Supporting information for

Multifunctional dithiolane monomers for multi-scale recyclable light-driven additive

manufacturing

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Figure S1. LAPEO synthesis scheme.



Figure S2. ¹H NMR of LAPEO monomer after synthesis. Inset shows the full spectrum.



Figure S3. ¹³C NMR of LAPEO monomer after synthesis.



Figure S4. FTIR of LAPEO monomer after synthesis.



Figure S5. 2 arm dithiolane monomer synthesis scheme.



Figure S6. ¹H NMR of 2 arm dithiolane monomer after synthesis. Inset shows the full spectrum.



Figure S7. ¹³C NMR of 2 arm dithiolane monomer after synthesis.



Figure S8. FTIR of 2 arm dithiolane monomer after synthesis.



Figure S9. Decadic molar extinction coefficient of LAPEO as measured by UV/Vis spectroscopy.



Figure S10. Depth of penetration from absorbance measurements of different concentrations of LAPEO in toluene with 0.5 wt% BAPO at both 365 nm and 405 nm.



Figure S11. DMA of polymerized films in tension after solvent removal (monomer at 53 w/w%, with 0.5 w/w% BAPO added, polymerized with 20 mW/cm² 405 nm light for 5 min per side, 100 μ m samples, solvent removed at 60°C for 18 hours).



Figure S12. DSC of polymerized LAPEO (monomer at 53 w/w%, with 0.5 w/w% BAPO added, polymerized with 20 mW/cm² 405 nm light for 5 min per side, 100 μ m samples, solvent removed at 60°C for 18 hours).



Figure S13. % Transmittance through a 200 μ m LAPEO film at various UV, visible, and IR wavelengths.



Figure S14. Disulfidation of LAPEO films *in situ* on a rheometer. Polymerized LAPEO films were swelled in 60 w/w % ethylene glycol vinyl ether in acetone for 18 hours. Films were exposed to 405 nm light (20 mW/cm² for 5 minutes per side) and solvent was removed at 60°C for 18 hours prior to stress relaxation experiments. Dashed line indicates light exposure. Modulus values are normalized to the initial storage modulus prior to light exposure.



Figure S15. Tensile testing of LAPEO films at 0.5% strain/s (monomer polymerized at 53 w/w%, with 0.5 w/w% BAPO added, irradiated with 20 mW/cm² 405 nm light for 5 min per side, 100 μ m samples, solvent removed at 60°C for 18 hours). Three replicate traces are shown. Young's modulus = 3.0 ± 0.1 MPa, ultimate tensile strength = 1.6 ± 0.2 MPa, strain to break = 110 ± 10%. Red traces indicate disulfidation reaction performed. Young's modulus = 10.2 ± 0.9 MPa, ultimate tensile strength = 1.7 ± 0.3 MPa, strain to break = 25 ± 3%.



Figure S16. % Transmittance through 200 μ m LAPEO film with and without disulfidation at various UV, visible, and IR wavelengths.



Figure S17. GPC of virgin LAPEO and recycled LAPEO.



Figure S18. Comparison in gelation times for LAPEO and 2 arm dithiolane monomer. Storage modulus displayed as a fraction of ultimate modulus achieved (monomer at 53 w/w% in toluene, 20 mW/cm² 405 nm light). a) With initiator (0.5 w/w % BAPO) b) without initiator.



Figure S19. DLP printed LAPEO objects. Scale bar = 5 mm. a) Recreation of Boulder's flatirons landscape. b) 3D knot pattern.



Figure S20. Array of 2PL printed reconstructions of *La Pietà*. Scale bar = 50 μ m.