Electronic supplementary information (ESI) for

Rapid Sulfur-Oxazoline Polymerization for Biobased Dynamic Polyamide Networks

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Materials. Sublimed sulfur (S_8,99%) was purchased from Xilong Chemical Co., Ltd. Eugenol (99%), potassium hydroxide (KOH,95%),2-ethyl-2-oxazoline, 2-phenyl-2-oxazoline,2-chloroethylamine hydrochloride (98%) were purchased from Energy. Chloroacetic acid (98%), ethanolamine (99%), 10-undecenoyl chloride (98%), triethylamine (TEA,99%), sodium hydroxide (NaOH, 95%), sodium bicarbonate ($NaHCO_3$,99.5%), and anhydrous magnesium sulfate ($MgSO_4$, 98%) were purchased from Macklin. Thionyl chloride ($SOCl_2$, 98%) were purchased from Rhon. 5,5-dimethyl-1-pyrrolinen-oxide (DMPO, 97%), 2-methyl-2-oxazoline (95%) was purchased from Bide Pharmatech. Dichloromethane (DCM) (99.5%, AR) and methanol (95%, AR) are from General agents. All chemicals were used as received without further purification.

Characterizations. A 600 MHz Agilent DD2 branch magnetic resonance spectrometer was used to confirm the synthesized organic compounds using $CDCl_3$ and $(CD_3)_2SO$ as the solvent. Tetramethylsilane (TMS) was used as internal reference compound. Fourier transform infrared spectroscopy (FT-IR) was measured by tensor II Fourier transform 5 infrared spectrometer and the spectra were obtained by attenuated total reflection (ATR) technology. The scanning range is 400-4000 cm^{-1} with a resolution of 4 cm^{-1}, and the scanning speed is 32 times per second. The thermal stability of the polymers was measured by thermal gravimetric analysis (TGA instrument, Netzsch 209F3). The sample (about 5.0 mg) was heated to 100 ^oC at a heating rate of 10 ^oC/min and maintained for 5 mins. After cooling down to room temperature, it was heated to 700 ^oC under nitrogen atmosphere (80 ml/min flow rate). Netzsch 200F3 DSC was used to check the glass transition temperature (T_g) of polymer samples. First, the sample (around 5 mg) was heated from room temperature to 160 ^oC and kept at equilibrium for 3 min to remove the heat history. Then, the temperature was decreased to -60 ^oC in 3 mins before being gradually increased to 160 ^oC at 10 ^oC /min. DMA 242E /1/G (tension mode) was used to test the dynamic mechanical properties. The cured samples were cut into cuboids of 2.05 mm $*$ 25 mm $*$ 0.7 mm for testing from -5 to 150 ^oC (heating rate = 5 ^oC /min) with a frequency of 1 Hz. The uniaxial tensile test was carried out on the UTM2502 universal testing machine equipped with 100N sensor at 25 ^oC. The tensile sample was prepared into standard bone like spline with a cutting knife and tested at the speed of 10 mm/min. All rheological characterization of polysulfide materials was performed on a rotational rheometer (Discovery HR-1, TA Instruments, USA) equipped with a 25 mm diameter parallel-plate geometry. Angular frequency sweep measurements were conducted under nitrogen atmosphere, with a dynamic oscillation frequency range of 500 to 0.05 rad/s and a constant strain of 0.5%. The electron paramagnetic resonance (EPR) experiment was conducted using a continuous-wave X-band EPR spectrometer (Elexsys E500, Bruker BioSpin), which is equipped with a rectangular resonator operating in the TE_{102} mode. For samples with added spin-trapping agents, the experimental measurement temperature was set at approximately 300 K (room temperature). The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) with G1316A detector, Agilent 1260 HPLC pump and PL gel (MIXED-A, effective molecular weight range 200-2,000,000). The samples were dissolved in N, N-dimethylformamide (DMF), and filtered by a 0.22 µm filter before testing. The insoluble content of cross-linked materials is tested by placing approximately 0.2

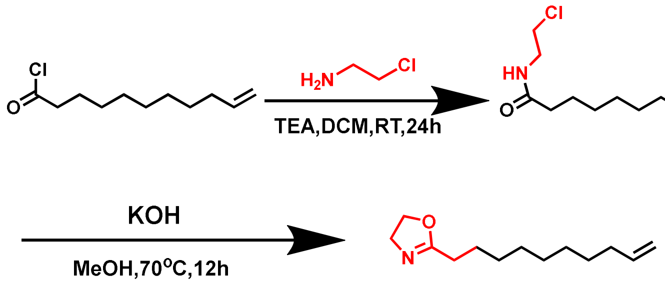
grams of the cross-linked film in THF, DCM, and DMF, soaking at 60 °C for 24 hours, and then weighing the completely dried material to calculate the weight difference. Field emission scanning electron microscope (FE-SEM) were separately used to investigate the morphologies and elemental components of the films. The samples were firstly sputter-coated with a 2 nm layer of platinum and then observed on a Hitachi S-4800 operating at 15 kV.

Model reactions of oxazoline compounds (2-ethyl-2-oxazoline, 2-phenyl-2-oxazoline, 2-methyl-2-oxazoline) with sulfur. The model reactions between sulfur (S_8) and 2-ethyl-2-oxazoline/2-phenyl-2-oxazoline/2-methyl-2-oxazoline were conducted by adding the reactants into 20 ml glass vials at a mass ratio of 1:1. The total mass of each reaction mixture was maintained at 3.0 g. A magnetic stir bar was introduced, and the mixtures were stirred and heated at 120 ^{o}C, 140 ^{o}C, and 160 ^{o}C for 10 mins, with sampling performed every 2 mins for ^{1}H NMR and FT-IR analysis. Notably, sulfur and 2-phenyl-2-oxazoline were reacted at 160 ^{o}C at a mass ratio of 1:1 for 24 hours. Sulfur reacts with 2-methyl-2-oxazoline in a model reaction at a 1:1 mass ratio at 140 °C. The reaction mixture is heated for 10 minutes, and samples are taken every 2 minutes for nuclear magnetic resonance analysis (^{1}H NMR, ^{13}C NMR). Additionally, sulfur (S_8) and 2-ethyl-2-oxazoline were reacted at varying mass ratios (1:9, 3:7, 5:5, 7:3, 9:1) at 160 °C for 10 mins. After cooling to room temperature, the samples were collected.

The qualitative detection of hydrogen sulfide gas. Charge 5g of sulfur and 5g of EUO in a 50 ml glass vial, and attach DI water wetted lead acetate test paper to the mouth of the vial. Wetting the test paper with distilled water is necessary to activate its reactivity with hydrogen sulfide. Then, the vial was heated at 160°C and hydrogen sulfide was generated. Ensure that the test paper is fully exposed to the gas escaping from the vial. During the reaction process, a gradual color change of the test paper was observed. Taking care to do the test inside a fume hood, since hydrogen sulfide has a strong rotten egg odor and is toxic, so please exercise caution during the operation.

Electron Paramagnetic Resonance (EPR) Analysis Sample Preparation. Place methyl oxazoline (1g) or ethyl oxazoline (1g), and sulfur (1g) in an oil bath with a temperature of 140°C and react under stirring for 6 mins. Then, cool the system to 80°C and add 0.2 mL of 5,5-dimethyl-1-pyrroline N-oxide (DMPO). The mixture was maintained at 80°C for 5 mins. After the system was cooled to room temperature, dilute the sample by adding 0.5 mL of DMSO to prepare a solution for EPR test. To ensure uniform mixing, gently shake the EPR tube for 30 seconds before conducting the electron paramagnetic resonance (EPR) experiment.

Synthesis of undecenyl oxazoline (UCO, Scheme S1)



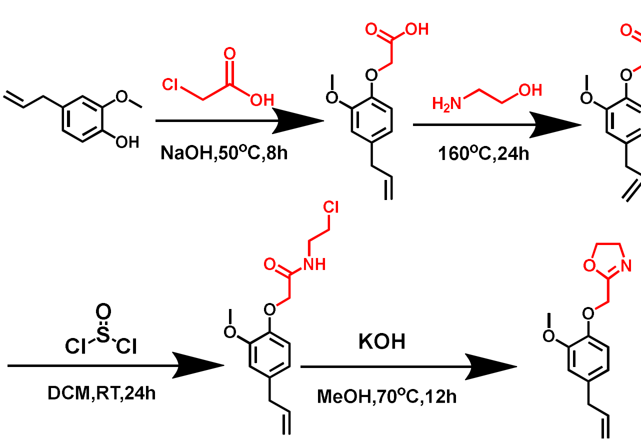
UCO

Scheme S1. Synthetic route of UCO.

Procedures (1) Synthesis of the intermediate: Chloroethylamine hydrochloride (6.38 g, 0.055 mol) was dissolved in anhydrous DCM and transferred to a three-necked flask. Triethylamine (12.65 g, 0.125 mol) was added, followed by N_2 purging (5–10 min) under ice-bath cooling. Undecenoyl chloride (10.136 g, 0.05 mol) was slowly added dropwise, and the mixture was stirred at rt for 24 h. After completion, the aqueous phase was separated, and the organic layer was washed with DCM twice, washed three times with H_2O, and washed one times with saturated NaCl solution. Drying over anhydrous $MgSO_4$ overnight, filtration, and solvent removal by rotary evaporation yielded the crude product,the product yield is 67.98%.

