

Supplementary Information

Bio-based, Robust, Shape Memory, Self-Healing and Recyclable Elastomer Based on Semi-interpenetrating Dynamic Network

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Shape memory tests program

- 1) Apply a force of 0.001N to make the sample vertical, then heat to 70°C (5°C/min) and keep it for 5 minutes;
- 2) Raise the stress to 0.5N (0.2N/min);
- 3) Maintain a constant stress of 0.5N, reduce the temperature to -10°C (5°C/min), and keep it for 5 minutes;
- 4) Reduce the stress to 0.001N (0.2N/min);
- 5) Raise the temperature to 70°C (5°C/min) and keep it for 5 minutes;
- 6) Raise the temperature to 160°C (10°C/min), then increase the stress to 0.2N (0.2N/min), keep it for 1 hour;
- 7) Keep a constant temperature of 160°C, reduce the stress to 0.001N (0.2N/min), and keep it for 10 minutes;
- 8) Cool to 70°C (5°C/min);
- 9) Raise the stress to 0.6N (0.2N/min);
- 10) Cool to -10°C (5°C/min) and keep it for 5 minutes;
- 11) Reduce the force to 0.001N (0.2N/min);
- 12) Raise the temperature to 70°C (5°C/min) and keep it for 5 minutes.

Table S1 Detailed composition of E_x-DTSA_y

Sample name	EEUG (phr)	EUG (phr)	DTSA (phr)	IM (phr)	Zn(Ac) ₂ (phr)	4010NA (phr)
E0-DTSA0.5	100	0	0.5	0.06	0.15	1
E10-DTSA0.5	100	10	0.5	0.06	0.15	1
E20-DTSA0.5	100	20	0.5	0.06	0.15	1
E30-DTSA0.5	100	30	0.5	0.06	0.15	1
E40-DTSA0.5	100	40	0.5	0.06	0.15	1
E50-DTSA0.5	100	50	0.5	0.06	0.15	1
E30-DTSA0.8	100	30	0.8	0.1	0.24	1
E30-DTSA1.0	100	30	1.0	0.12	0.30	1
E30-DTSA1.5	100	30	1.5	0.18	0.45	1

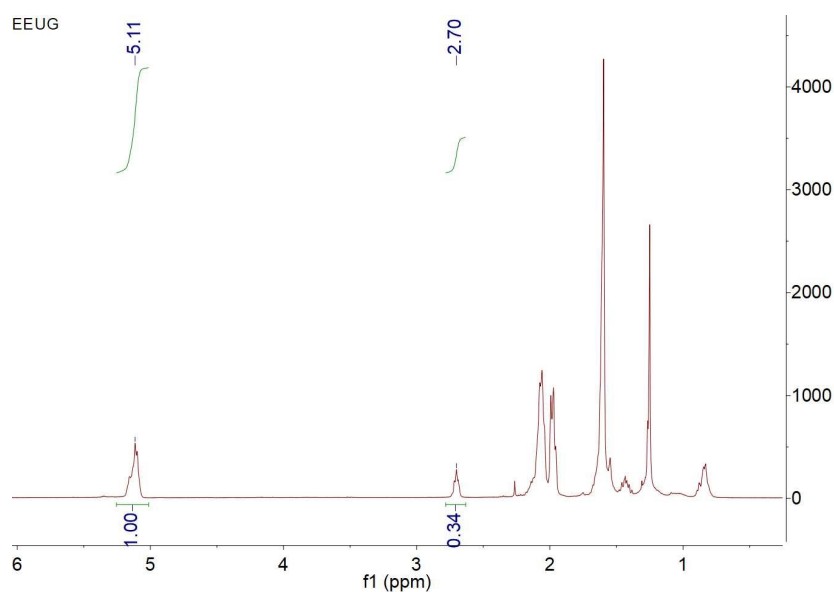


Figure S1. ¹H NMR spectrum of EEUG. The peaks at 5.11 ppm, 2.70 ppm are attributed to the proton resonance peak of C=C and epoxy groups separately. Epoxy content = $A_{2.70}/(A_{5.11}+A_{2.70}) * 100$, where $A_{2.70}$ and $A_{5.11}$ are resonance peak area of protons epoxy groups and C=C separately.^[1]

