

Electronic Supplementary Information

High Strength, Epoxy Cross-Linked High Sulfur Content Polymers from One-Step Reactive Compatibilization Inverse Vulcanization

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Experimental Procedures

Materials and Chemicals

Sulfur powder (S₈, sublimed, -100 mesh, 99.5%, Alfa Aesar), allyl glycidyl ether (AGE, >99.0%, TCI), allyl butyl ether (ABE, >97.0%, TCI), butyl glycidyl ether (BGE, 95%, Sigma-Aldrich), dimethyl terephthalate (DMT, ReagentPlus[®], >99%, Sigma-Aldrich), chloroform-d (CDCl₃, 99.8 atom % D, Sigma-Aldrich), hydrochloric acid (HCl solution, ACS reagent, 37%, Sigma-Aldrich) were purchased and used as received without further purification. 1,1-Dimethyl allyl glycidyl ether (DAGE) was prepared following previously reported procedures.¹

Instrumentation and Characterization

Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, USA) or a Tensor 27 IR (Bruker, USA) using ATR mode. Field emission scanning electron microscope (FE-SEM) images of the polymers and corresponding energy dispersive X-ray spectroscopy (EDX) elemental mapping were obtained using a Zeiss Sigma 300 FE-SEM equipped with Bruker XFlash 6 |10 detector. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 4000 (Perkin-Elmer, USA). Thermogravimetric analysis (TGA) was conducted on TGA Q500 (TA Instruments, USA) from room temperature to 600 °C with a heating rate of 10 °C/min under N₂ atmosphere. ¹H nuclear magnetic resonance (NMR) spectra were obtained using a Avance III 400 MHz NMR spectrometer (Bruker, USA). Chemical shifts were referenced to residual CHCl₃ (δ: 7.26 ppm) in CDCl₃. Solid-state ¹³C NMR spectra were obtained using Avance I solid-state NMR (Bruker, USA) with 7 Tesla magnet with 300 MHz ¹H resonance frequency) under 5 kHz sample spinning at the magic angle. Tensile strength was measured using a universal testing machine (Instron 5567, USA). Dynamic mechanical analysis for quantifying the shape memory effect was conducted using DMA Q800 (TA instruments, USA). Powder X-ray

diffraction (PXRD) was conducted on a X'Pert Pro X-ray diffractometer (Malvern PANalytical, 1.35 kW). Elemental analysis was conducted with Flash EA1112 CHNS (Thermo Scientific).

Synthesis of 1,1-Dimethyl Allyl Glycidyl Ether (DAGE)

Epichlorohydrin (240 mmol, 18.8 mL) and tetrabutylammonium bromide (3 mmol, 0.97 g) were added to a 40% w/w NaOH aqueous solution (100 mL) at 0 °C. The mixture was stirred vigorously, and 2-methyl-3-buten-2-ol (60 mmol, 6.27 mL) was slowly added to the reaction mixture over 30 minutes using a syringe pump. The reaction mixture was then removed from ice bath and stirred for 15 hours under ambient temperature. The reaction mixture was diluted with water (100 mL) and extracted with diethyl ether (3 x 50 mL). The organic layers were collected, washed with brine (100 mL), dried over MgSO₄, and concentrated *in vacuo*. The crude product was purified using flash column chromatography (ethyl acetate : hexanes = 1 : 5) to give the title compound as a clear oil (4.1 g, 48 %). ¹H NMR (400 MHz, CDCl₃, 20 °C, TMS): δ = 5.81 (m, 1H; CH₂CH), 5.12 (m, 2H; CH₂CH), 3.48 (m, 1H; OCH₂), 3.33 (m, 1H; OCH₂), 3.09 (s, 1H; OCH), 2.79 (m, 1H; OCH₂), 2.60 (m, 1H; OCH₂), 1.28 ppm (s, 6H; CCH₃). ¹³C NMR (100 MHz, CDCl₃, 20 °C, TMS): δ = 143.5 (CHCH₂), 114.4 (CHCH₂), 75.7 (C(CH₃)₂), 64.0 (OCH₂), 51.4 (OCH), 45.1 (OCH₂), 25.8 (CH₃)

Preparation of Poly(S-r-AGE) Samples

S₈ and AGE were added to a 20 mL glass vial equipped with a magnetic stir bar. The sulfur content of each sample varies from 30 wt% to 80 wt%. The mixture was heated to 150 °C under magnetic stirring for several hours until vitrification of the reaction mixture. The reaction product was extracted by a spatula and spread out on a silicone film mold. Further curing of the product in an oven held at 150 °C for ~5 hours yielded a free-standing film of poly(S-r-AGE) copolymer.

