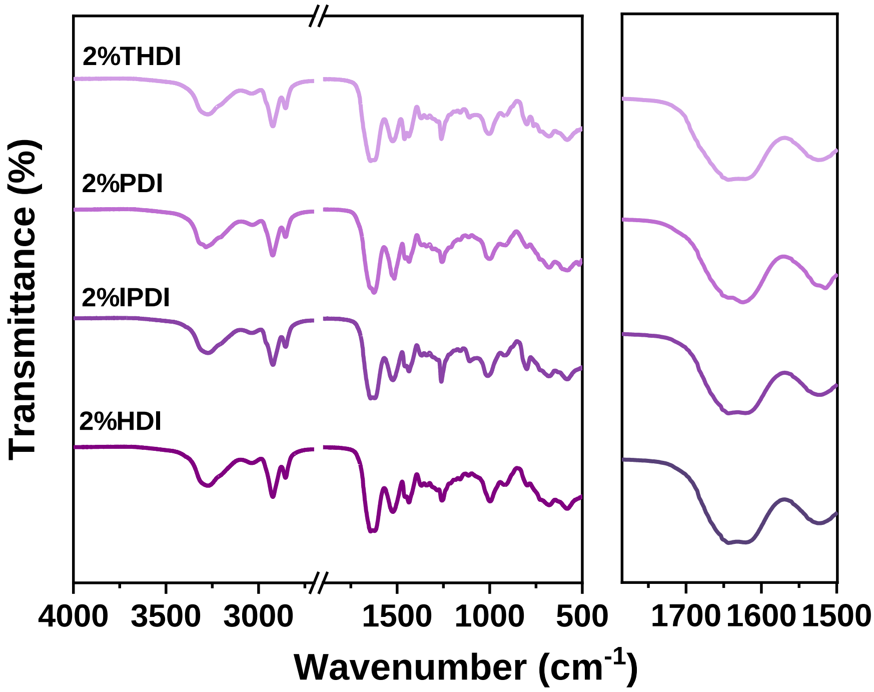


Figure S2. FTIR spectra of poly(TAH) with various crosslinkers, the molar ratio of crosslinkers is 2%.

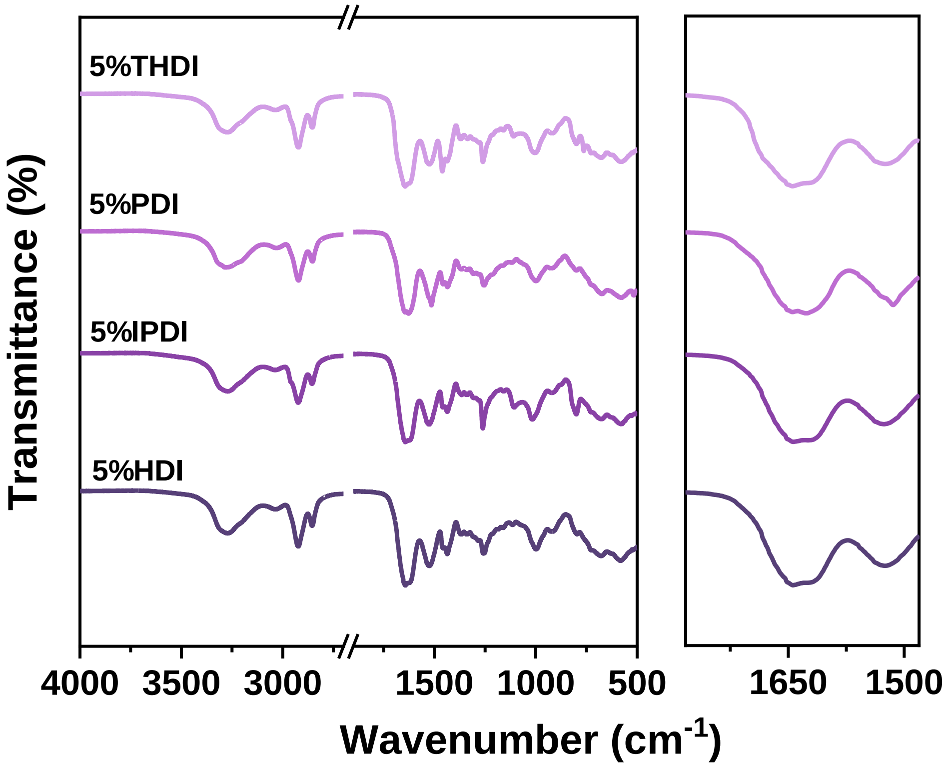


Figure S3. FTIR spectra of poly(TAH) with various crosslinkers, the molar ratio of crosslinkers is 5%.

