

Electronic Supporting Information (ESI)

A photopolymerizable thermoplastic with tunable mechanical performance

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Experimental

Materials

All chemicals were used as received without further purification. 1,6-hexane dithiol (HDT, $\geq 97\%$ FG) was purchased from Millipore Sigma. Diallyl terephthalate (DAT, $\geq 98.0\%$ GC), diallyl isophthalate (DAI, $\geq 98.0\%$ GC), diallyl phthalate (DAP, $\geq 98.0\%$ GC) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, $> 98.0\%$ HPLC) were purchased from TCI America. Dichloromethane (DCM), dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were purchased from Fisher Scientific. N-Methyl-2-pyrrolidone (NMP) was purchased from Acros Organics. Toluene was purchased from Macron Fine Chemicals.

Methods

Film preparation: A stoichiometric ratio of dithiol and diene monomers were well mixed in a 20 mL scintillation vial (VWR) with 1 mol% TPO photoinitiator (with respect to either functional group; corresponding to 0.87 wt% of the total formulation). Films were prepared between 4.50" x 5.25" glass plates (Sellstrom) with 250 μm plastic shims (Precision Brand) lining the perimeter to control the thickness with binder clips used to clamp the slides together. A 405 nm LED source (ECO UV Bar) was used to irradiate the samples at an intensity of approximately 7 mW/cm² at 405 nm for 5 – 10 minutes.

Fourier Transform Infrared Spectroscopy (FTIR): Fourier transform infrared spectroscopy was used to monitor the polymerization of the thiol and carbon-carbon double bonds. A Thermo Scientific Nicolet 6700 FTIR spectrometer was used with a 405 nm LED source (Thorlabs) using a myDAQ device (National Instruments) synchronized to a computer for timed and defined illuminations at 1-10 mW cm⁻². Optically thin samples were prepared between two salt (NaCl) plates using 15 μm spacers. Thiol conversion (c_{thiol}) and vinyl conversion (c_{vinyl}) were monitored using a series scan, integrating over the ranges 2550-2600 cm⁻¹ and 1778-1650 cm⁻¹ respectively. Conversion of functional groups (C) was calculated with the equation,

$$C = \left(1 - \frac{A_{\text{final}}}{A_{\text{initial}}}\right) * 100\% \quad (1)$$

where A_{initial} is the area of the unconsumed functional group peak, and A_{final} is the area under the thiol or C=C peak after the thiol-ene reaction.

Size exclusion chromatography with multi-angle light scattering and viscometry (SEC-MALS-IV): A size-exclusion chromatography instrument (Tosoh EcoSEC) equipped with a UV and differential refractive index detector (temperature: 40°C; injection volume: 100 μL) was used with a multi-angle light scattering detector (Wyatt Treos II) and an online viscometer (Wyatt Viscostar). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL/min.

Polarized microscopy: A Nikon Eclipse Ci microscope was used with a commercial DLP (Mightex Polygon 400) to either flood cure or photopattern basic structures. For large area images a Nikon Ti inverted microscope was used.

Photo-rheology: A rotational rheometer (ARES-G2, TA Instruments) with a parallel plate geometry using a photocuring geometry equipped with mirrors and a 20 mm diameter quartz plate for in-situ irradiation using a 405 nm LED (Thorlabs) at an intensity of 10 mW/cm².

Differential scanning calorimetry (DSC): Differential scanning calorimetry (DSC) was conducted with a TA Instruments DSC2500 at a heating and cooling rate of 2°C/min under a N₂ atmosphere. Approximately 5-7 mg of polymer sample was measured into a hermetically sealed aluminum pan.

Dynamic mechanical analysis (DMA): DMA was performed with a TA Instruments RSA-G2 on rectangular film specimens with a heating rate of 3°C/min and a frequency of 1 Hz, with a fixed strain of 0.05%.

Mechanical tensile testing: A uniaxial tensile tester (Exceed Model E42 – MTS) was used on thiol-ene films cut into ASTM D638 Type V dogbones ranging in thickness (120 – 250 µm) and tested with a strain rate of 5 mm/min at ambient temperature.

