

Supporting Information for

Structure-reactivity based control of radical-mediated degradation in thiol-Michael hydrogels

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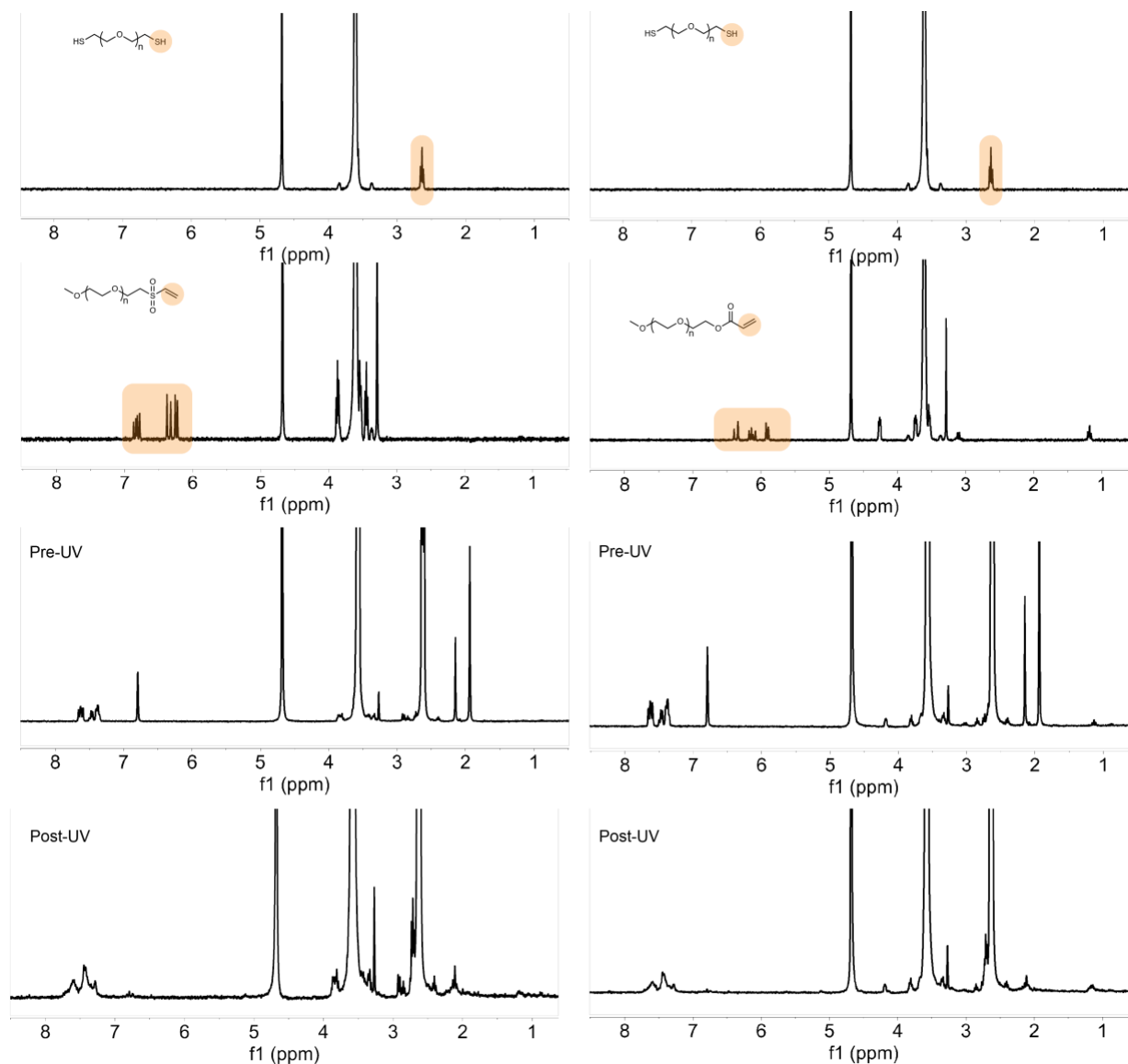


Fig. S1 | NMR of linear polymer alkene and thiol starting materials and thiol-Michael products before and after exposure. Disappearance of alkene protons (highlighted between 7.0-5.5 ppm) and thiol protons (highlighted at ~2.75 ppm) but retention of methyl group peak (~3.3 ppm) indicates essentially quantitative conversion of functional groups to thioethers. Post-UV (in the presence of LAP), spectra broaden and become noisy, making precise identification of molecular degradation products challenging.