The dogbone-shaped specimen for tensile strength measurement was prepared in a similar procedure, except using a Sylgard 184 polydimethylsiloxane (PDMS) mold. The PDMS mold was prepared by mixing the base and curing agent in a 10:1 weight ratio and poured onto a standard dogbone specimen placed in a flat petri dish. The elastomer was degassed and cured at 60 °C for 6 h. The standard specimen was then removed from the mold and the poly(S-r-AGE) prepolymer was poured on the PDMS mold, followed by curing at 150 °C for 5 hours to yield a dogbone specimen of poly(S-r-AGE) copolymer.

Bending Test

A straight rectangular strip of Poly(S-r-AGE) of size 90 x 12 x 1 mm was used for the test. The polymer was deformed to an angle ($\theta_{max} = 180^\circ$) at a temperature $T_{trans} + 20^\circ\text{C}$. Then the polymer was cooled below T_{trans} to fix the deformation and the resultant deformation was measured by angle (θ_i). Then the deformed polymer was heated to $T_{trans} + 20^\circ\text{C}$ and the recovered angle (θ_f) was recorded.

$$\text{Shape Recovery (\%)} = \frac{\theta_i - \theta_f}{\theta_i} \times 100$$

$$\text{Shape Fixity (\%)} = \frac{\theta_{max} - \theta_i}{\theta_{max}} \times 100$$

Shape-Reconfiguration of Poly(S-r-AGE) Film

Poly(S-r-AGE) prepolymer was spread and cured on aluminum foil to obtain the polymer/Al foil bilayer specimen. Above T_{trans} (T_g), the initial permanent shape (flat) was deformed to a desired shape (cube) and the temporary shape (cube) was fixed by cooling below T_{trans} . Reconfiguration of the permanent shape into the deformed (cube) shape was proceeded by annealing the specimen at 100°C for 30 minutes. Although the annealing temperature was above T_{trans} , the deformed shape did not return to the original shape with the help of aluminum foil. After the reprogramming, aluminum foil was removed by immersing the specimen in HCl solution. The deformed shape (cube) became the new permanent shape and shape-memory behavior was well-retained.

Time-resolved Quantitative ^1H NMR Analysis

DMT (dimethyl terephthalate) was used as an internal standard in the reaction mixture of S_8 and AGE. After DMT was completely dissolved in AGE, S_8 was added and the mixture was heated to 140°C . As the reaction proceeds with stirring, aliquots of the mixture were taken over time, dissolved in CDCl_3 and corresponding NMR spectra were obtained.

Reprocessing of Poly(S-r-AGE) samples

Poly(S-r-AGE) samples were grounded using a mortar and pestle. The grains of Poly(S-r-AGE) were filled in a mold and pressed with vertical pressure of 2290 Pa in an 170°C oven for 2 hours. New free-standing film was obtained and it also showed shape memory behavior.

Detailed Analysis Conditions of Solid-State ^{13}C NMR

A poly(S-r-AGE) was crushed and filled into a 7mm ZrO_2 solid-state NMR rotor. Sample spinning stability was ensured by manually mixing in talc powder. Measurements took place in a Bruker Avance 1 spectrometer with 7 Tesla magnet (300 MHz ^1H resonance frequency), under 5 kHz sample spinning at the magic angle. ^{13}C spectroscopy was performed, using indirect excitation with ^1H – ^{13}C cross-polarization for semi-quantitative and sensitive spectroscopy, as well as direct excitation with short (2 s / non-quantitative) and long (40 and 120 s / quantitative) scan recycle delays. Acquisition was performed under high-power heteronuclear proton-decoupling, for 30 ms per scan. Fourier transform was performed with 30 Hz exponential line broadening. Manual baseline correction was applied.