(2) Synthesis of Undecenyl Oxazoline (UCO): Undecenylchloroethylamine (8.35 g, 0.035 mol) and KOH (2.47 g, 0.044 mol) were dissolved in 40 mL anhydrous methanol each and combined in a 100 mL round-bottom flask. The reaction was heated at 70 °C for 12 h. Upon cooling, KCl was removed by filtration, and methanol was evaporated. Persistent precipitates were redissolved in DCM, filtered, and concentrated to afford a colorless liquid product, the product yield is 58%.

Synthesis of eugenol oxazoline (EUO, Scheme S2)



EUO

Scheme S2. Synthetic route of EUO.

Procedures (1) Etherification: eugenol (4.93 g, 0.03 mol) was added to a 100 mL round-bottom flask. Under ice-bath cooling, NaOH solution (4.8 g dissolved in 200 mL H_2O) was added dropwise, forming a yellow precipitate. Chloroacetic acid solution (5.67 g, 0.06 mol dissolved in 10 mL H_2O) was subsequently added dropwise, partially dissolving the precipitate. After 1 h of aging in an ice bath, the mixture was stirred at 50 ^oC for 8 h. Upon cooling, concentrated HCl was added dropwise, initially dissolving the white precipitate before yielding a milky suspension. The product was extracted with hexane, stirred overnight, and filtered to obtain a white solid, the product yield is 93.1%.

(2) Amidation: product from the previous step (20 g, 0.09 mol) and ethanolamine (6.6 g, 0.1 mol) were charged into a 100 mL round-bottom flask.After purging with N_2 for 5-10 min, the reaction was heated at 160 ^oC for 24 h. The crude product was dissolved in DCM, washed three times with water and washed one times with saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation to afford a solid product,the product yield is 71.21%.

(3) Chlorination: product from the previous step (17 g, 0.064 mol) was dissolved in 320 mL DCM. Thionyl chloride (19 g, 0.16 mol) was added dropwise under ice-bath cooling, and the mixture was stirred for 24 h. The reaction was quenched with saturated $NaHCO_3$ solution, washed with water twice, and concentrated under reduced pressure to yield a liquid product the product yield is 83.7%.

(4) Cyclization to make EUO: product from the previous step (5 g, 0.017 mol) was dissolved in 20 mL anhydrous methanol and transferred to a 250 mL round-bottom flask. A solution of KOH (1.3 g, 0.023 mol) in 20 mL anhydrous methanol was added dropwise, and the mixture was stirred at 70 ^oC for 24 h. After filtration and solvent removal by rotary evaporation, the target product was obtained,the product yield is 39.5%.

Preparation of sulfur-modified polyamide networks. Sulfur powder (S_8), EUO, and UCO were combined in specific molar ratios within a 20 mL glass vial. The total mass of each reaction mixture was maintained at 3.0 g. A magnetic stirrer bar was introduced, and the mixture was stirred and heated at 160 oC for 30 minutes. Upon cooling to room temperature, the sample was collected to obtain the final product.

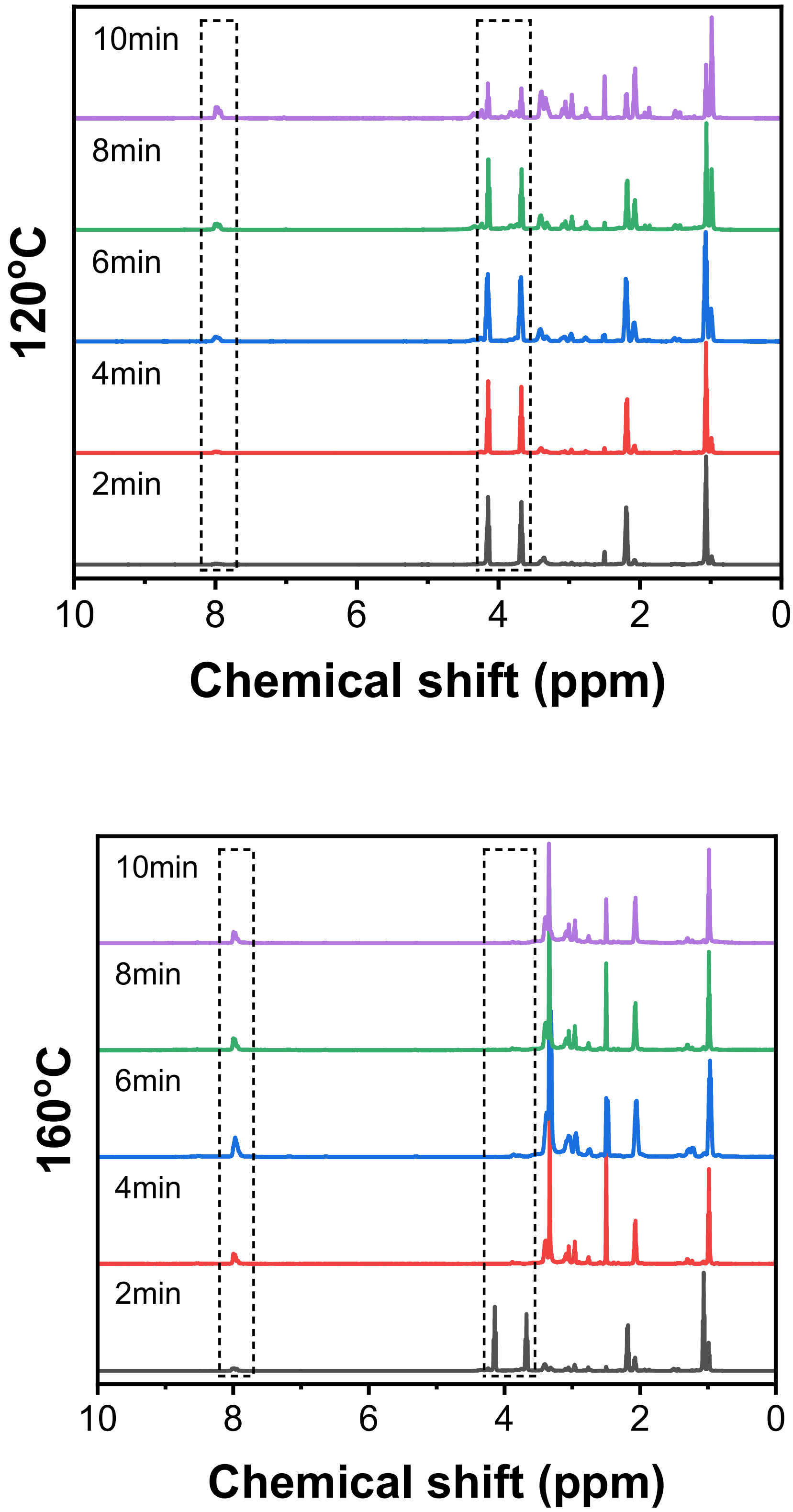


Figure S1. ^{1}H NMR spectra of the model reactions between sulfur and 2-ethyl-2-oxazoline at 120 °C and 160 °C.

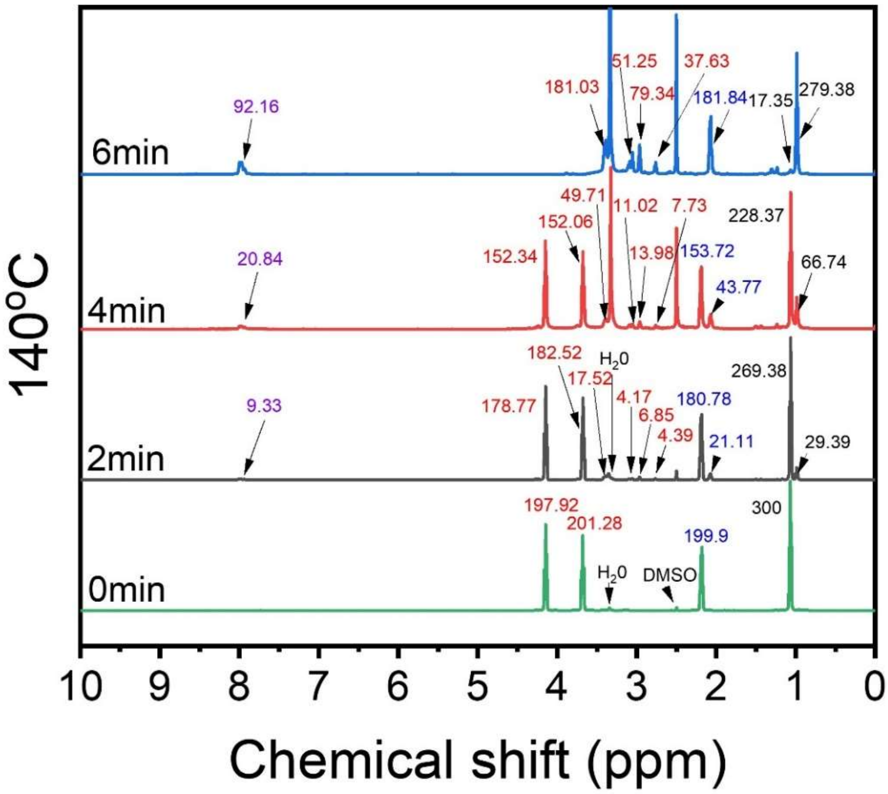


Figure S2. ^{1}H NMR peak integration values for the model reaction at 140 ^{o}C.