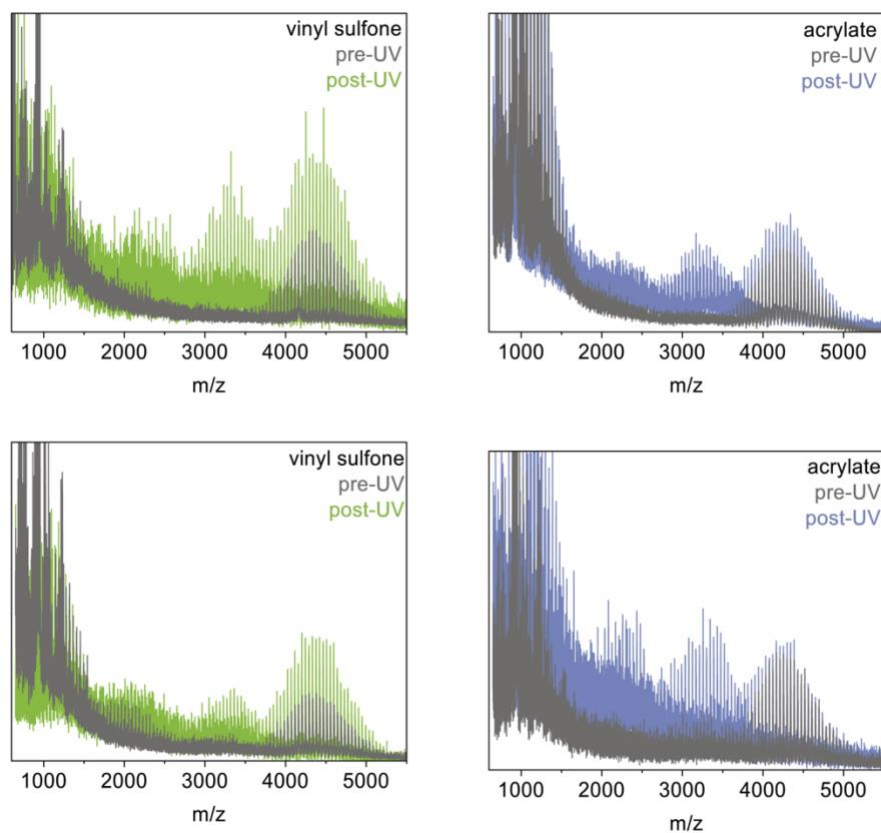


Fig. S2 | Complete MALDI spectra of samples prepared with 0.3 M (top) and 0.05 M (bottom) triethanolamine, with 4 kDa species before irradiation indicating the presence of Michael adduct species and lower-MW species emerging following light exposure in the presence of LAP.