Thermal Analysis

TGA was performed to provide the weight changes of poly(S-r-AGE) compared with pure S_8 and a simple mixture of S_8 and AGE. The samples were heated from 30 °C to 600 °C at a ramp rate of 10 °C/min under nitrogen atmosphere. DSC was utilized to examine thermal transitions of poly(S-r-AGE) copolymers in a temperature range of -50 °C to 120 °C with a 10 °C /minute ramp rate under nitrogen atmosphere. The heating and cooling cycles were repeated three times and the second cycle was used for analysis. Also, DSC was utilized to investigate the heat flow during the copolymerization in an isothermal condition under a nitrogen atmosphere. The samples were heated from 32 °C to 150 °C with a 20 °C /min ramp rate and then held for 900 minutes at 150 °C.

Supplementary Figures

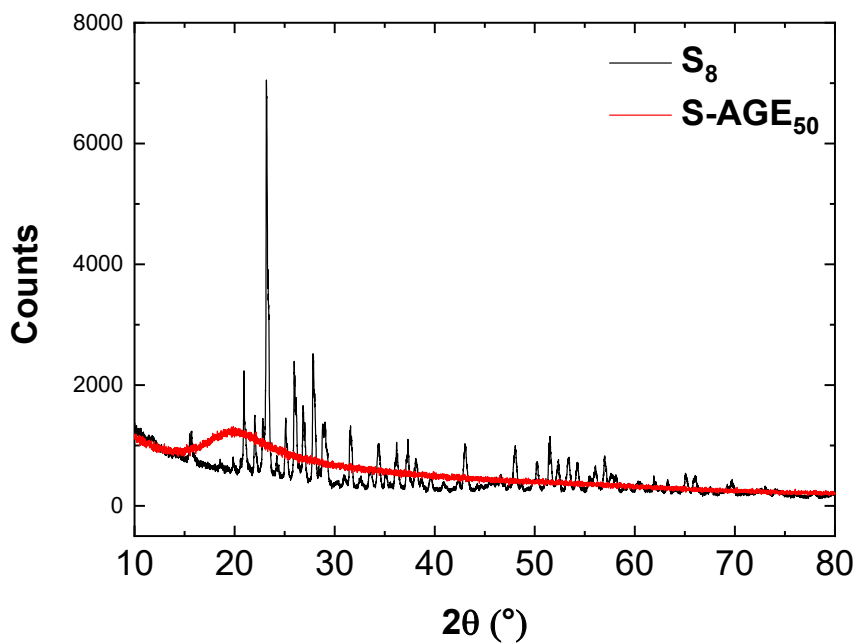


Figure S1. Powder X-ray diffraction pattern of elemental sulfur (black) and poly(S-r-AGE) with 50 wt% sulfur (red).

Table S1. Elemental analysis (CHNS) result of poly(S-r-AGE) with 50 wt% sulfur. Theoretical values were calculated assuming a complete reaction between elemental sulfur and AGE.

Element	Observed (%)	Theoretical (%)
Carbon	31.6983	31.57
Hydrogen	4.3350	4.415
Sulfur	51.7436	50