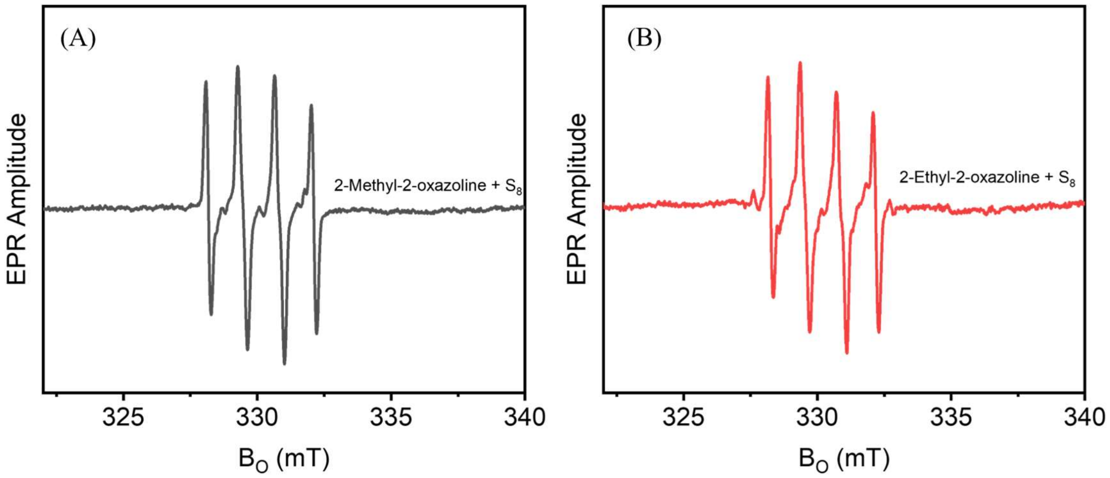
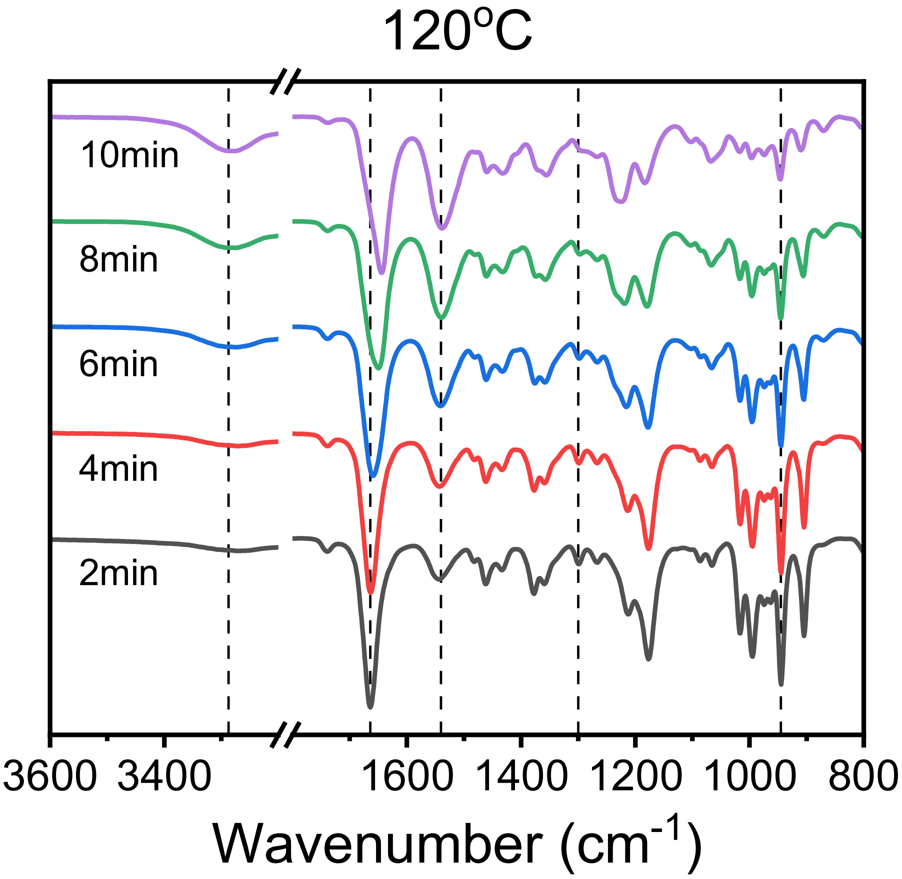
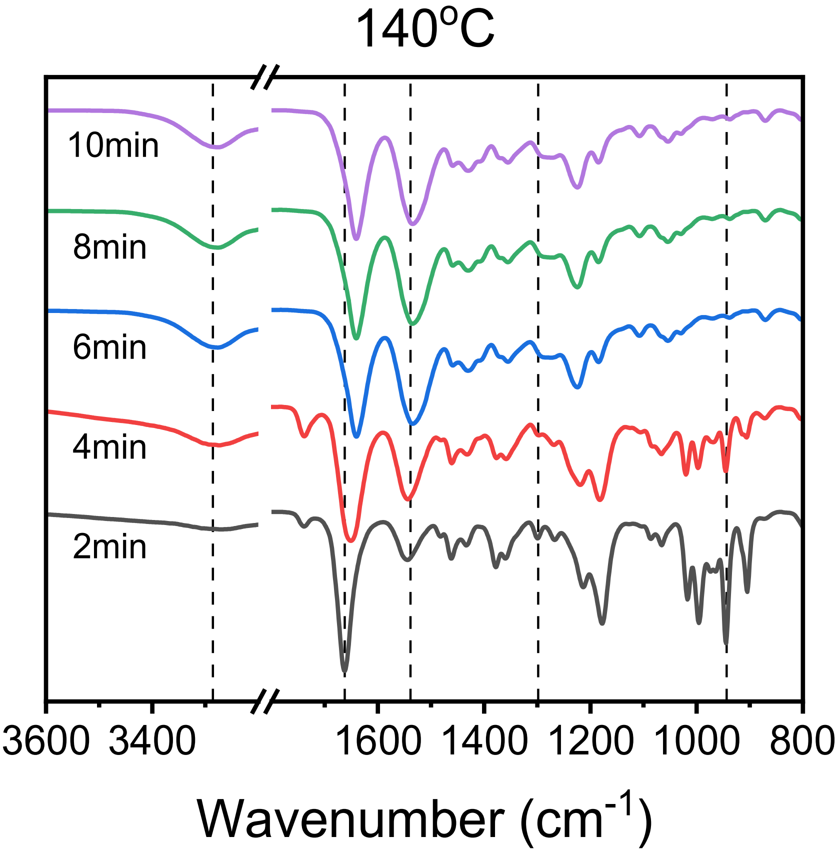


Figure S3. EPR analysis of sulfur reactions with (A) 2-ethyl-2-oxazoline and (B) 2-methyl-2-oxazoline.


120°C

10min
8min
6min
4min
2min
3600
3400
1600
1400
1200
1000
800
Wavenumber (cm^{-1})


140°C

10min
8min
6min
4min
2min
3600
3400
1600
1400
1200
1000
800
Wavenumber (cm^{-1})