SLA 3D printing: 3D printing resins were formulated using 4 wt% TPO-L, 0.07 wt% carbon black as an absorber with 1 wt% of a proprietary additive supplied by Colorado Photopolymer Solutions (CPS) with the stoichiometric HDT-DAT formulation. A DLP production-grade commercial printer (Origin) was used for the QC, batarang and ring prints. The rest of the prints were made using a desktop projector-based (Solus) 3D printer. The QC .stl file was provided by CPS and all other .stl files were downloaded from Thingiverse.

Characterization

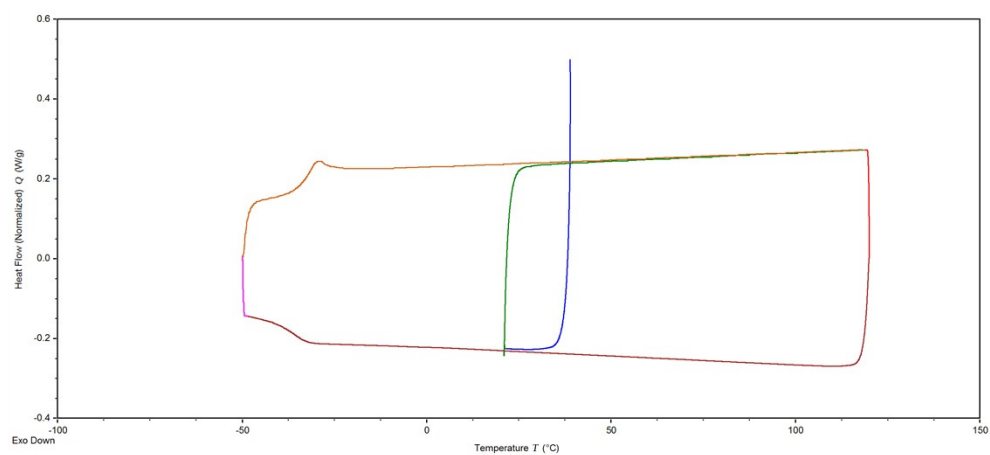
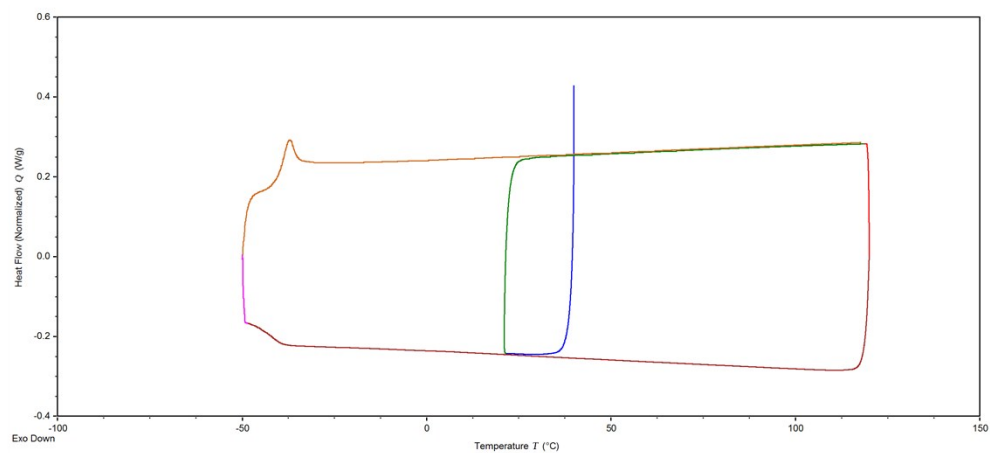


Figure S1. DSC trace of HDT-DAP with no discernable peaks.

Figure S2. DSC trace of HDT-DAI with no discernable peaks.