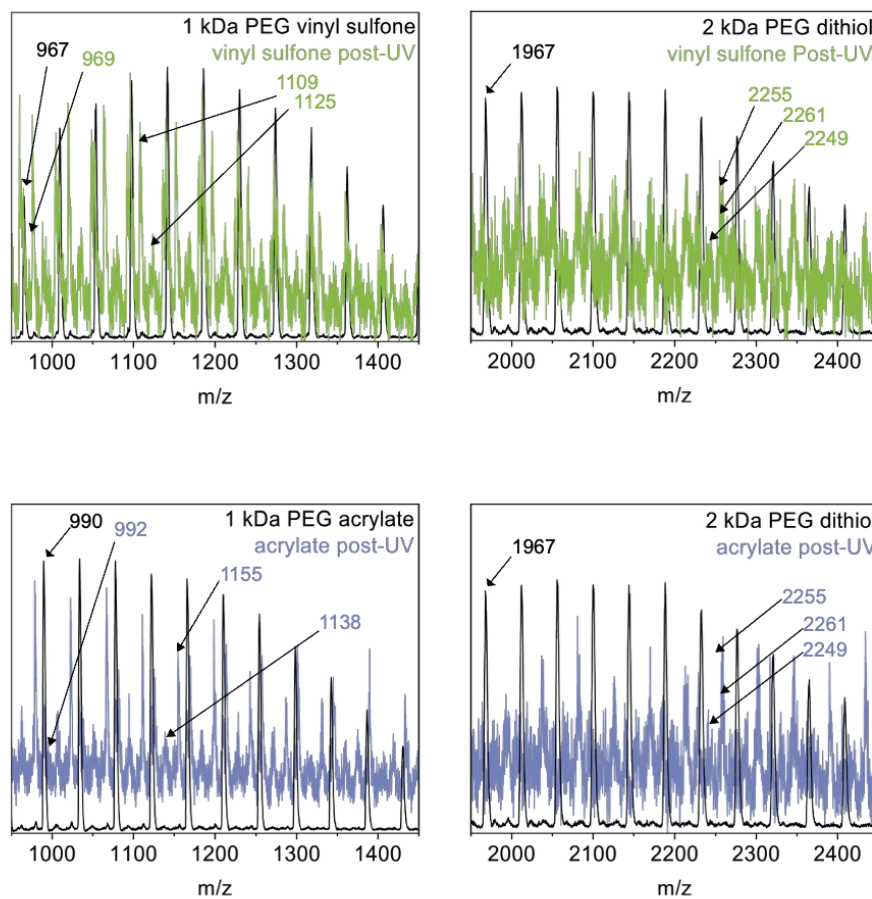


Fig. S3 | MALDI spectra of thiol-Michael adducts prepared with 0.05 M triethanolamine. Peaks indicating product complexes with triethanolamine are less pronounced than those in Fig. 2 (0.3 M triethanolamine) but identified product peaks are consistent.