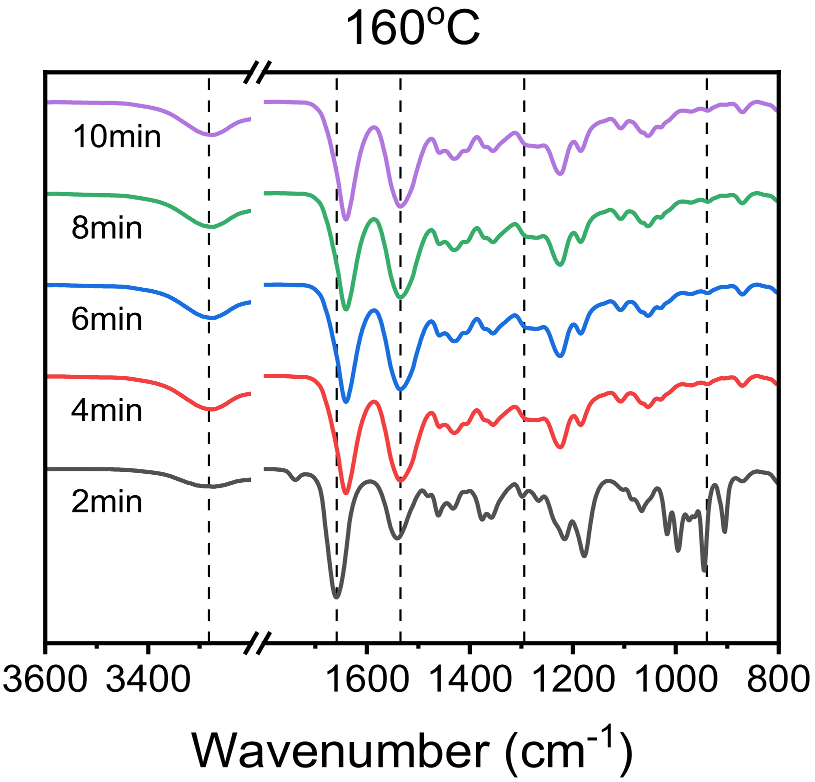
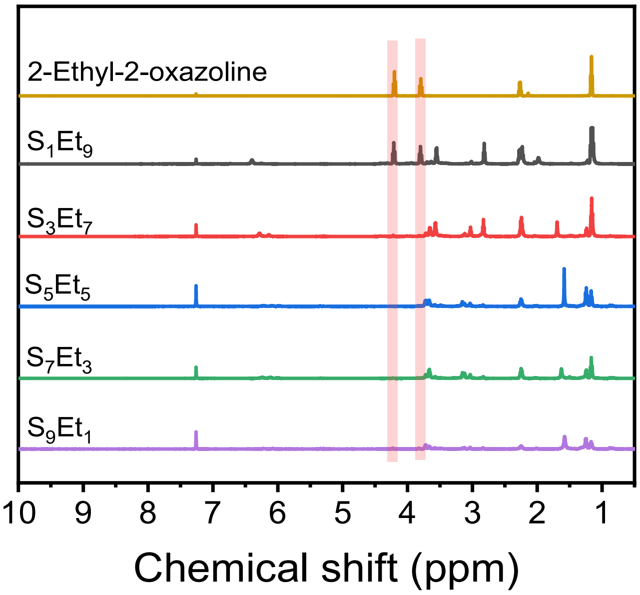
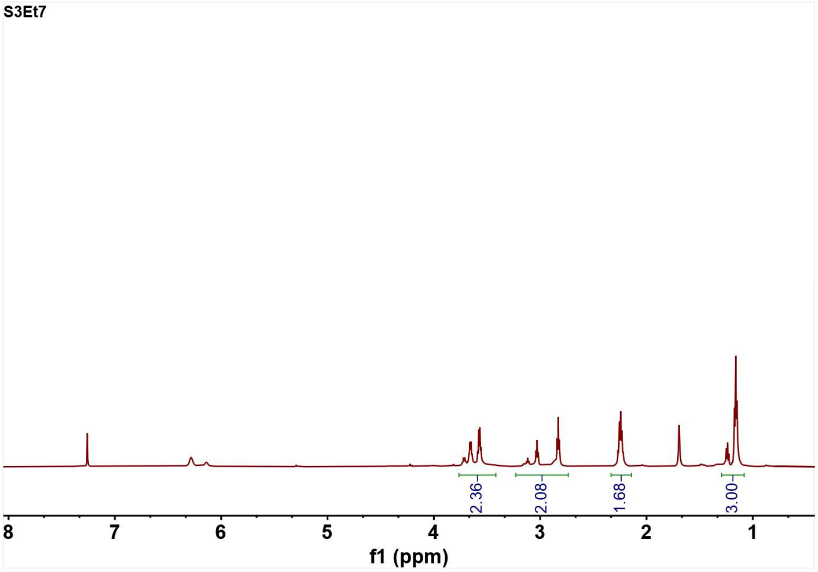
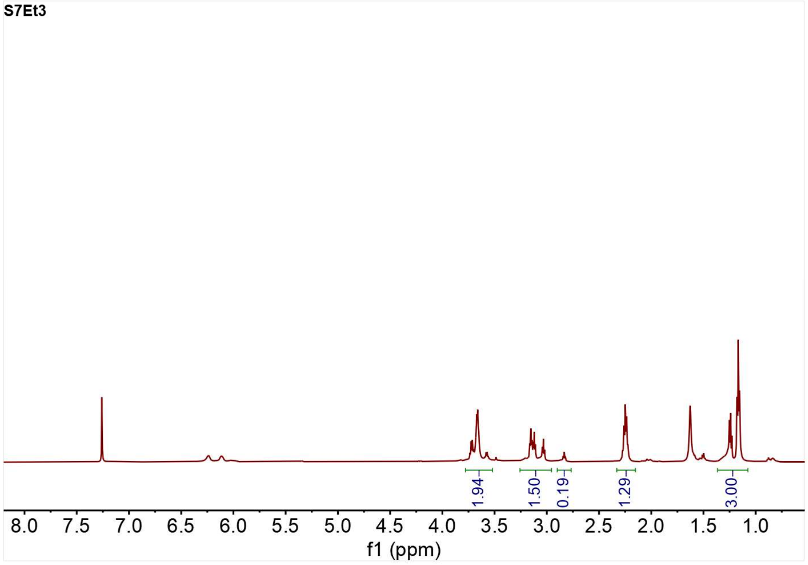


Figure S4. FT-IR spectra of the model reactions between sulfur and 2-ethyl-2oxazoline at 120 °C, 140 °C, 160 °C.

Figure S5. Digital photographs of reaction mixtures with varying weight ratios of sulfur to 2-ethyl-2-oxazoline after heating at 160 °C for 10 minutes and cooling.


2-Ethyl-2-oxazoline
S_1Et_9
S_3Et_7
S_5Et_5
S_7Et_3
S_9Et_1
10
9
8
7
6
5
4
3
2
1
Chemical shift (ppm)


S3Et7
2.36
2.08
1.68
3.00
8
7
6
5
4
3
2
1
f1 (ppm)


S7Et3
1.94
1.50
0.19
1.29
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

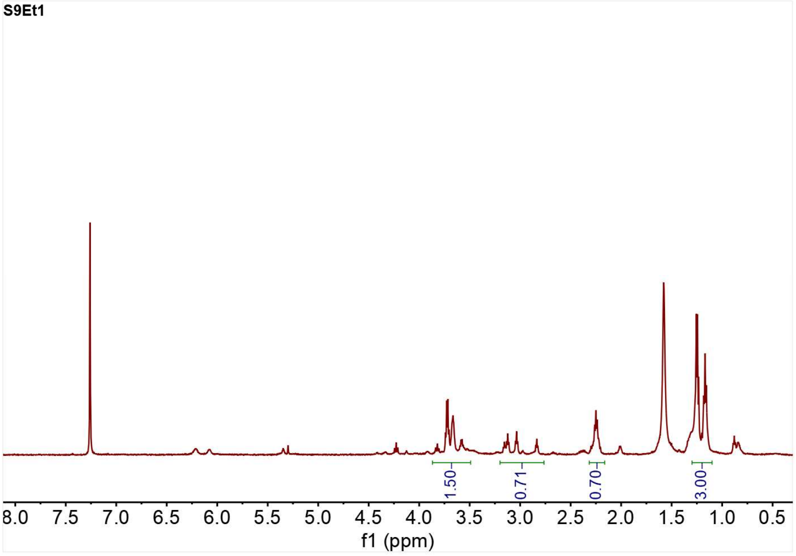


Figure S6. ^{1}H NMR spectra of reaction mixtures with varying weight ratios of sulfur to 2-ethyl-2-oxazoline after heating at 160 ^{o}C for 10 minutes and cooling; ^{1}H NMR spectral integration corresponding to the samples of S_3Et_7, S_7Et_3, and S_9Et_1.

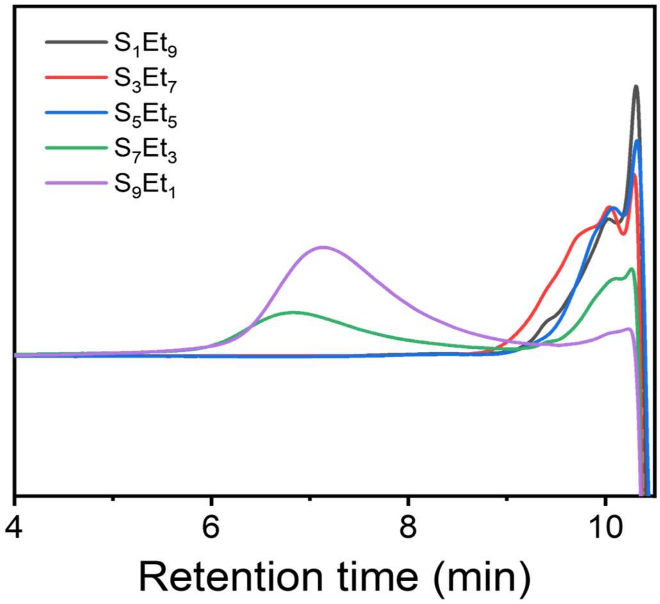


Figure S7. GPC analysis of products from the reactions between varying weight ratios of sulfur and 2-ethyl-2-oxazoline after heating at 160°C for 10 minutes.

Table S1. Molecular weight information from GPC analysis of the products from the sulfur & 2-ethyl-2-oxazoline polymerizations after heating at 160 °C for 10 minutes.

Samples	M_n (g/mol)	M_w (g/mol)	Đ
S_1Et_9	1040	1220	1.17
S_3Et_7	1410	1710	1.21
S_5Et_5	1020	1180	1.16
S_7Et_3	84810	414220	4.88
S_9Et_1	28860	255750	8.86