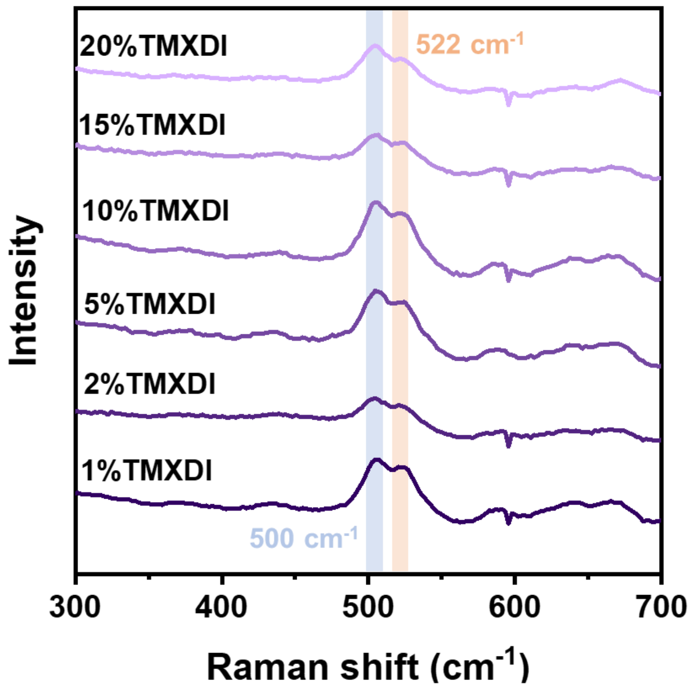


Figure S4. Raman spectra of poly(TAH) with various molar ratio of TMXDI, the molar ratio of crosslinkers ranging from 1% to 20%.

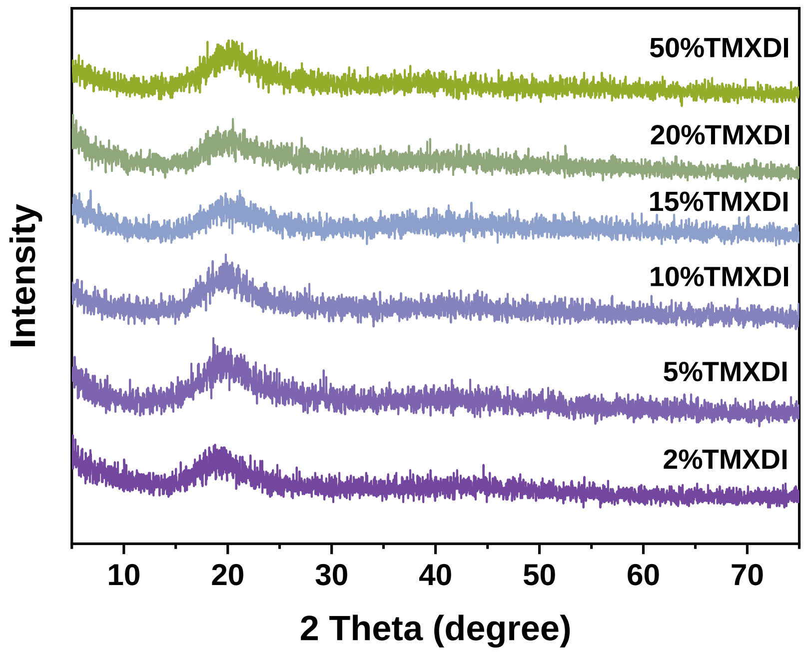


Figure S5. XRD analysis of poly(TAH) with various molar ratio of TMXDI, the molar ratio of crosslinkers ranging from 2% to 50%.

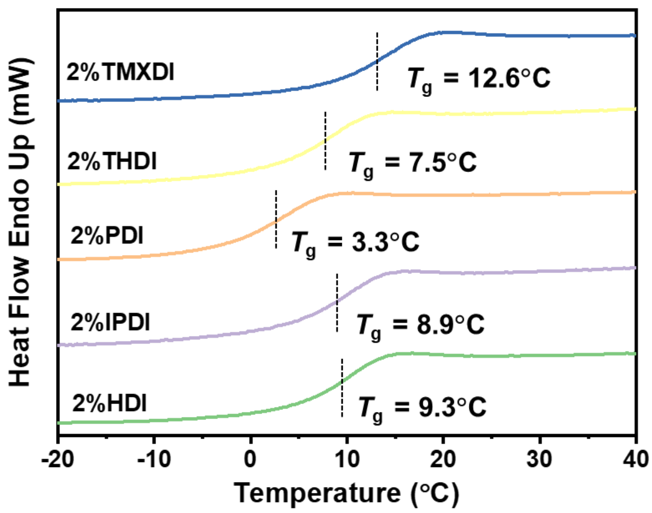


Figure S6. DSC analysis of poly(TAH) with various crosslinkers. DSC thermograms for materials from -20°C to 40°C at a temperature-increasing rate of 10°C/min. Tg refers to the glass-transition temperature, and the molar ratio of crosslinkers is 2%.