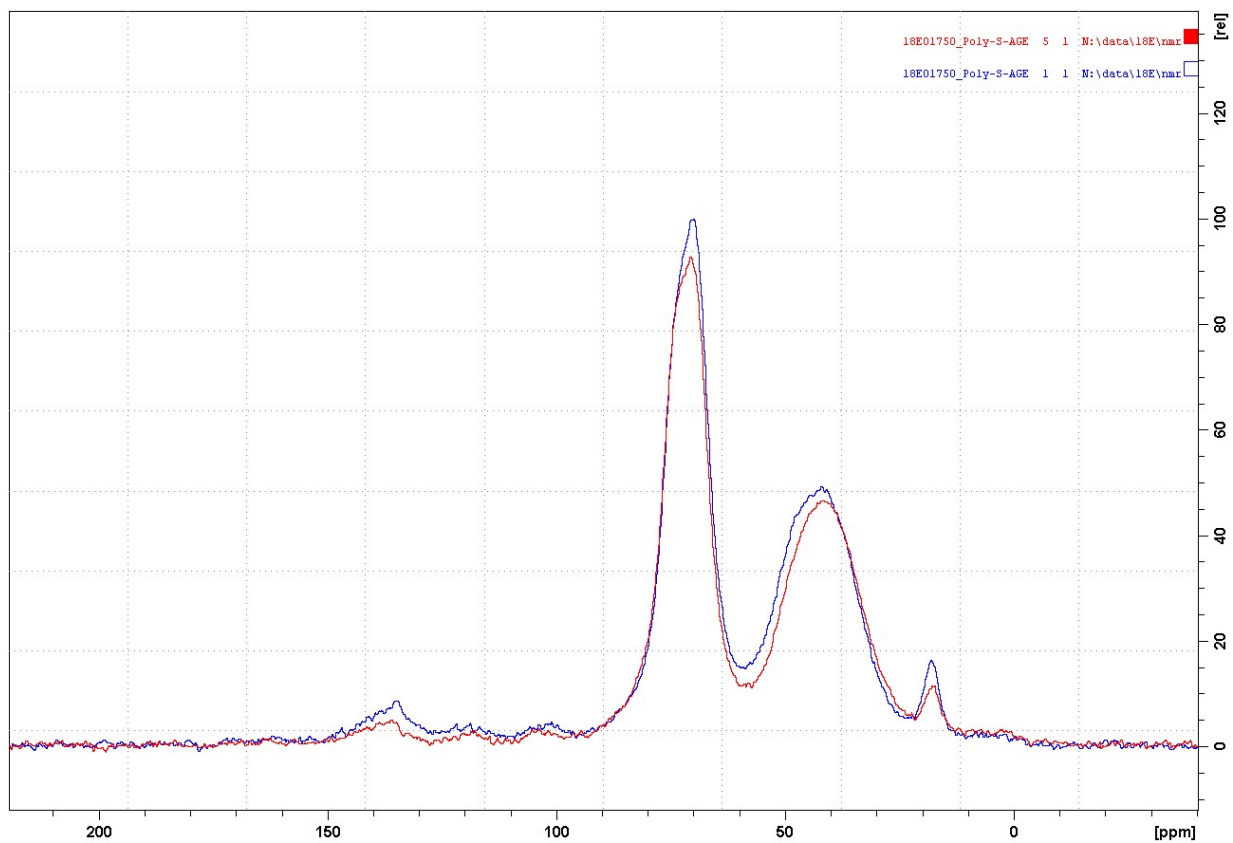


Figure S2. ^1H - ^{13}C cross-polarization solid-state NMR of poly(S-r-AGE) with contact times of 1 ms (blue) and 0.1 ms (red).