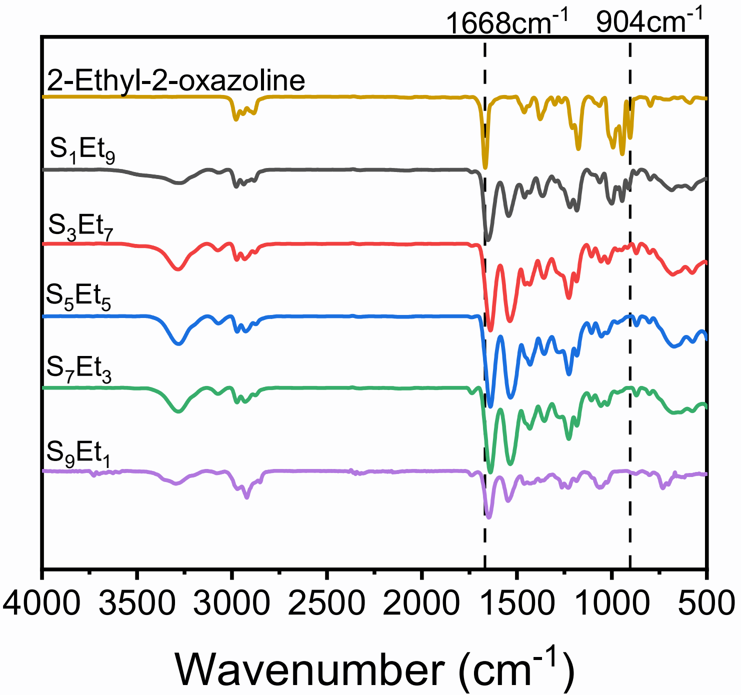
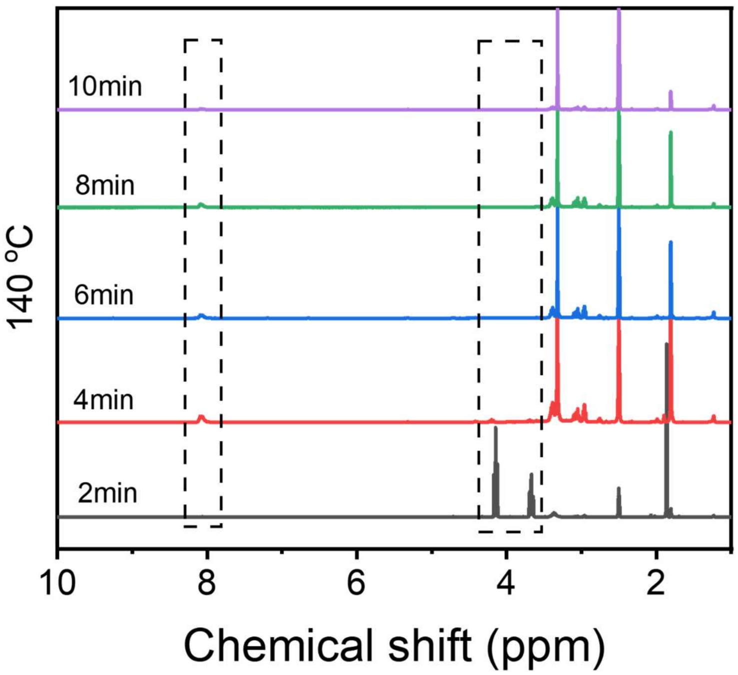


Figure S8. FT-IR spectra of products from the reactions between varying weight ratios of sulfur and 2-ethyl-2-oxazoline after heating at 160°C for 10 minutes.



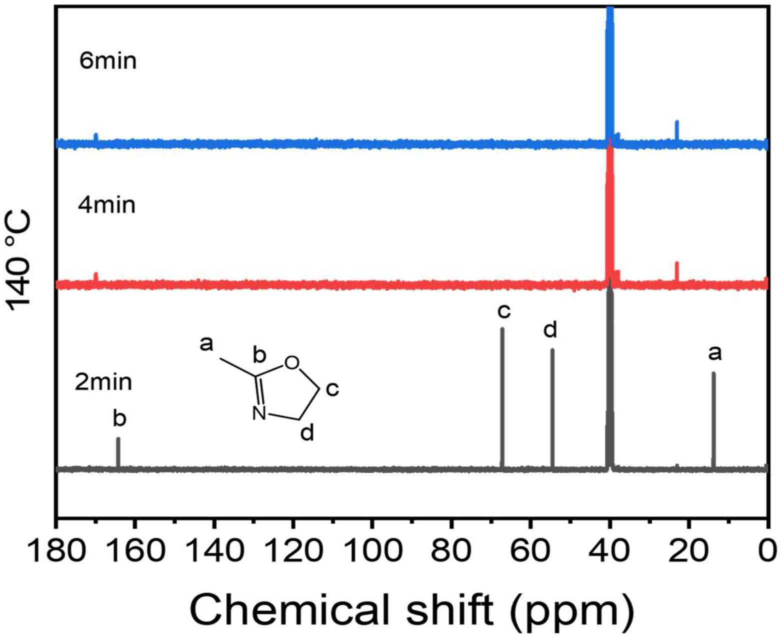
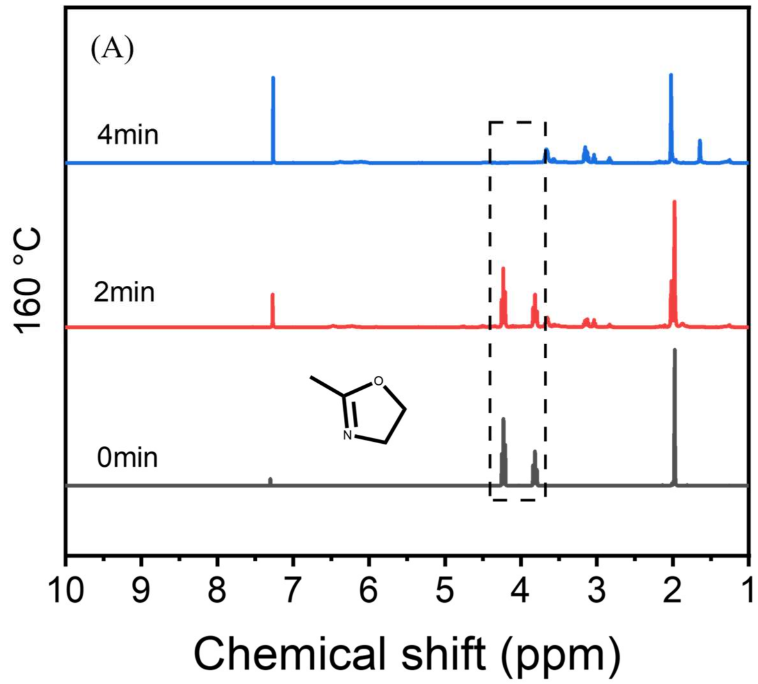
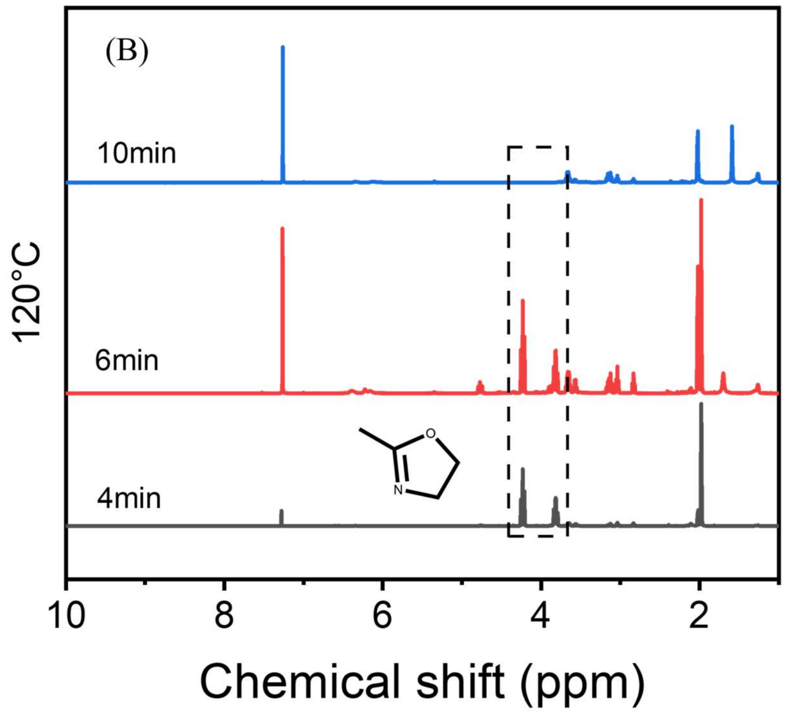


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of the model reactions between sulfur and 2-methyl-2-oxazoline at 140 °C.


(A)
160 °C
4min
2min
0min
O
N
10
9
8
7
6
5
4
3
2
1
Chemical shift (ppm)


(B)
120°C
10min
6min
4min
O
N
10
8
6
4
2
Chemical shift (ppm)

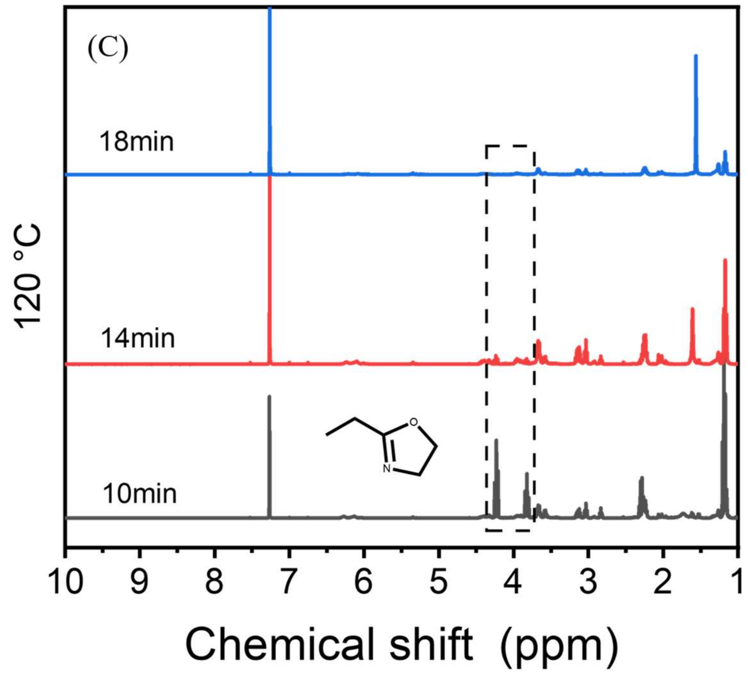


Figure S10. ^{1}H NMR spectra of the model reactions between sulfur and 2-methyl-2-oxazoline at (A) 160 ^{o}C and (B) 120 ^{o}C, (C) ^{1}H NMR spectra of the model reactions between sulfur and 2-ethyl-2-oxazolin at 120 ^{o}C after 10 mins.