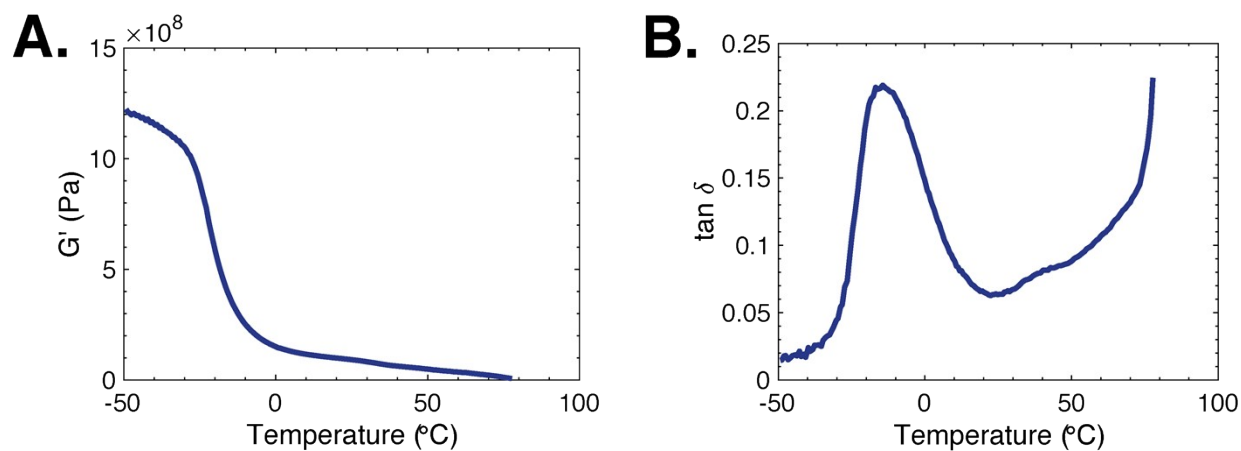


Figure S3. DMA plot for the HDT-DAT photopolymer. A) Storage modulus (G') versus temperature. B) Tan δ versus temperature.

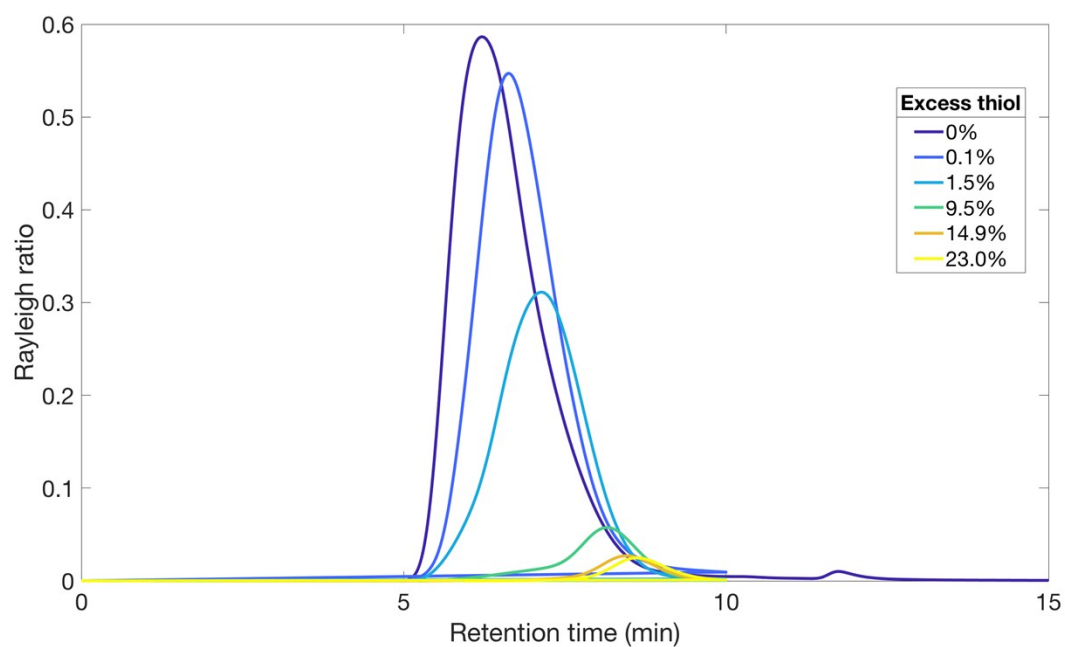


Figure S4. Light scattering for off-stoichiometric HDT-DAT systems with varying amounts of excess thiol. As the amount of excess thiol increases, the molecular weight of the polymer decreases dramatically as observed by the reduced Rayleigh ratio values of the peaks observed at delayed relation times.

