Supporting Information

Directing Network Degradability Using Wavelength-Selective Thiol-Acrylate Photopolymerization

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Figure S1. ¹H NMR spectrum of the TBD-HBPh₄ photobase generator.



Figure S2. ¹H NMR spectrum of the thiol-acrylate photoresin having a stoichiometric balance between thiol and acrylate groups.

(A) Main photochemical pathway of Eosin Y + TBD-HBPh₄



Figure S3. (A) Eosin Y's main photochemical pathway of activating TBD-HBPh₄ to release TBD base under green light irradiation; (B) Side reactions involving Eosin Y ketyl radicals that generate unwanted free radicals; and (C) Radical scavenging by TEMPO.



Figure S4. ¹H NMR spectrum of the completely decrosslinked X_{Green} sample.

The ¹H NMR spectrum in **Figure S4** shows signals of the terminal thiol proton (peak **a** at 1.57 ppm; 1 mol of **a** protons correspond to 1 mol of [SH] groups) and the proton closest to the thiol-acrylate linkage (peak **g** at ~ 3 ppm; 6 mol of **g** protons correspond to 1 mol of triacrylate molecule). The intensity ratio between peaks **a** and **g** in **Figure S4** is ~1:0.4. Notably, in order to decrosslink the thiol-acrylate network, 1 mol of Thioplast G4 molecules were added (i.e., ~5 mol of [S-S] bonds and ~2 mol of [SH] groups corresponding to ~2 mol of **a** protons) per 1 mol of dynamic [S-S] linkages (i.e., network formed by reacting ~0.2 mol of Thioplast G4 with ~0.14

mol of triacrylate corresponding to ~0.8 mol of **g** protons). Thus, the theoretically calculated intensity ratio between **a** and **g** protons for the completely decrosslinked materials should be ~2:0.8 (i.e., ~1:0.4). Overall, the ¹H NMR result in **Figure S4** demonstrates the complete decrosslinking of the X_{Green} network. Owing to the unique degradation mechanism via thiol-disulfide exchange, the amount of [SH] groups should remain unchanged and can undergo recrosslinking with a stoichiometric amount of triacrylate monomers, if needed.¹



Figure S5. ¹H NMR spectrum of the soluble fraction of the X_{UV} sample.

REFERENCE

1. Alfarhan, S.; Brown, J.; Liu, B.; Long, T.; Jin, K., Chemically recyclable crosslinked thiol-ene photopolymers via thiol-disulfide exchange reactions. *Journal of Polymer Science* **2022**, *60* (24), 3379-3390.