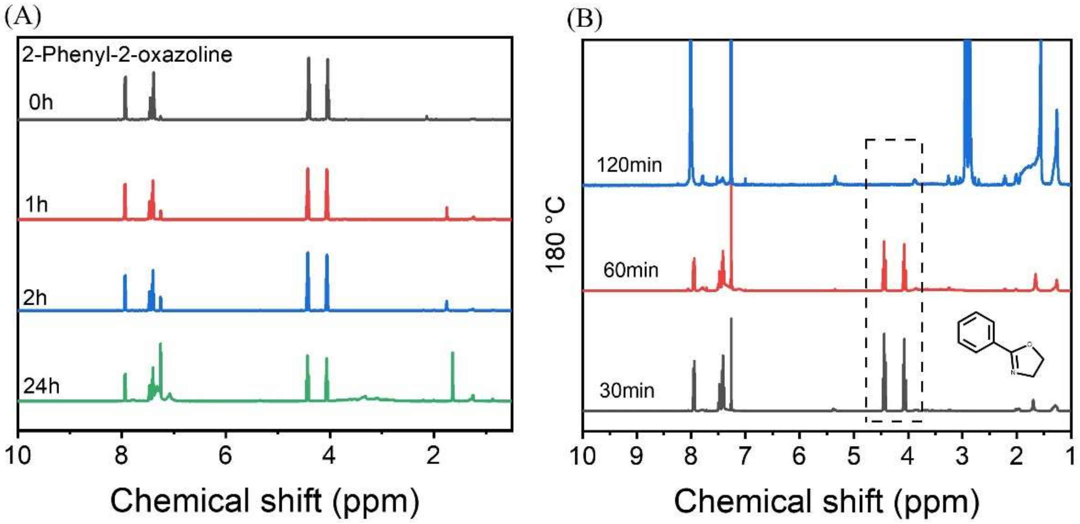


Figure S11. ^{1}H NMR spectra of the reaction between sulfur and 2-phenyl-2-oxazoline (A) at 160 °C and (B) at 180 ^{o}C.

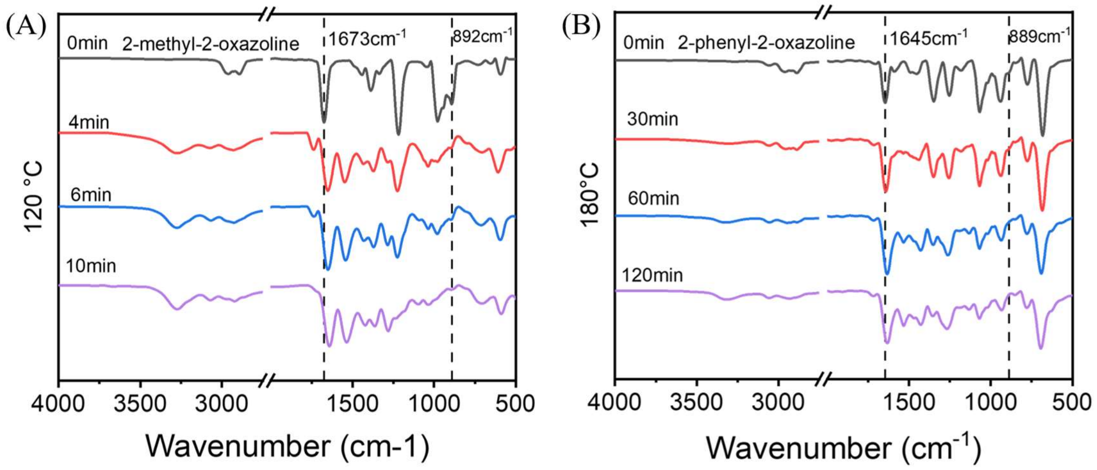
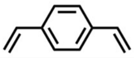
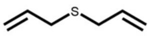
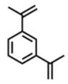
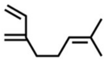
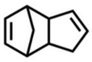
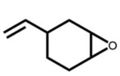
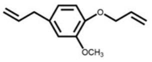
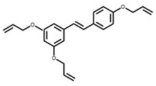
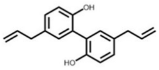
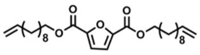
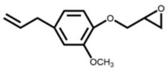
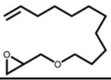
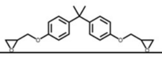
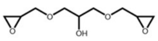
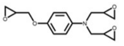
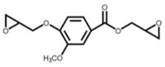
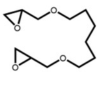


Figure S12. FT-IR spectra of the model reactions. (A) sulfur and 2-methyl-2-oxazoline at 120 ^{o}C, (B) sulfur and 2-phenyl-2-oxazoline at 180 ^{o}C.

Table S2. Structures of reported organic compounds to react with sulfur, with the curing time, curing temperature, mechanical properties summarized.

S_X	Reactant	Chemical structure	Samples	Catalyst	Curing time (h)	Temperature (°C)	Tensile strength (MPa)	Tensile strain (%)	Ref
S1	DVB		Sample 1	no	185 °C curing 0.25h, 120 °C 3h		/	/	*J. Power Sources 329 (2016) 72e78*
S2	DAS		Sample 2	no	1h	180 °C	/	/	*ACS Appl. Mater. Interfaces* 2019, 11, 38, 35312–35318
S3	DIB		Sample 3	$Zn(DTC)_2$	5h	135°C	/	/	*ACS Appl. Polym. Mater.* 2022, 4, 7, 4901–4911
S4	Myrcene		Sample 4	no	180 °C curing 2h, 140 °C 2h		/	/	*ACS Appl. Polym. Mater.* 2023, 5, 9, 6761–6765
S5	DCPD		Sample 5	no	1h	160°C	/	/	*Macromolecules* 2024, 57, 6, 2905–2914
S6	VE		Sample 6	no	16h	130°C	/	/	*Macromolecules* 2024, 57, 2, 470–480
S7	EAE		Sample 7	no	150 °C curing 1h, 180 °C 0.17h		/	/	*Mater. Chem. Front*, 2017,1, 1818-1822
S8	AER		Sample 8	no	4h	140 °C	/	/	*ACS Sustainable Chem. Eng.* 2024, 12, 46, 16924–16933
S9	Magnolol		Sample 9	no	5.5h	160 °C	/	/	*ACS Sustainable Chem. Eng.* 2023, 11, 51, 18041–18050
S10	UF		Sample 10	$Zn(DTC)_2$	5h	130 °C	0.52 ± 0.03	180 ± 11	*Macromolecules* 2024, 57, 12, 5849–5859
			Sample 11				1.58 ± 0.12	47 ± 2	
			Sample 12				1.97 ± 0.21	35 ± 5	
S11	EGE,UGE	 	Sample 13	no	4h	160 °C	2.7±.2	119.7±10.6	*ACS Sustainable Chem. Eng.* 2023, 11, 30, 11259–11268
			Sample 14				6.4±0.4	70±12.0	
			Sample 15				11.7±0.9	19.1±1.6	
S12	DGEBA		Sample 16	no	180 °C curing12h, 140 °C 12h		3.17	2.2	*Polym. Chem.*, 2024,15, 1748-1757
	DGEG		Sample 17	no	170 °C curing12h, 140 °C 12h		0.84	21.6	
	DGGA		Sample 18	no			0.58	0.5	
	DGENG		Sample 19	no			0.11	36.6	
S13	VDE,HDE	 	Sample 20	ZDC	4h	180 °C	1.4±0.1	54.6±2.5	ACS Appl. Polym. Mater. 2025, 7, 22, 15790–15798
			Sample 21				2.4±0.1	85.6±3.3	
			Sample 22				5.8±0.5	115.1±1.3	

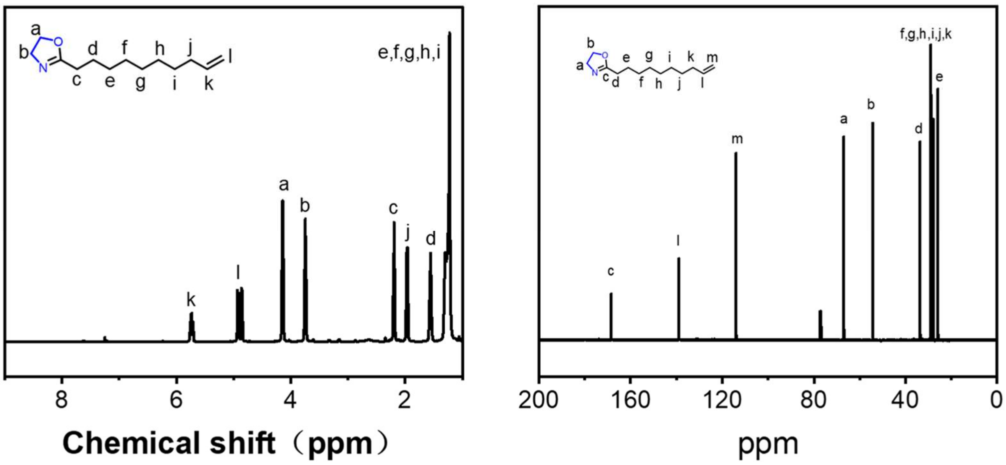


Figure S13. ^{1}H NMR and ^{13}C NMR spectra of undecyl oxazoline monomer (UCO).