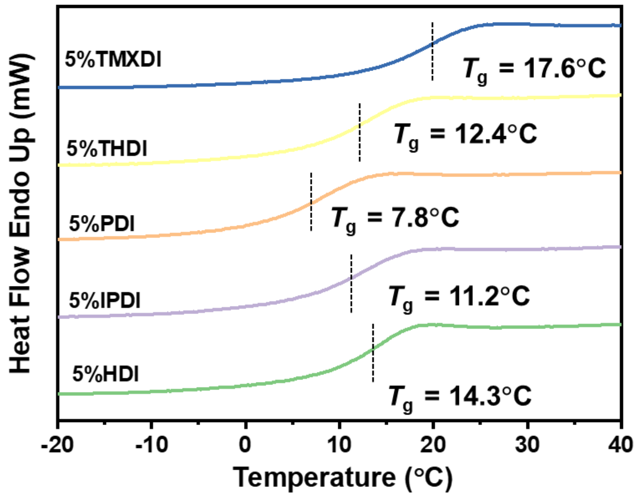


Figure S7. DSC analysis of poly(TAH) with various crosslinkers. DSC thermograms for materials from -20°C to 40°C at a temperature-increasing rate of 10°C/min. Tg refers to the glass-transition temperature, and the molar ratio of crosslinkers is 5%.

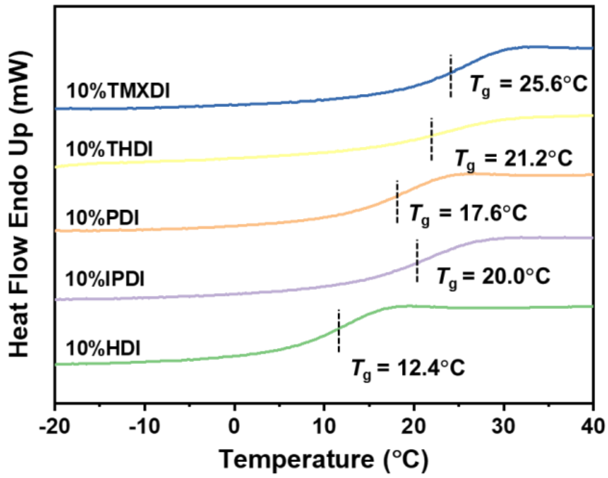


Figure S8. DSC analysis of poly(TAH) with various crosslinkers. DSC thermograms for materials from -20°C to 40°C at a temperature-increasing rate of 10°C/min. Tg refers to the glass-transition temperature, and the molar ratio of crosslinkers is 10%.

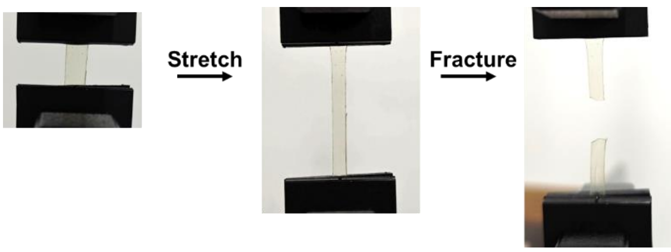
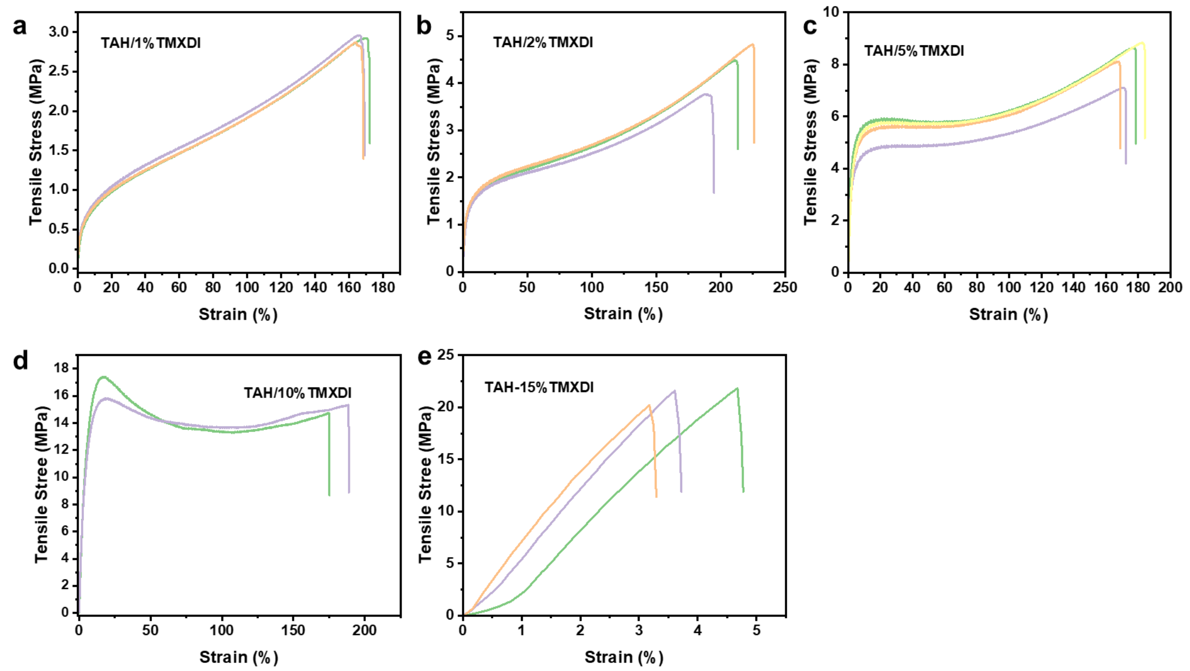