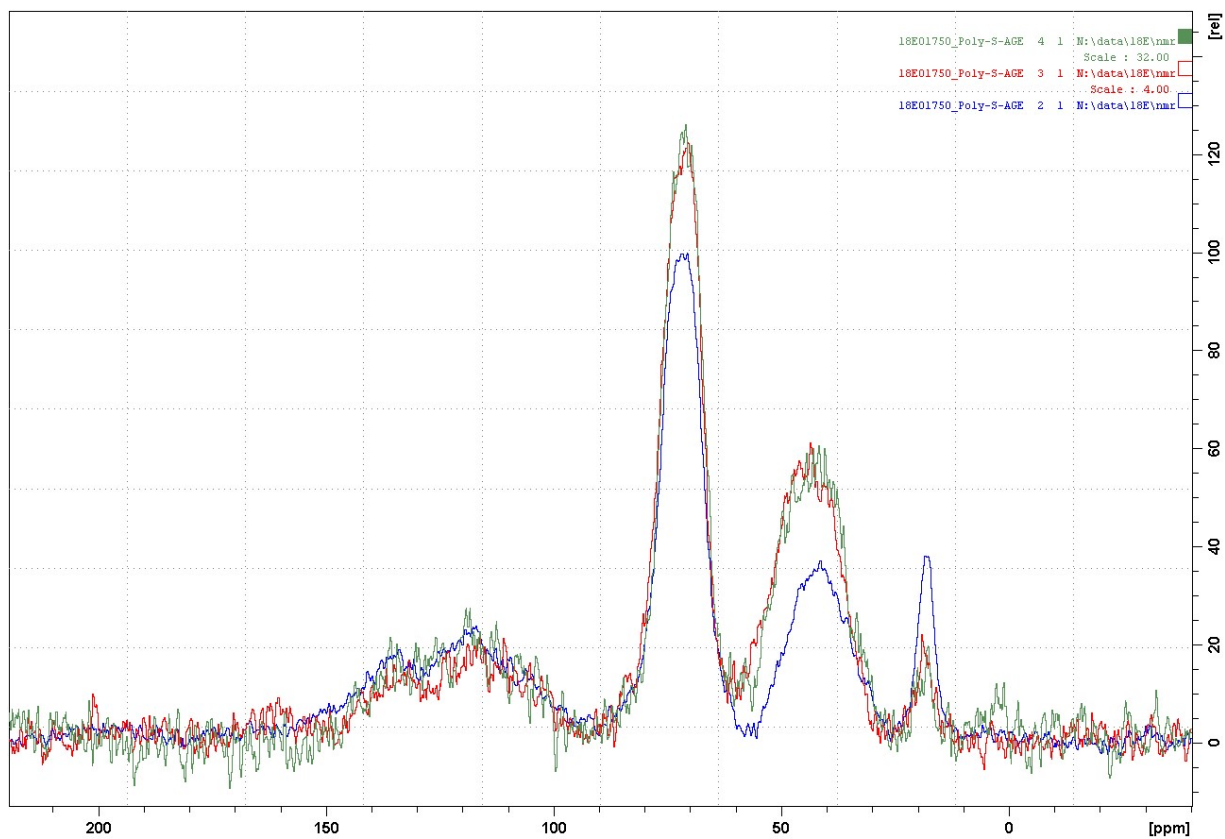


Figure S3. ^{13}C solid-state NMR of poly(S-r-AGE) with direct excitation and recycle delays of 120 s (green), 40 s (red), 2 s (blue), according to which the polarization at recycle delays of 40s and 120s can be considered fully relaxed, i.e. the spectra provide quantitative information.