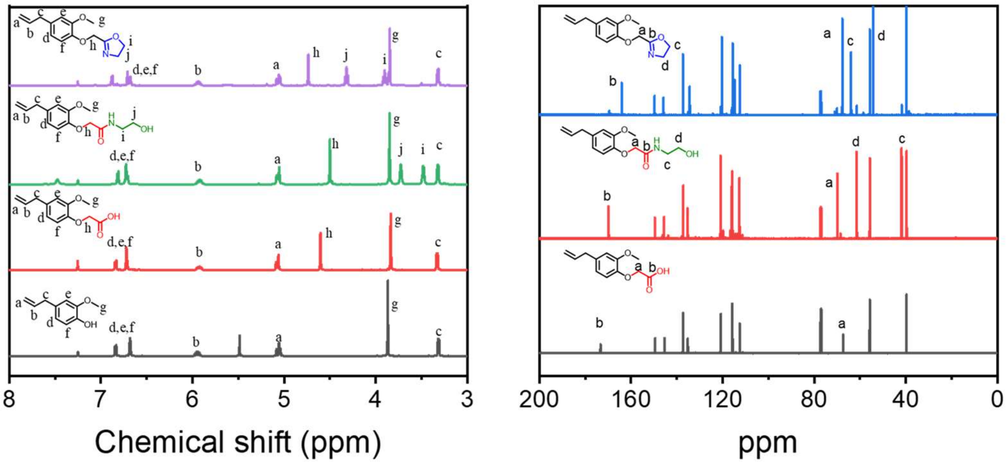
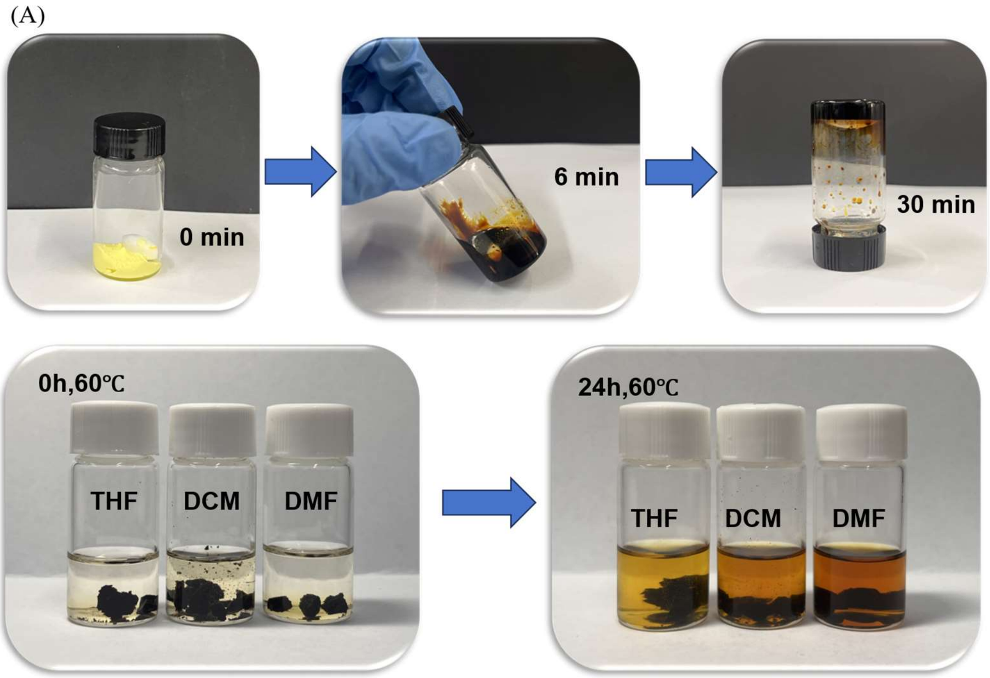


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of the intermediate and final product in $CDCl_3$ during the synthesis of eugenol oxazoline monomer (EUO).



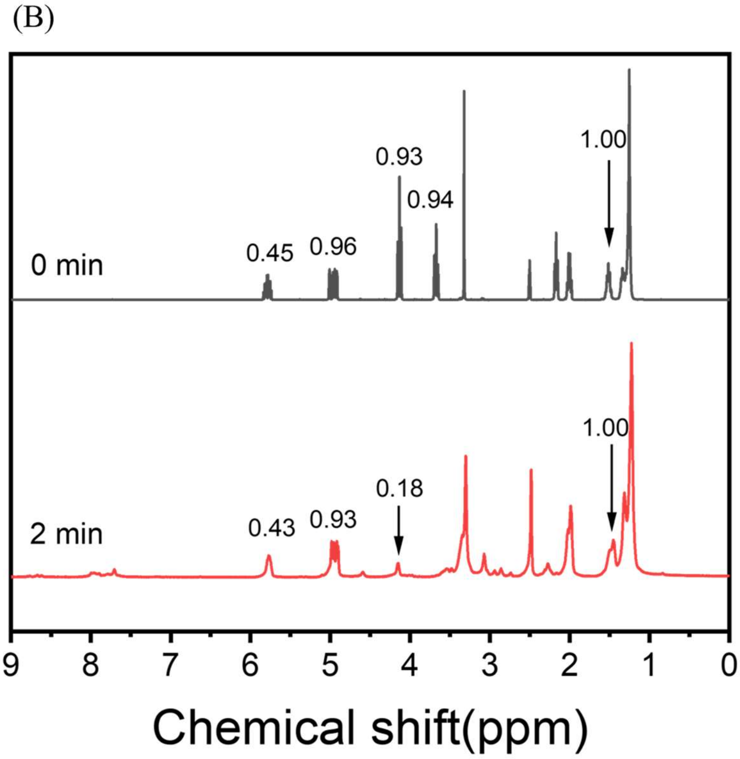


Figure S15. (A) Digital recording: sulfur-UCO mixture heated at 160 °C for 30 mins and solvent compatibility series*:* reaction product immersed in THF,DCM, and DMF; (B) ^{1}H NMR peak integration values for sulfur-UCO reaction heated at 160 °C for 2 mins.

Figure S16. Lead acetate test detection of H_2S generation in EUO-sulfur reaction at 160 °C.

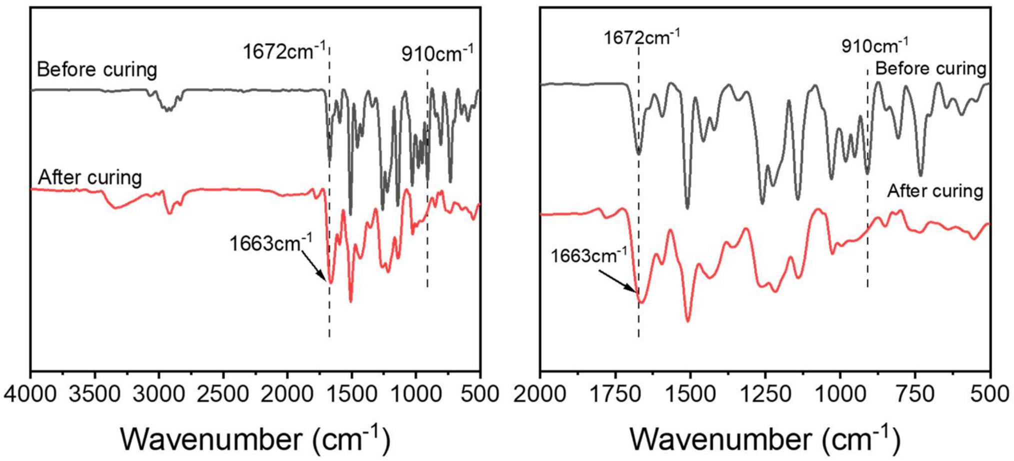


Figure S17. FT-IR spectra of eugenol oxazoline monomer (EUO) before and after polymerization with sulfur.

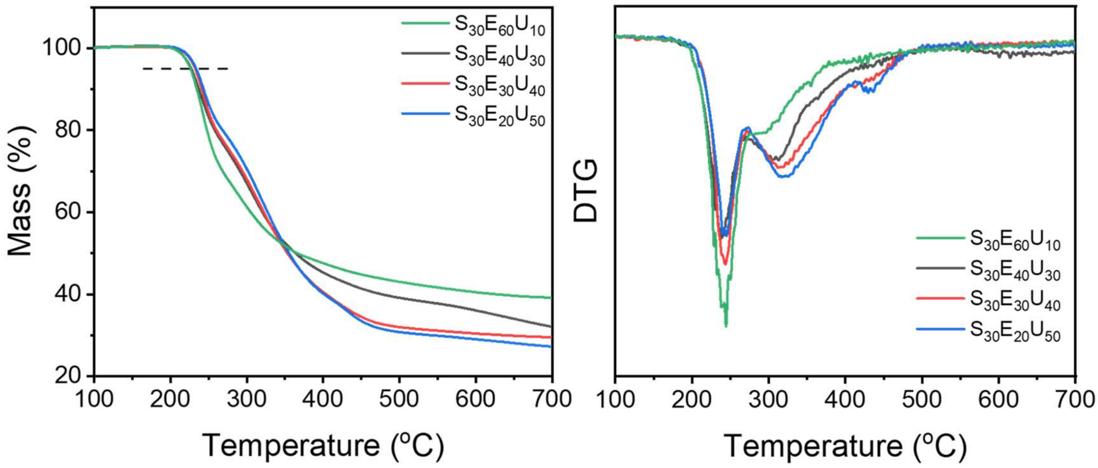


Figure S18. TGA and DTG results for the sulfur modified polyamide networks.