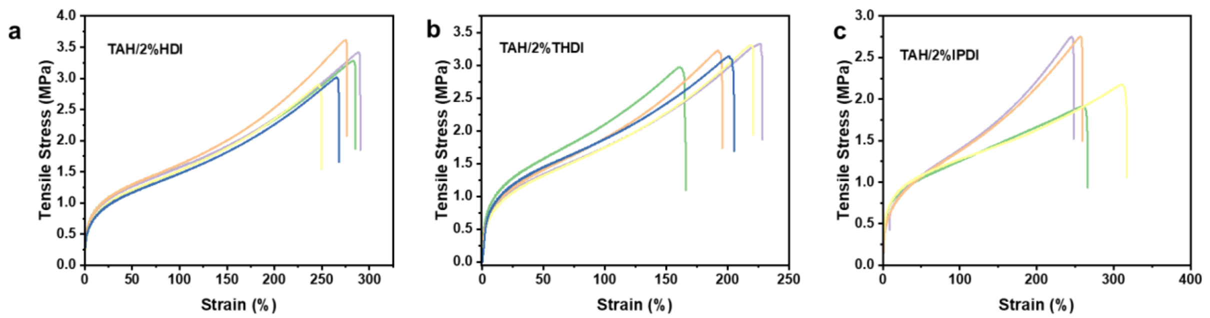
Figure S9. Photograph of the material was stretched and fracture.



f

Sample	Young's modulus (E, MPa)	Tensile toughness (U_T, MJ·m^{-3})	Tensile Strength (MPa)	Tensile Strain (%)
poly(TAH)-1% TMXDI	64.69±24.77	3.03±0.06	2.9±0.08	164±6.74
poly(TAH)-2% TMXDI	156.86±23.79	5.99±0.98	4.36±0.54	230.35±11.28
poly(TAH)-5% TMXDI	265.34±72.28	11.21±0.78	8.18±0.78	175.59±6.73
poly(TAH)-10% TMXDI	333.8±19.1	25.73±1.39	16.63±1.12	181.65±9.48
poly(TAH)-15% TMXDI	699.91±134.1	45.9±13.17	21.21±0.88	3.82±0.77

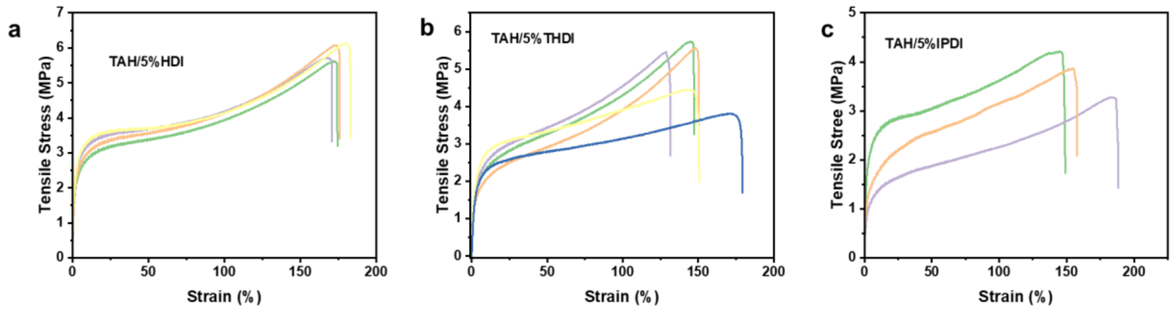
Figure S10. Tensile test: (a-d) Stress-strain curves of poly(TAH) with various ratio of TMXDI; (f) A summary of the mechanical data of the poly(TAH-TMXDI).



d

Sample	Young's modulus (E, MPa)	Tensile toughness (U_T, MJ·m^{-3})	Tensile Strength (MPa)	Tensile Strain (%)
poly(TAH)-2% THDI	88±6.8	4.12±0.30	3.19±0.15	199.97±24.51
poly(TAH)-2% IPDI	29.02±10.09	3.95±0.28	2.57±0.53	257.41±92
poly(TAH)-2% HDI	93.75±12.11	5.62±0.84	3.25±0.29	271.65±16.37

