Supplementary Information (SI) for RSC Applied Polymers.

Supporting Information

Phase Morphology–Structure–Property–Recyclability Relationships of Dynamically Crosslinked Thiol-Ene Photopolymers

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Additional Characterizations and Results

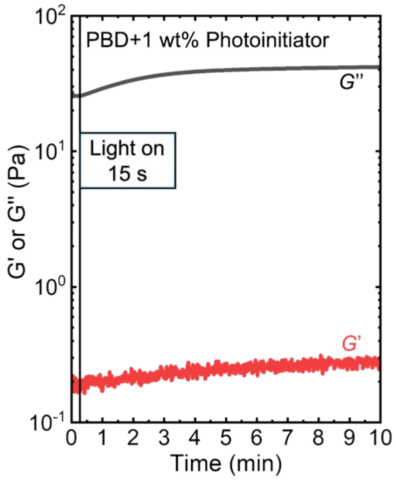

Figure S1. Photo-rheological analysis of neat PBD (containing 1 wt% photoinitiator) under UV irradiation (i.e., 10 mW/cm^2), showing the evolution of G' and G'' over time.

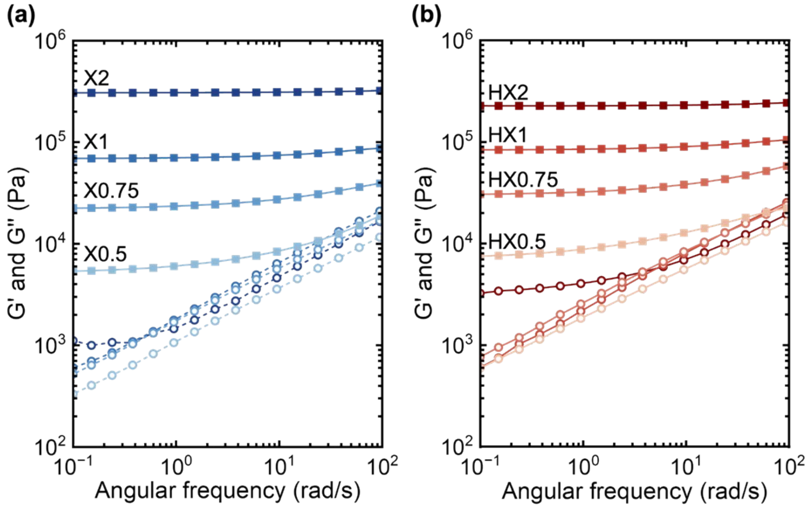

Figure S2. Room-temperature oscillatory rheological frequency sweep results for photocured PBD–G4 networks: **(a)** Phase-separated X0.5-X2 and **(b)** Phase-mixed HX0.5-HX2 samples. Solid symbols with solid lines denote the storage modulus (G'), and open symbols with dashed lines denote the loss modulus (G'').

Reactivity study of 1,4- and 1,2-unsaturation in PBD with thiol groups

The chemical composition of polybutadiene (PBD) was analyzed by ^{1}H NMR spectroscopy to determine the relative abundance of 1,4- and 1,2-unsaturation. As shown in **Figure S3**, the protons associated with 1,4-main-chain and 1,2-side-chain vinyl unsaturation give rise to distinct resonances (peaks **b** and **c**, respectively). Integration of these signals yielded an integral ratio of **b:c** ≈ 7.24:1.00, corresponding to approximately 88 mol% 1,4-unsaturation and 12 mol% 1,2-unsaturation. Based on the reported number-average molecular weight of PBD (5000 g/mol), this composition corresponds to an average of ~81 moles of 1,4-double bonds and ~11 moles of 1,2-vinyl double bonds per mole of PBD chains.

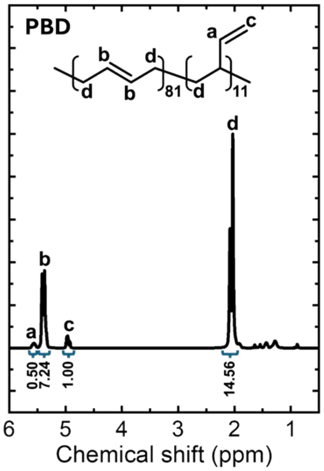

Figure S3. ^{1}H NMR spectrum of PBD in chloroform-d.