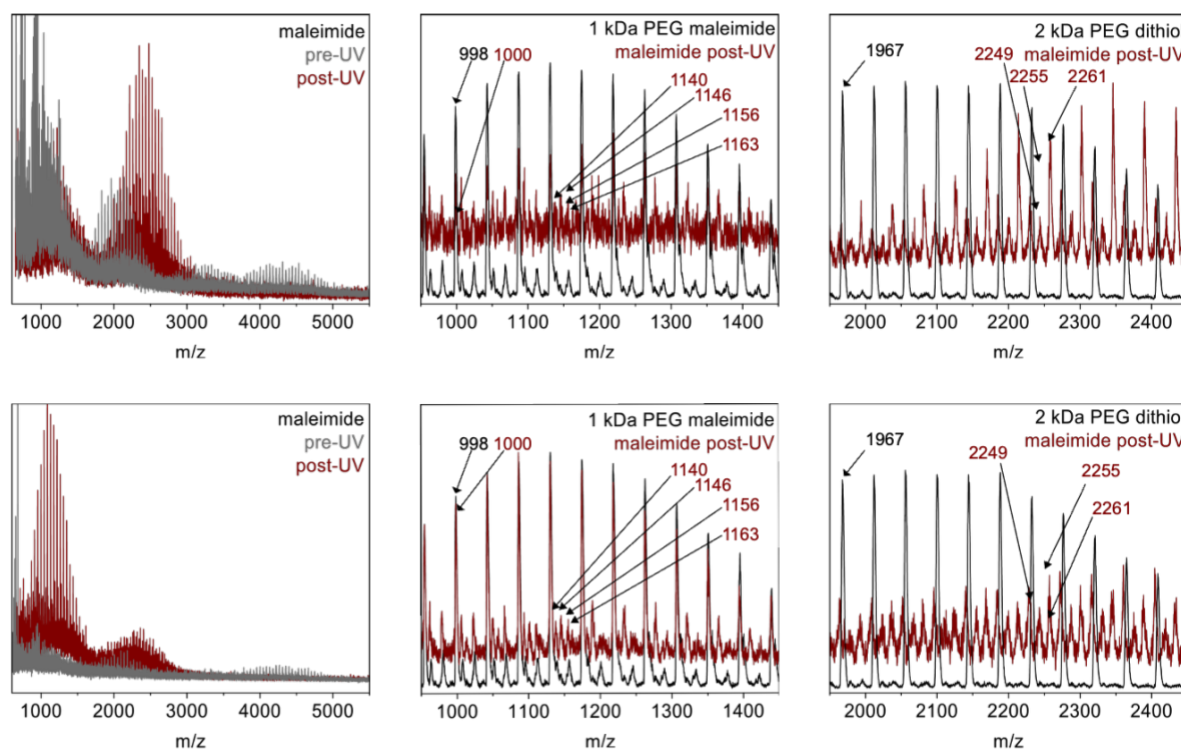


Fig. S4 | MALDI spectra of thiol-maleimide adduct degradation; polymers prepared with 0.3 M (top) and 0.05 (bottom) triethanolamine. Full spectra (left) reveal disappearance of 4 kDa product peak after irradiation in the presence of LAP, suggesting complete decomposition of thiol-Michael adducts. Magnified view of 1 kDa (alkene) starting materials and products (middle) shows alkyl products and complexes with initiator fragments and triethanolamine. Magnified view of 2 kDa (dithiol) starting materials and products (right) shows similar trends, with combinations of initiator fragments accounting for the observed shifts in molecular weight.

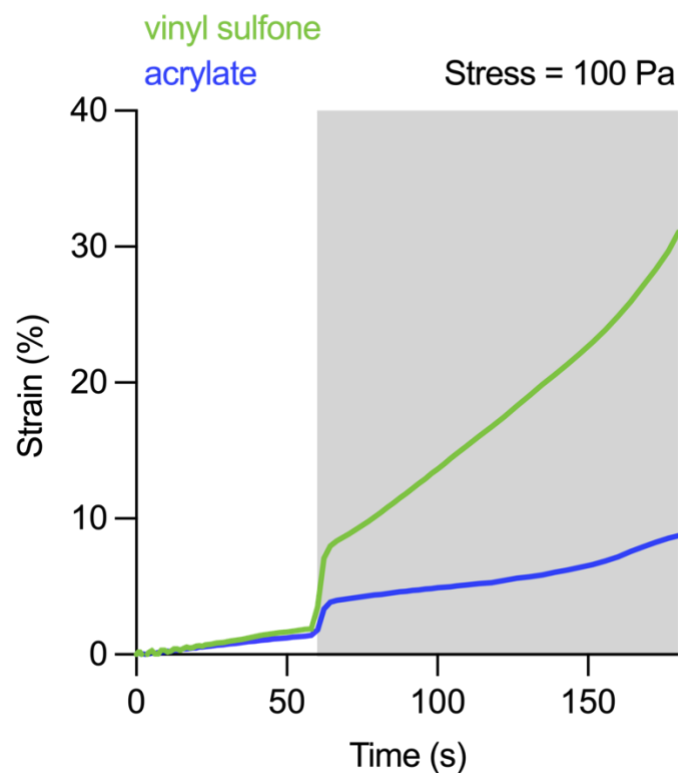


Fig. S5 | Photoinduced creep in on-stoichiometry thiol-Michael hydrogels formed from vinyl sulfone and acrylate precursors and containing 4 wt% LAP; vinyl sulfone shows dramatically increased creep, corresponding to enhanced softening responses seen with this chemistry. Shaded region = light on, 365 nm, 10 mW/cm². Strain data was baselined to 0 at t = 60 seconds in the raw data (shown above as t = 0) to eliminate noise from the creep measurement stabilizing.