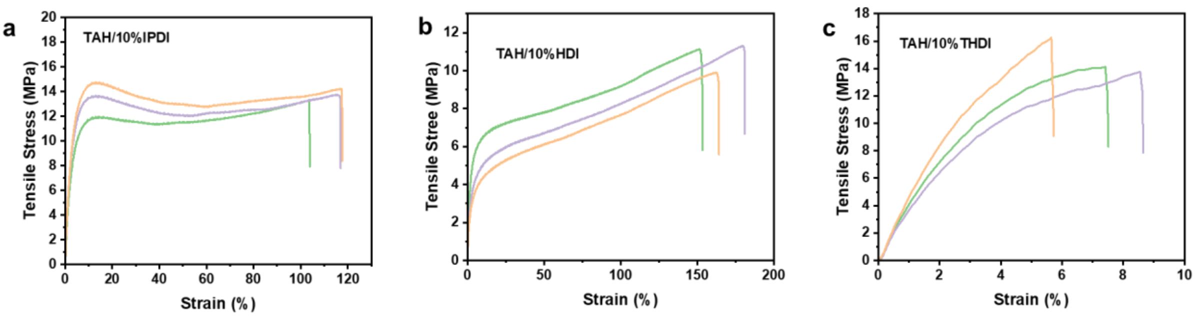
Figure S11. Tensile test: (a-c) Stress-strain curves of poly(TAH) with various crosslinkers; (d) A summary of the mechanical data of the poly(TAH-2% HDI), poly(TAH-2% THDI), poly(TAH-2% IPDI).



d

Sample	Young's modulus (E, MPa)	Tensile toughness (U_T, MJ·m^{-3})	Tensile Strength (MPa)	Tensile Stress (%)
poly(TAH)-5% THDI	186.85±9.66	5.26±0.31	5.3±0.58	140.9±8.5
poly(TAH)-5% IPDI	215.25±5.89	4.68±0.23	4.56±0.92	160.15±16.94
poly(TAH)-5% HDI	286.7±33.75	7.55±0.71	5.93±0.24	184.52±19.95

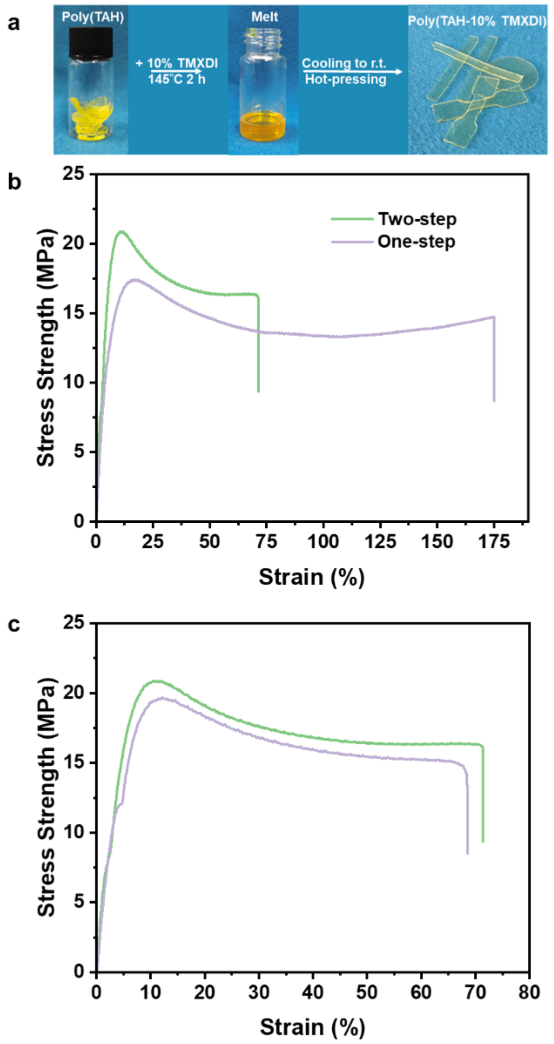
Figure S12. Tensile test: (a-c) Stress-strain curves of poly(TAH) with various crosslinkers; (d) A summary of the mechanical data of the poly(TAH-5% HDI), poly(TAH-5% THDI), poly(TAH-5% IPDI).



d

Sample	Young's modulus (E, MPa)	Tensile toughness (U_T, MJ·m^{-3})	Tensile Strength (MPa)	Tensile Stress (%)
poly(TAH)-10% THDI	422.19±12.93	0.71±0.14	14.7±1.34	7.2±1.46
poly(TAH)-10% IPDI	432.1±27.2	14.11±1.82	13.57±0.3	121.32±24.16
poly(TAH)-10% HDI	363.76±71.09	13.05±1.42	10.78±0.77	164.46±14.4

Figure S13. Tensile test: (a-c) Stress-strain curves of poly(TAH) with various crosslinkers; (d) A summary of the mechanical data of the poly(TAH-10% HDI), poly(TAH-10% THDI), poly(TAH-10% IPDI).