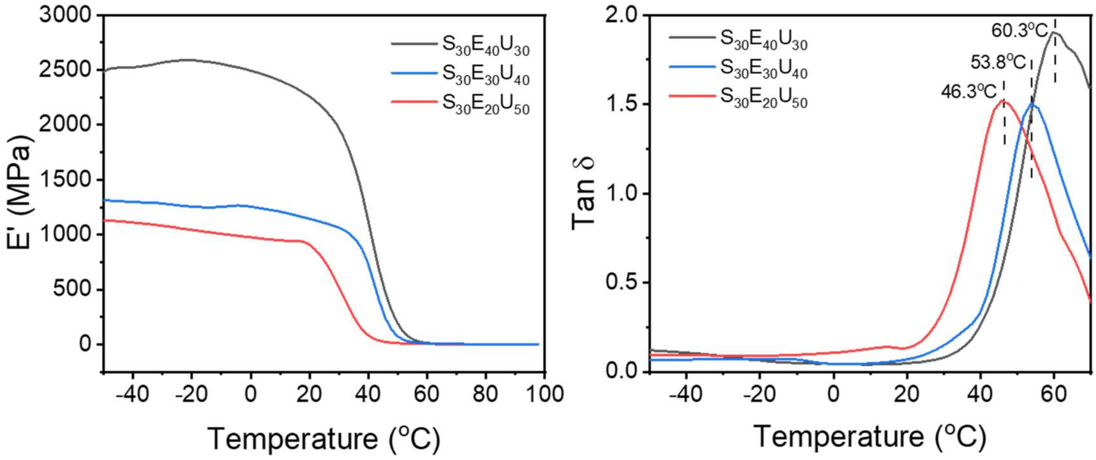


Figure S19. DMA thermograms for storage modulus and tan delta against temperature of the sulfur modified polyamide networks.

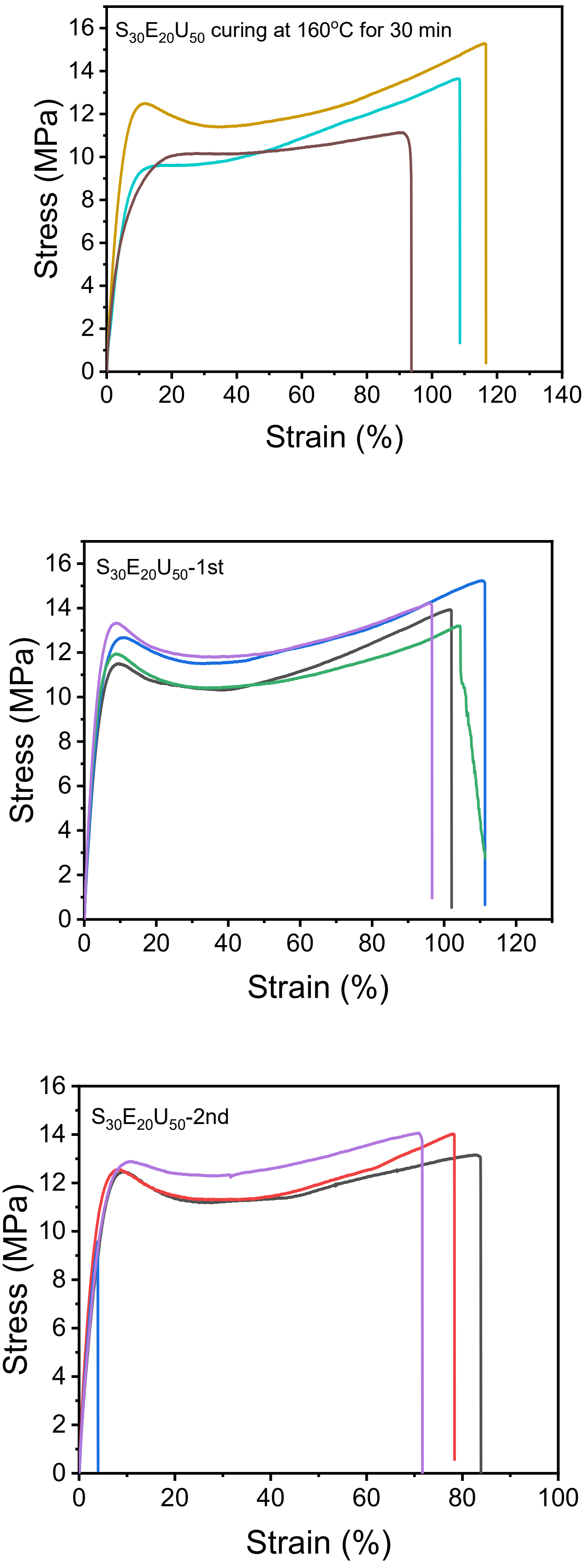


Figure S20. Mechanical properties of S$_{30}$E$_{20}$U$_{50}$ during repeated processing.

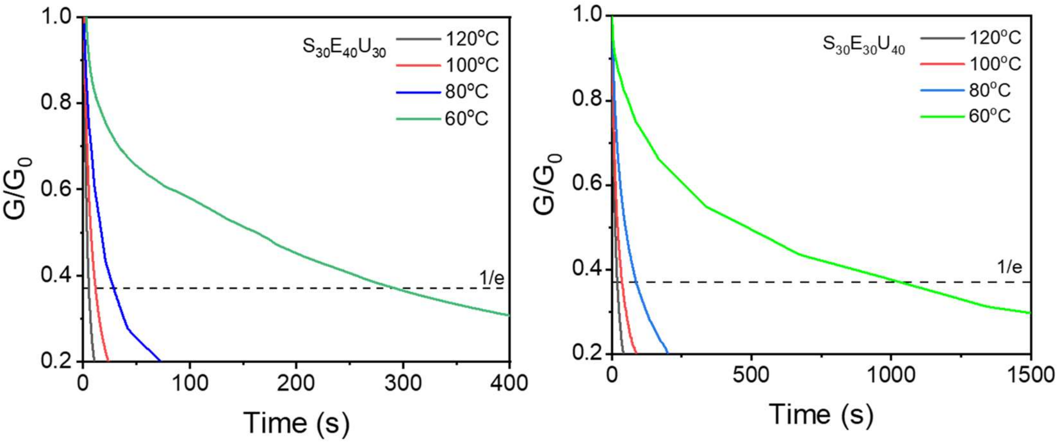


Figure S21. Stress relaxation tests of $S_{30}E_{40}U_{30}$ and $S_{30}E_{30}U_{40}$ samples.

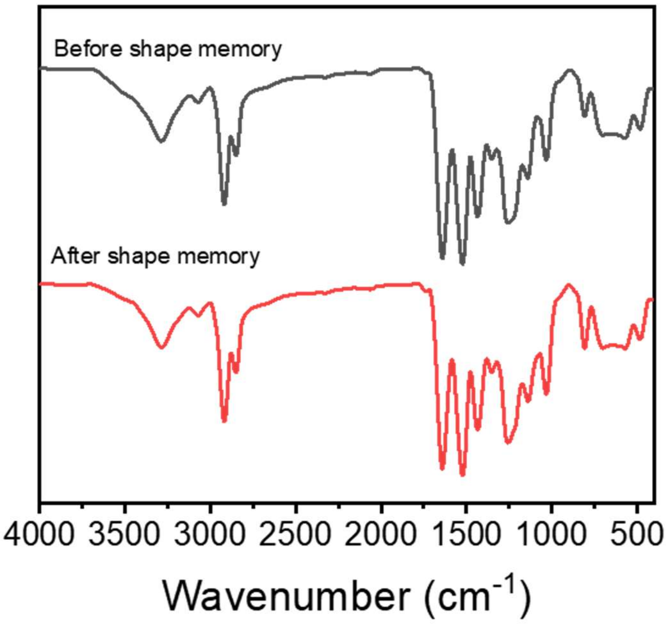


Figure S22. FT-IR characterization of shape memory materials before and after deformation test.

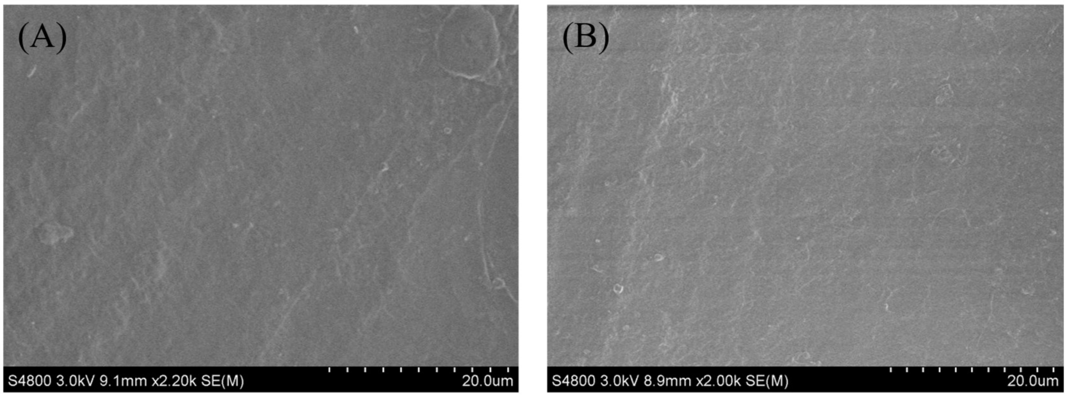


Figure S23 SEM images of the sample (A) before and (B) after shape memory test.