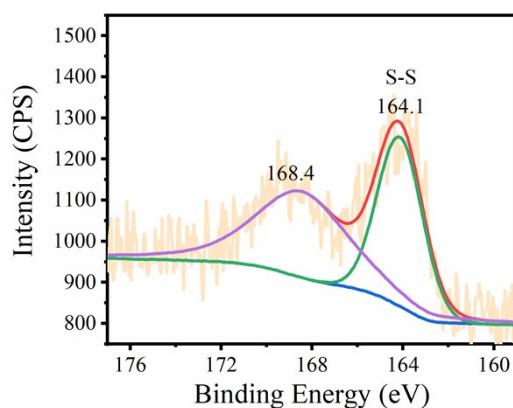


Figure S2. High-resolution XPS S 2p spectra of E_x -DTSA $_y$. The peak at 164.1 eV indicating the presence of disulfide bonds. Another peak at 168.0 eV was assigned to oxidized sulfur, probably generated by air oxidation of disulfide bonds. [2]

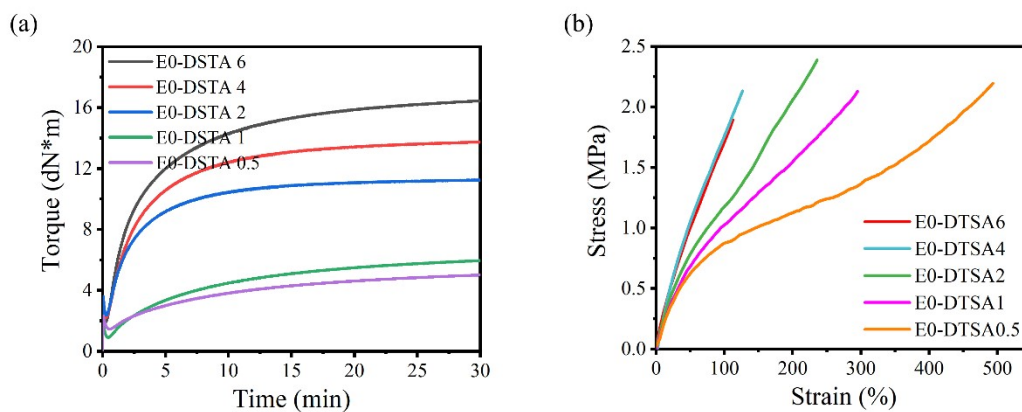


Figure S3. The effect of DTSA dosage on mechanical properties. (a) Vulcanization curves and (b) stress-strain curves of E0-DTSA $_y$ (with different DTSA content).