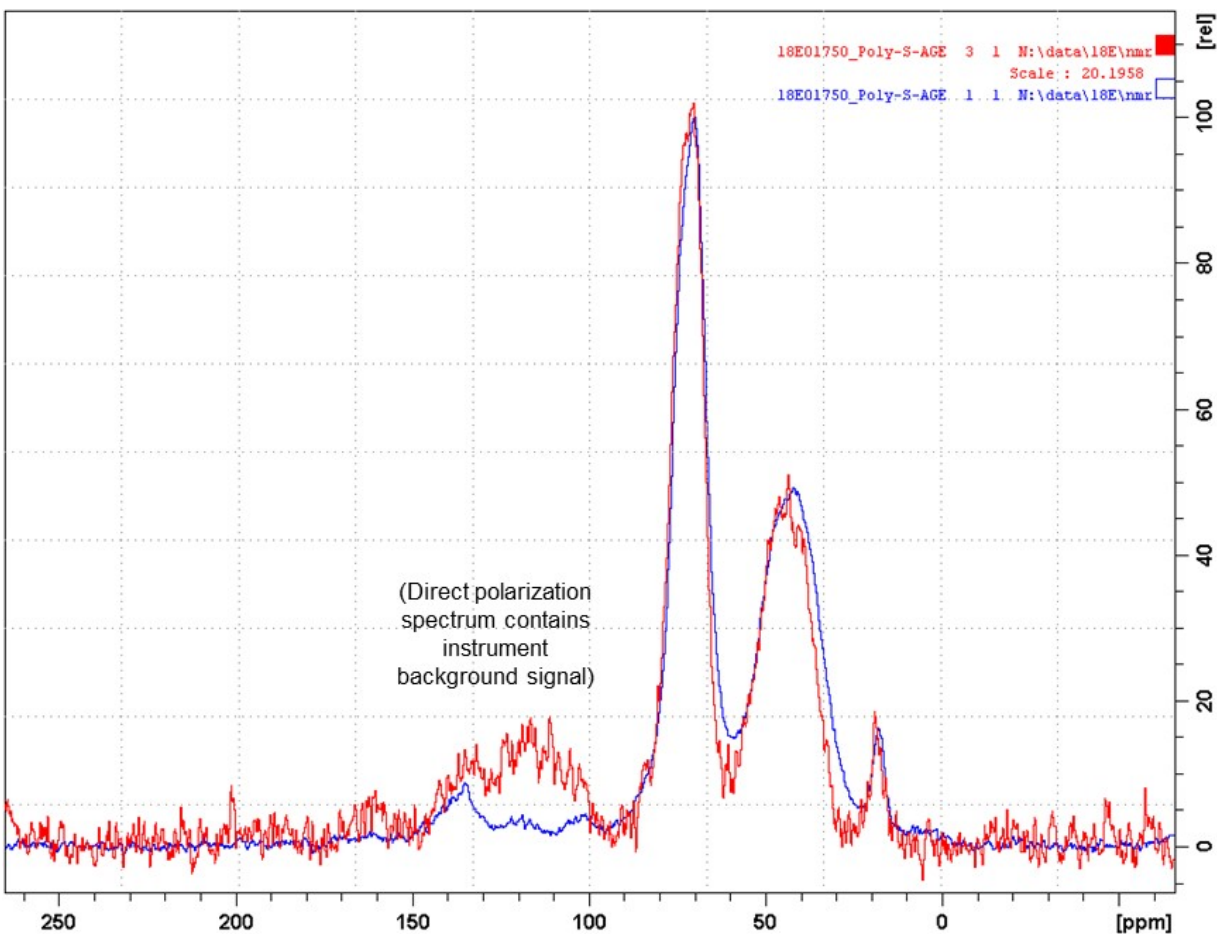


Figure S4. ^{13}C solid-state NMR of poly(S-r-AGE) with direct excitation and a recycle delay of 40 s (red), and from 1ms ^1H – ^{13}C cross-polarization (blue), according to which this cross-polarization spectrum provides quantitative information.

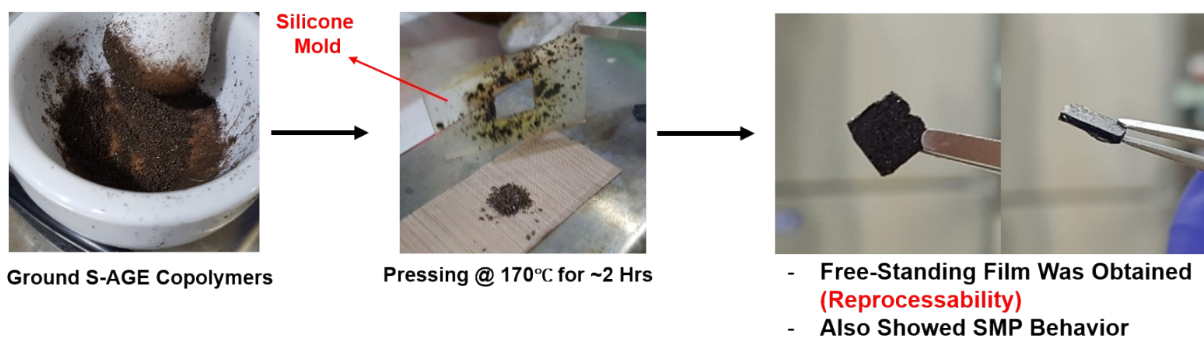


Figure S5. Demonstration of reprocessability of S-AGE copolymers using hot-press molding method due to high content of dynamic sulfur-sulfur bonds.

Supplementary Videos

Video S1. Spontaneous bending of 90 mm × 12 mm and 1 mm thick S-AGE (50 wt% sulfur).

Video S2. Spontaneous folding of S-AGE (50 wt% sulfur) film into a cube.

Supplementary Information Reference

1. *Eur. J. Org. Chem.* **2015**, 2960–2964