Sample	Young's modulus (E, MPa)	Tensile toughness (U_T, $MJ \cdot m^{-3}$)	Tensile Strength (MPa)	Tensile Strain (%)
Two step	330.83±31.89	11.52±0.84	20.28±0.86	69.63±2.13

Figure S14. (a) The two-step polymerization of poly(TAH-10% TMXDI); (b) Stress-strain curves of poly(TAH-10% TMXDI) prepared by one-step and two-step methods respectively. (c) Stress-strain curves of poly(TAH-10% TMXDI) prepared by two-step, a summary of the mechanical data of the poly(TAH-10% TMXDI) prepared by two-step.

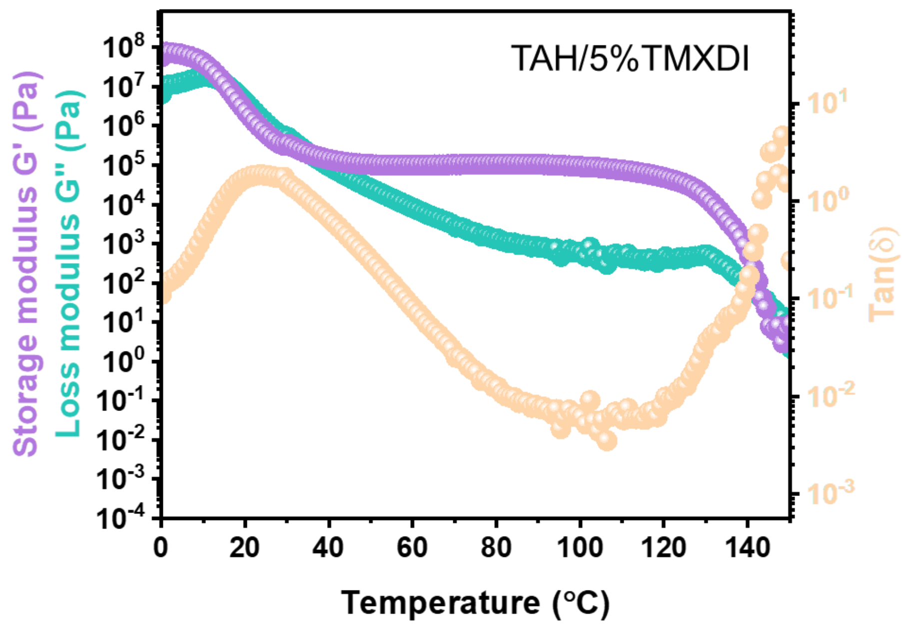


Figure S15. Temperature-dependence of rheological curves of poly(TAH-5% TMXDI) at 1 Hz.

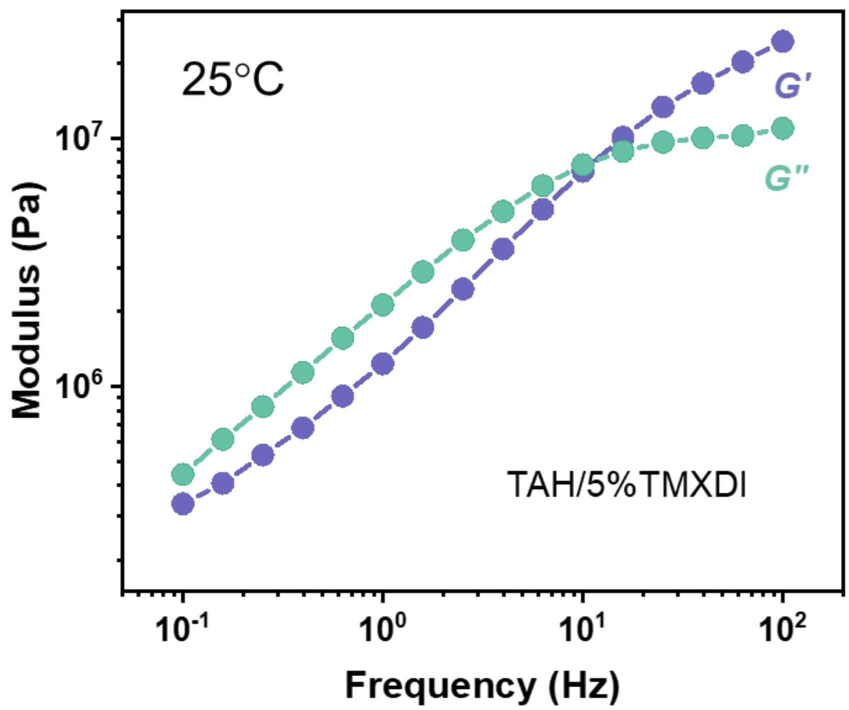


Figure S16. Frequency-dependence of rheological curves of poly(TAH-5% TMXDI) at 25°C.