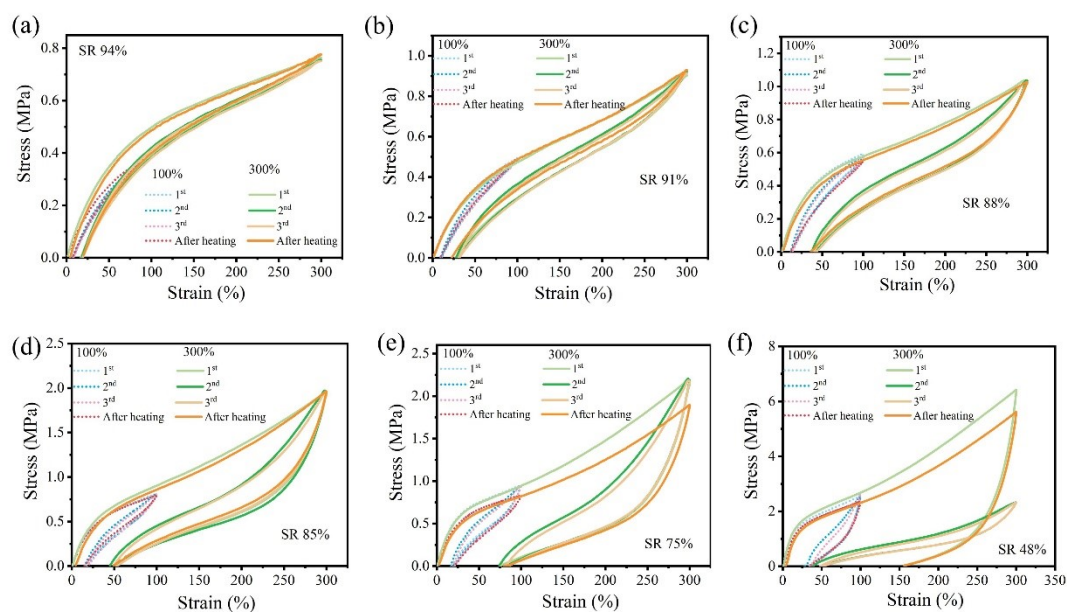


Figure S4. Loading–unloading curves of (a) E0-DTSA0.5, (b) E10-DTSA0.5, (c) E20-DTSA0.5, (d) E30-DTSA0.5, (e) E40-DTSA0.5, (f) E50-DTSA0.5, under strain of 100% and 300%.

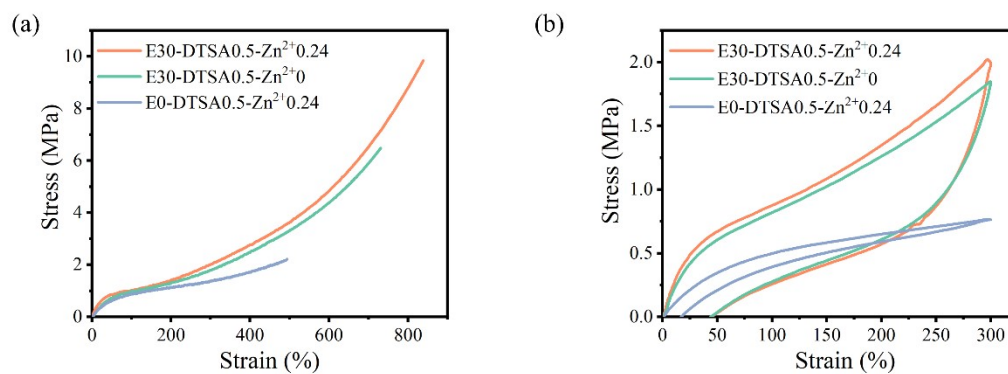


Figure S5. Contrast of energy dissipation between coordination bonds and EUG crystals. (a) stress-strain curves and (b) Loading–unloading curves of E0-DTSA0.5- $Zn^{2+}0.24$ (only coordination bonds), E30-DTSA0.5- $Zn^{2+}0$ (only EUG crystals), E0-DTSA0.5- $Zn^{2+}0.24$ (coordination bonds and EUG crystals).