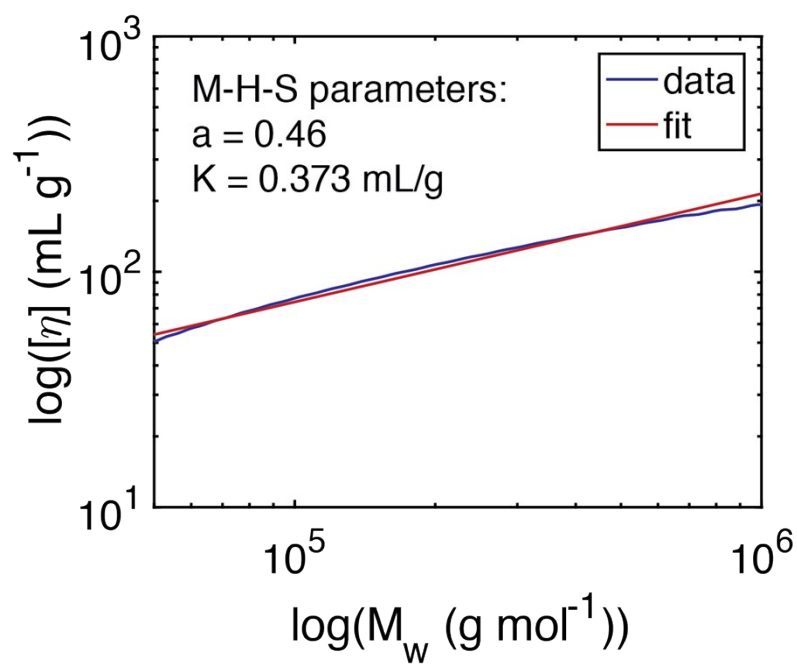


Figure S5. Log-log plot (Mark-Houwink-Sakurada) of intrinsic viscosity $[\eta]$ versus absolute M_w for a nominally stoichiometric HDT-DAT system. The Mark-Houwink-Sakurada parameters from the fitted data indicate a random coil morphology.

Table S1. Solubility table of HDT-DAT polymers in various organic solvents tested at a concentration of 1 mg/mL at ambient temperature.

DCM	DMSO	NMP	toluene	THF	water
soluble	insoluble	soluble	insoluble	soluble	insoluble

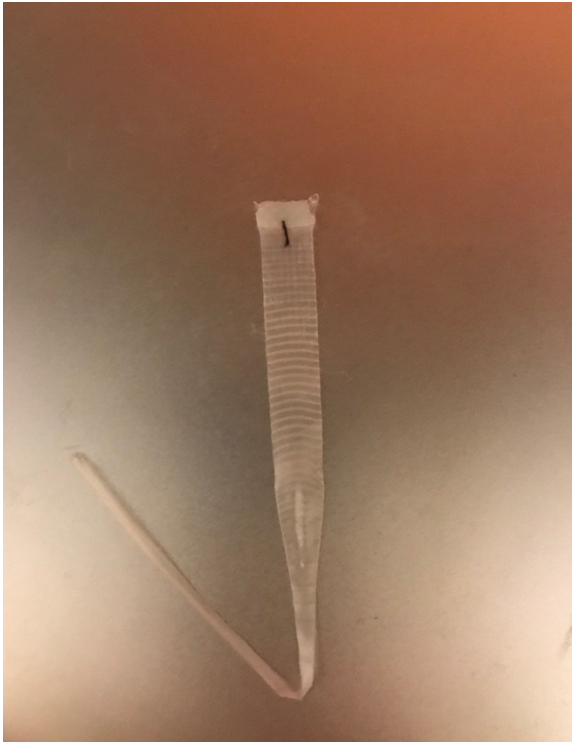


Figure S6. Photograph of a typical ASTM D638 Type V dogbone sample of HDT-DAT deformed in tension until failure showing the periodic striations of opaque and translucent regions.