To evaluate the relative reactivity of 1,4- and 1,2-unsaturation toward thiol–ene addition, a monofunctional thiol, 2-(2-methoxyethoxy)ethanethiol (ME), was used as a model compound (**Figure S4**). PBD and ME were mixed at two PBD:ME molar ratios of 1:1 and 1:5, both with 1 wt% photoinitiator, and irradiated by UV light at 10 mW/cm^2 for 5 min per side. **Figure S5a** illustrates the thiol–ene photopolymerization between PBD and ME. ^{1}H NMR spectra were collected before and after UV irradiation (**Figure S5b-e**). For quantitative analysis, the methyl protons of ME were used as an internal reference and normalized to an integral value of 1.

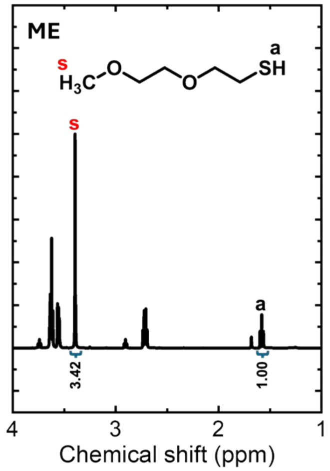

Figure S4. ^{1}H NMR spectrum of ME in chloroform-d.

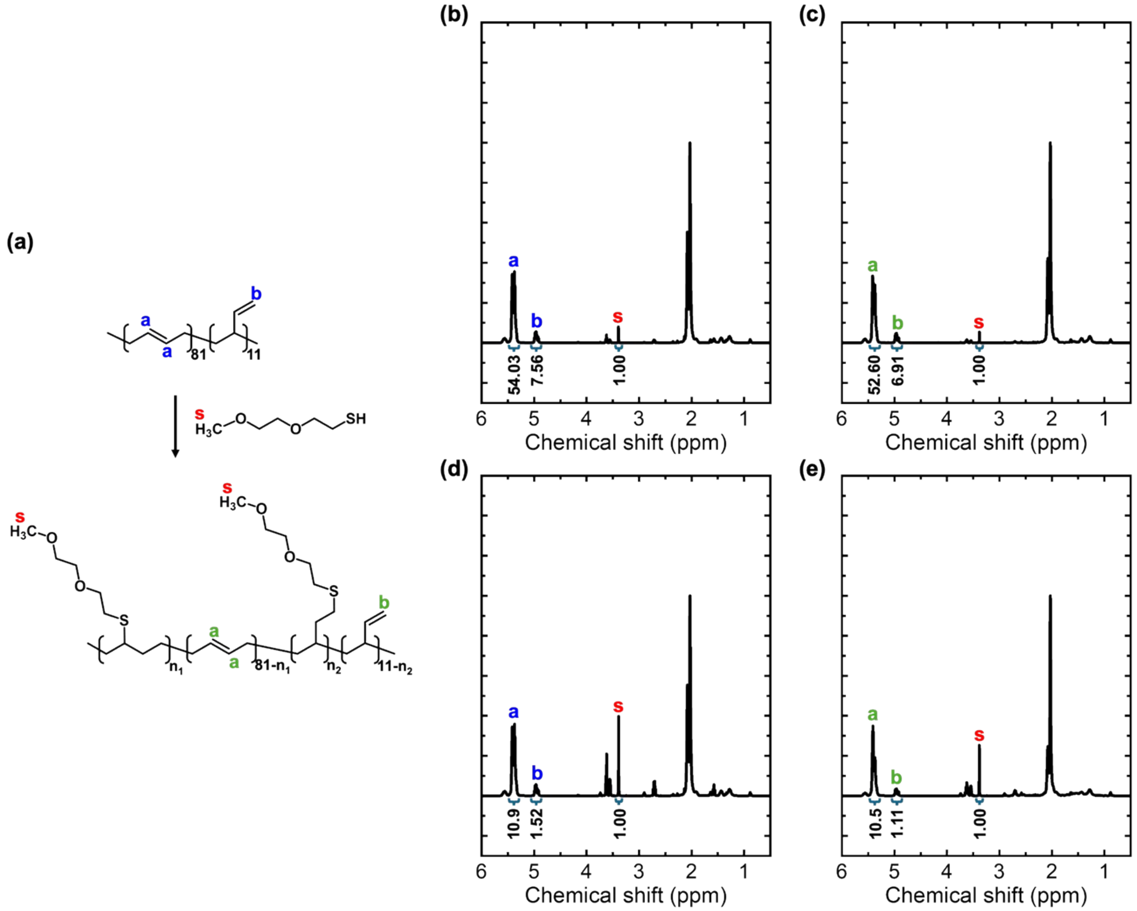

Figure S5. (a) Scheme of the reaction between PBD and ME; ^{1}H NMR spectra of PBD:ME = 1:1 **(b)** before and **(c)** after curing in chloroform-d; ^{1}H NMR spectra of PBD:ME = 1:5 **(d)** before and **(e)** after curing in chloroform-d.