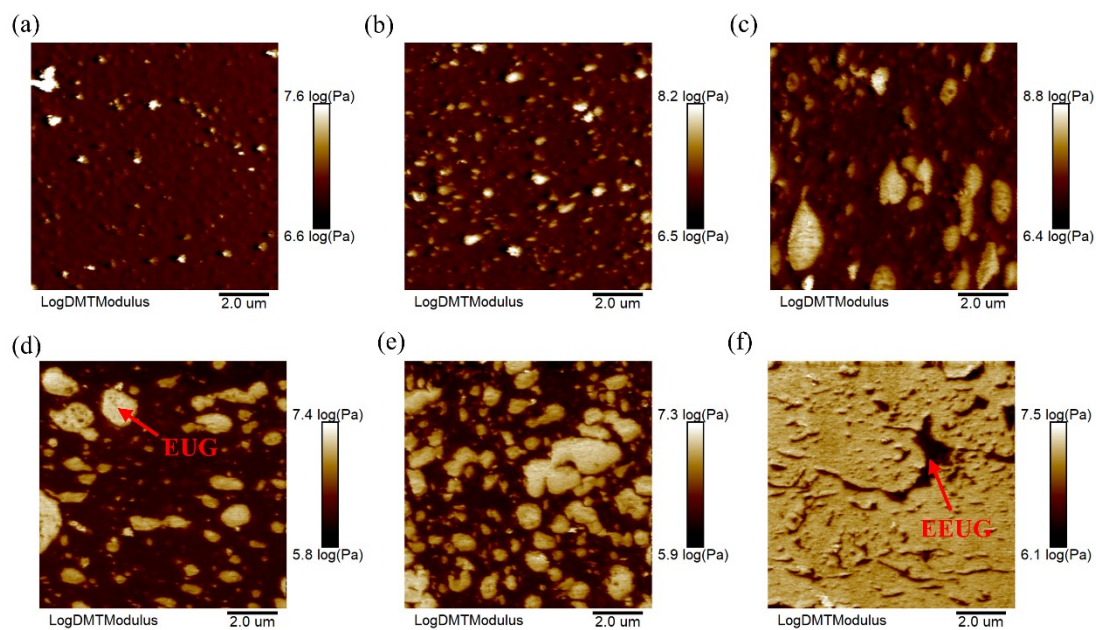


Figure S6. AFM LogDMTModulus image of (a) E0-DTSA, (b) E10-DTSA, (c) E20-DTSA, (d) E30-DTSA, (e) E40-DTSA, (f) E50-DTSA.

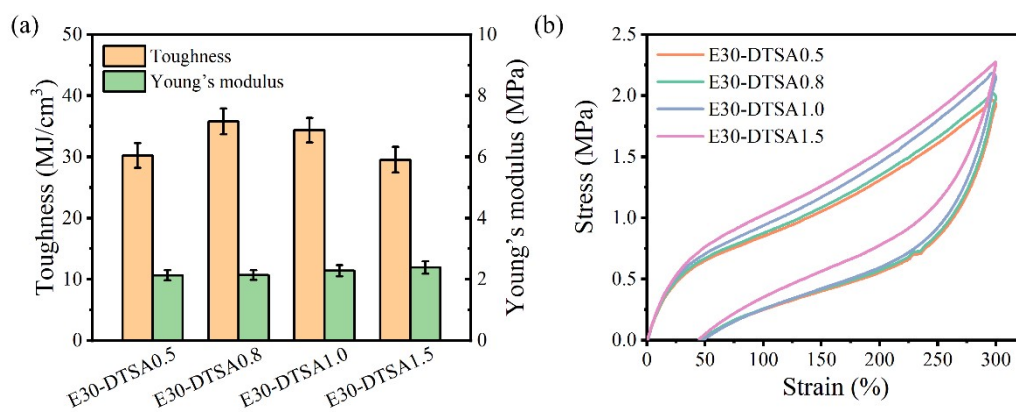


Figure S7. (a) Toughness and Young's modulus of E30-DTSA_y. (b) Loading-unloading curves for E30-DTSA_y under strain of 300%.

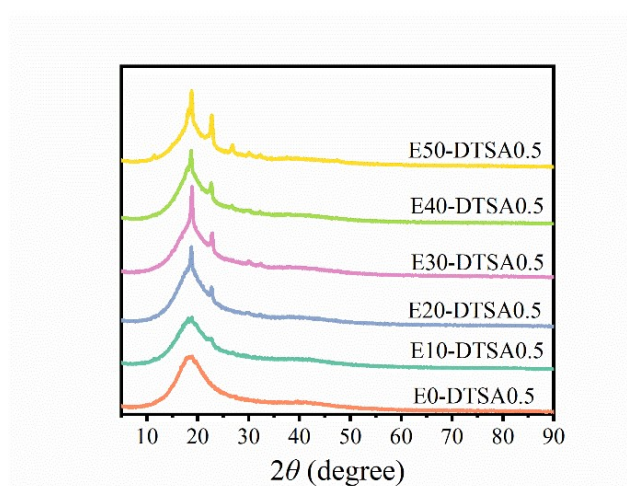


Figure S8. WAXD patterns of E_x -DTSA0.5.

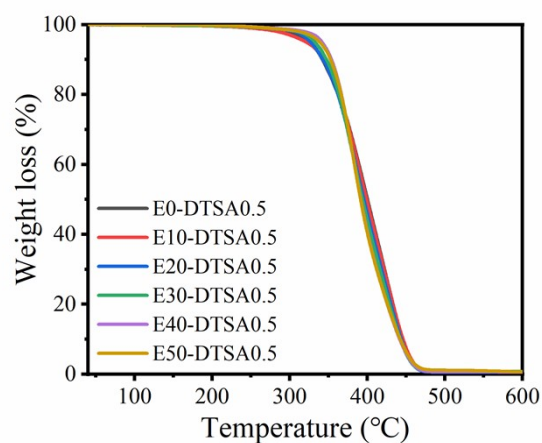


Figure S9. TGA curves of E_x -DTSA0.5.