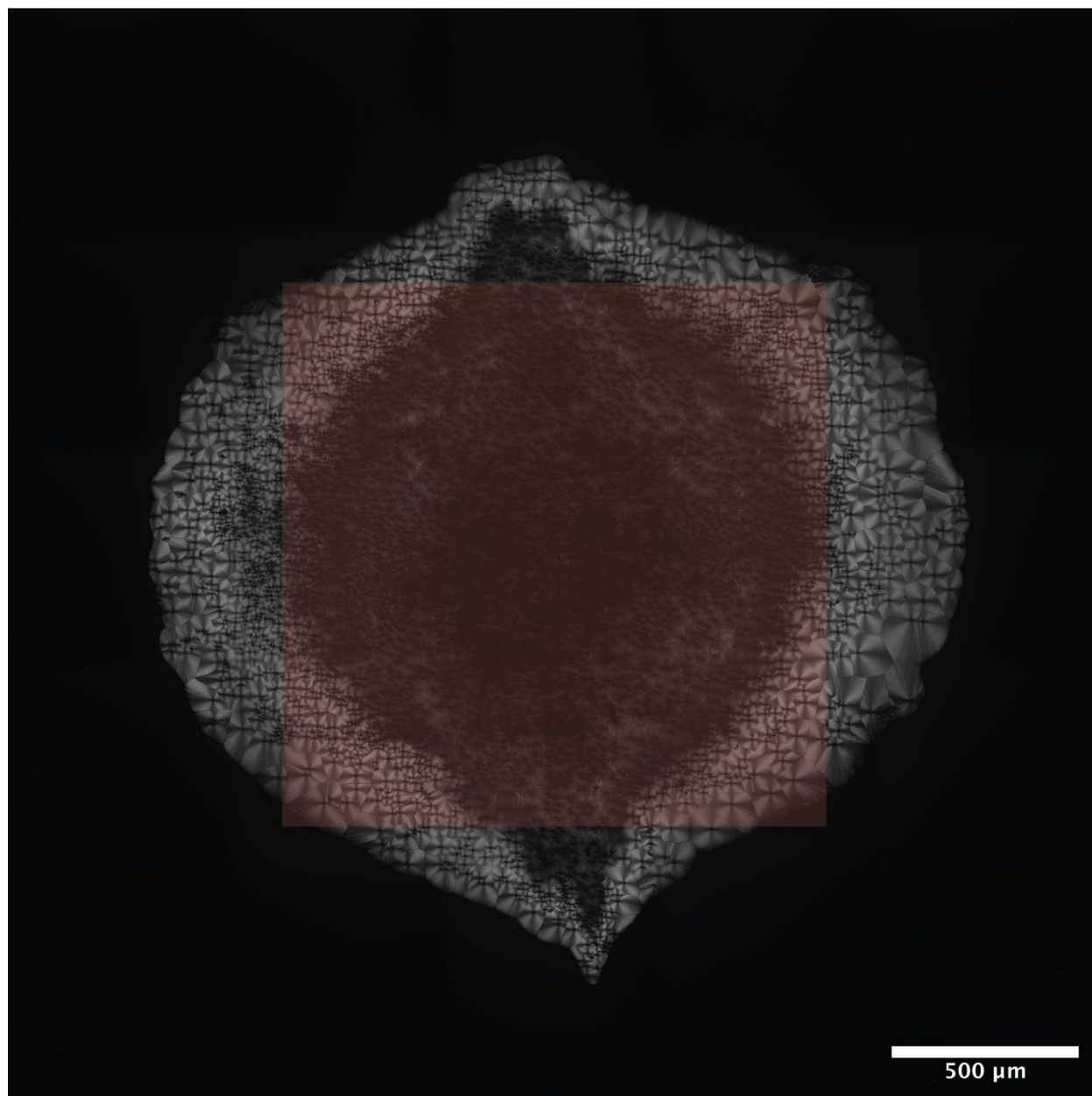


Figure S7. A high resolution differential interference contrast (DIC) image showing over-cure due to reaction-diffusion from a square exposure pattern (shaded in red) of neat HDT-DAT irradiated with a high intensity 405 nm scanning laser.