After photopolymerization, the thiol groups in ME were completely consumed under the applied thiol–ene reaction conditions based on the ^{1}H NMR spectra (**Figure S5**). The proton signals corresponding to both 1,4- and 1,2-unsaturation (peaks **a** and **b** in **Figure S5**) decreased relative to the reference peak **s**, indicating that both types of double bonds participated in thiol–ene addition. Notably, the ratio of the integrals associated with 1,4- to 1,2-unsaturation increased after curing, demonstrating preferential consumption of 1,2-vinyl double bonds. The relative reactivity ratio (RR) was estimated by comparing the fractional consumption of 1,2- and 1,4-double bonds under identical conditions. The calculated RR values were approximately 18 and 10 for PBD:ME molar ratios of 1:1 and 1:5, respectively. An average RR of ~14 was thus adopted to represent the relative reactivity of 1,2- versus 1,4-unsaturation toward thiol–ene addition.

$$RR = \left\{\frac{[1{,}2-]_b - [1{,}2-]_f}{[1{,}2-]_b}\right\} / \left\{\frac{[1{,}4-]_b - [1{,}4-]_f}{[1{,}4-]_b}\right\}$$

$$[1{,}2-]_b = \frac{[b]}{[a]+[b]} \times 92$$

$$[1{,}4-]_b = \frac{[a]}{[a]+[b]} \times 92$$

$$[1{,}2-]_f = \frac{[b]}{[a]+[b]} \times (92-x)$$

$$[1{,}4-]_f = \frac{[a]}{[a]+[b]} \times (92-x)$$

Where RR is the reactivity ratio of 1,2-unsaturation to 1,4-unsaturation towards thiol groups, $[1{,}2-]_b$ and $[1{,}4-]_b$ represent the concentrations of 1,2- and 1,4-type carbon–carbon double bonds before curing, while $[1{,}2-]_f$ and $[1{,}4-]_f$ represent their corresponding concentration after curing, respectively. The parameter $\boldsymbol{x}$ denotes the molar ratio between ME and PBD. **[a]** and **[b]** correspond to the integral value of 1,4- and 1,2-unsaturation signals, where blue and green refer the spectra collected before and after curing, respectively.

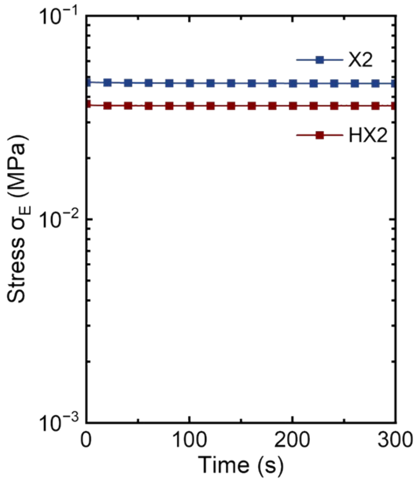

Figure S6. Stress relaxation behavior of X2 and HX2 measured at room temperature under 5% strain.

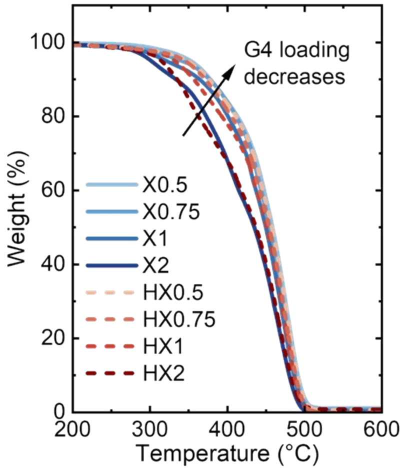

Figure S7. TGA spectra of photocured PBD–G4 networks: Phase-separated X0.5-X2 *vs.* Phase-mixed HX0.5-HX2 samples.