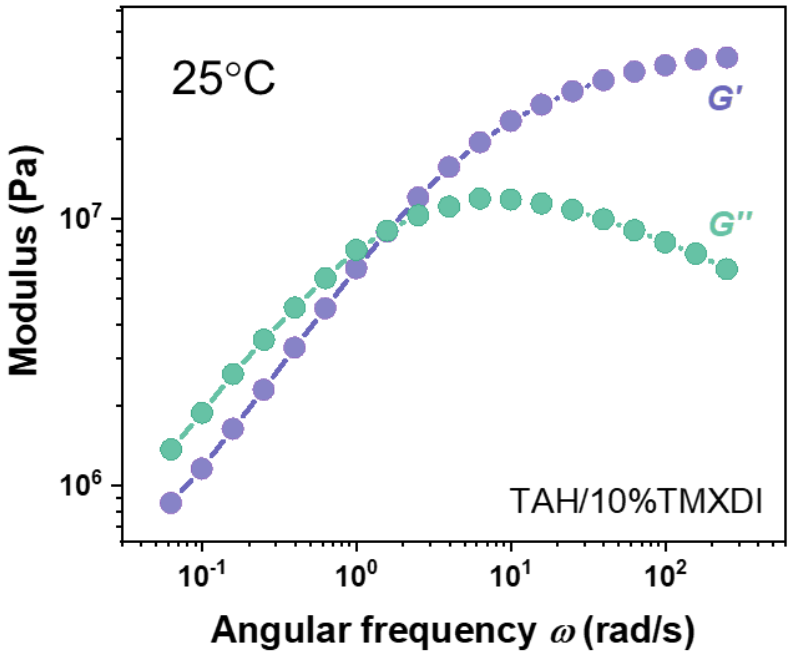


Figure S17. Frequency-dependence of rheological curves of poly(TAH-10% TMXDI) at 25°C.

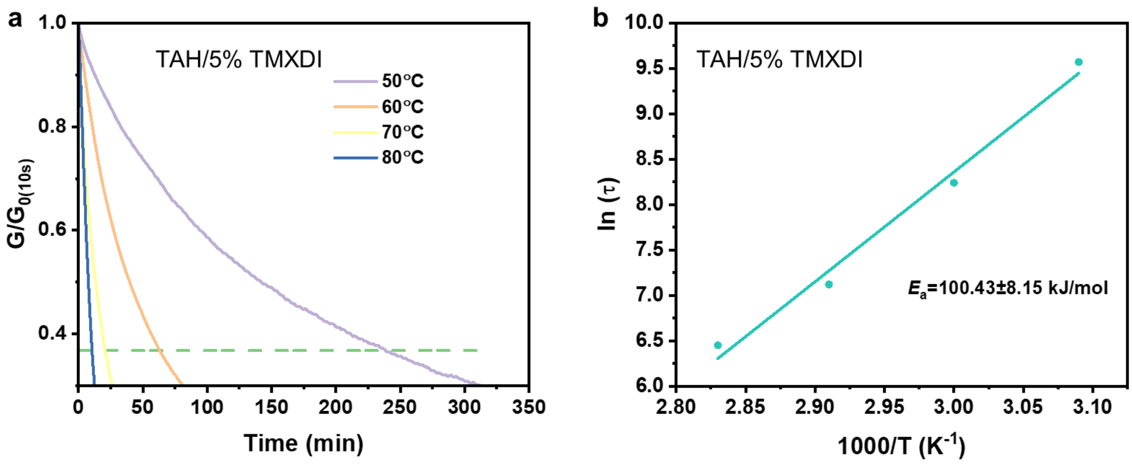


Figure S18. (a) Temperature-dependent stress relaxation curves for poly(TAH-5% TMXDI); (b) Arrhenius-type behavior of poly(TAH-5% TMXDI) with apparent activation energy of 100.43 kJ/mol.

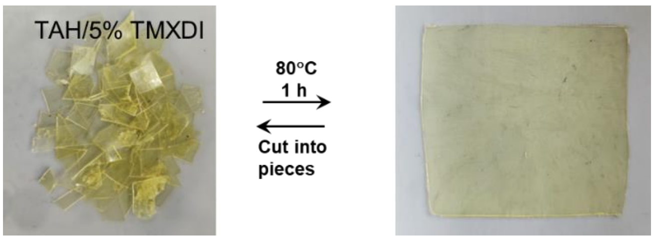


Figure S19. Diagram showing the reprocessing experiment of poly(TAH-5% TMXDI). The pressure is calculated to be about 10 MPa.