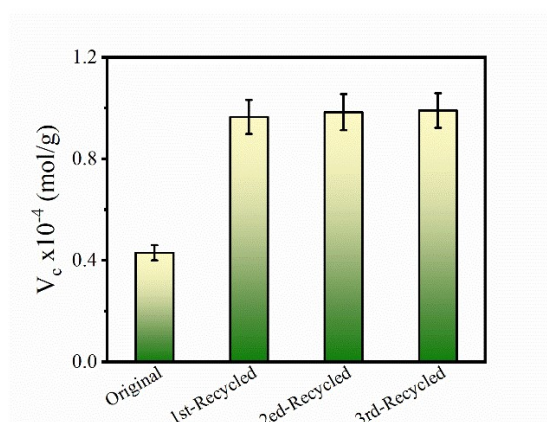


Figure S10. Crosslinking density of E30-DTSA0.5 after recycling by hot pressing. The crosslink density was evaluated by using the Flory–Huggins equations.

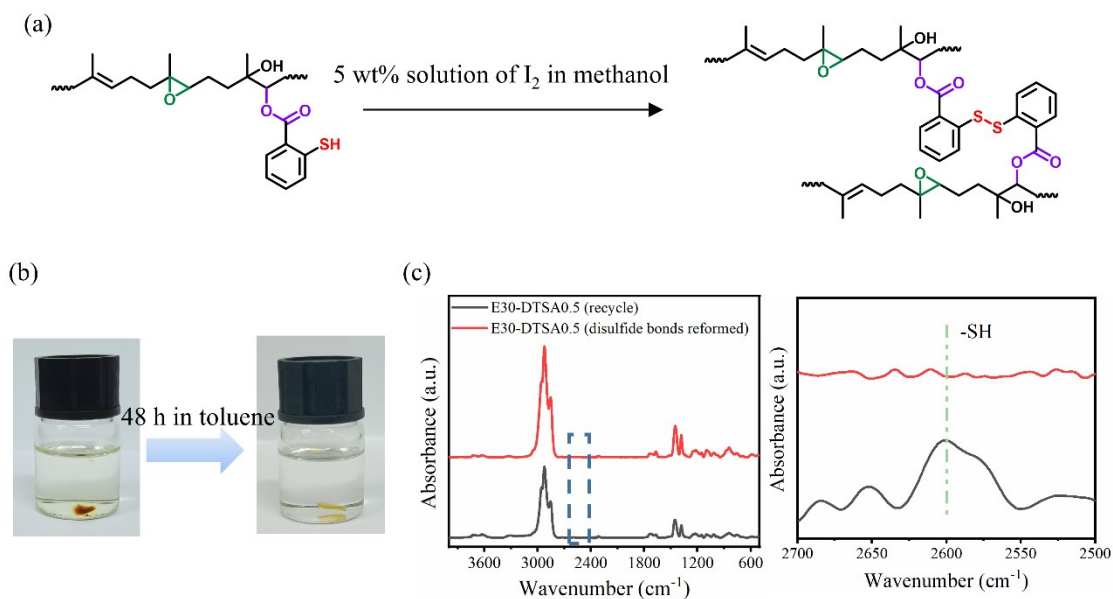


Figure S11. Disulfide bond reformed of the recovered samples. (a) Equation for the oxidation of thiol to disulfide bonds. (b) Photos of samples soaked in toluene for 48 h after disulfide bond reformed. Only swelling occurred in the sample, indicating that a new cross-linking network was established. (c) FT-IR spectra of samples before and after disulfide bonds reformed. When the thiol was oxidized to disulfide, the stretching vibration peak of the thiol at 2600cm^{-1} disappeared.

Reference

- [1] F. Yang, Q. Liu, X. Li, L. Yao, Q. Fang, *Polymer Bulletin* 2017, 74, 3657.
- [2] Masahiro Furutani, K. Okuma, K. Arimitsu, *Journal of Photopolymer Science and Technology* 2019, 32, 623.