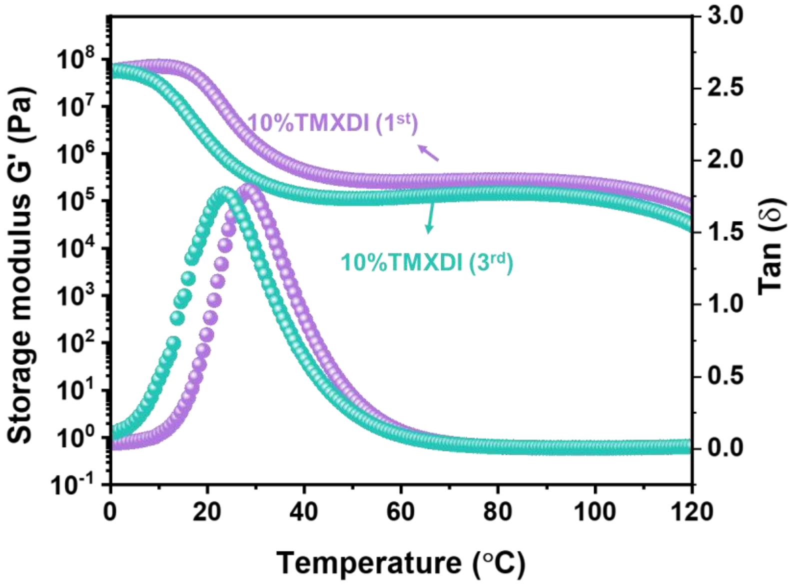


Figure S20. Temperature-dependent rheological analysis of poly(TAH-10% TMXDI) before and after reprocessing with two cycles.

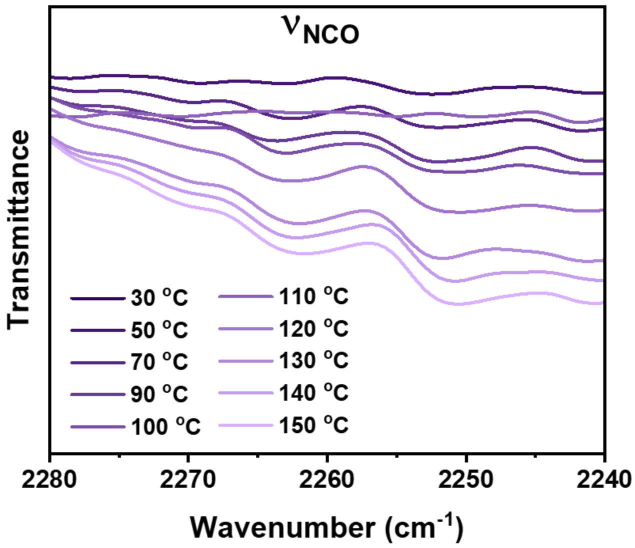


Figure S21. FTIR spectra of (polyTAH-20% TMXDI) between 30 and 150°C.

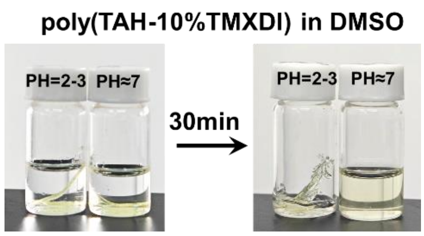


Figure S22. Photographs of poly(TAH-10% TMXDI) in DMSO with distinct pH value.

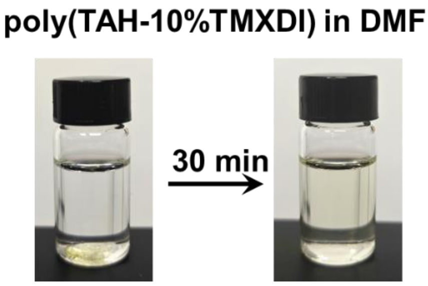


Figure S23. Photographs of poly(TAH-10% TMXDI) in DMF.

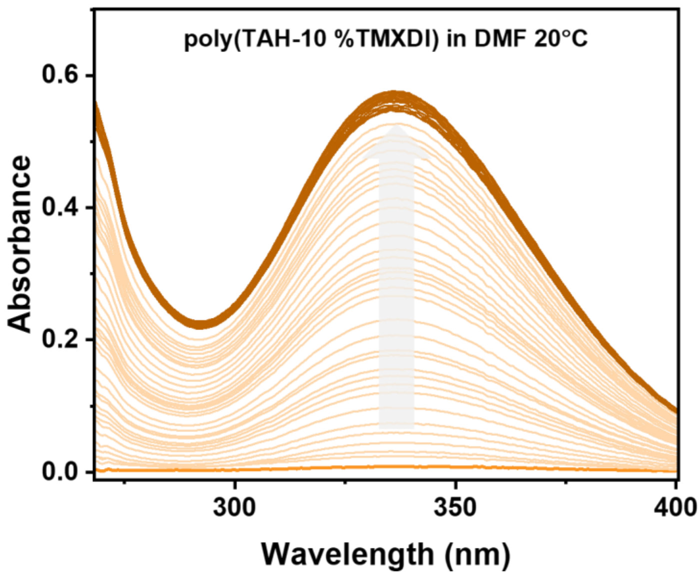


Figure S24. Real-time UV-Vis monitoring depolymerization of poly(TAH-10% TMXDI) in DMF at 20°C.