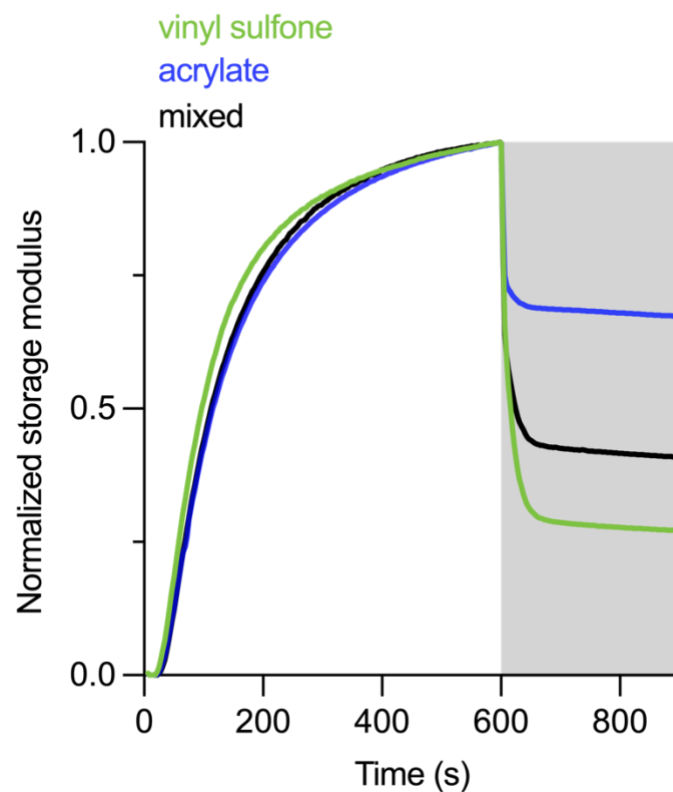


Fig. S6 | Photosoftening of on-stoichiometry thiol-Michael hydrogels containing isolated and mixed (1:1) alkene macromers and 2 wt% LAP; mixed macromers show an intermediated degradation profile. Shaded region = light on, 365 nm, 100 mW/cm².

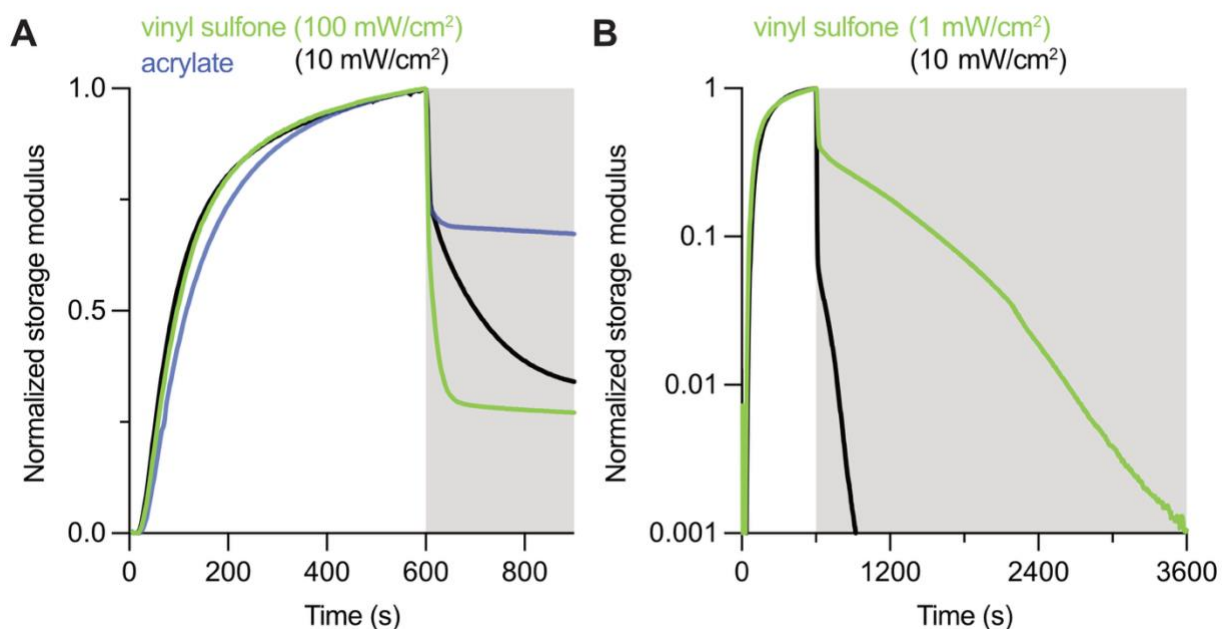


Fig. S7 | Photosoftening of thiol-Michael hydrogels with alternative light intensities. (A) High-intensity (100 mW/cm^2) irradiation does not increase the extent of degradation in hydrogels containing 2 wt% LAP. The y-axis is linearly scaled to more clearly illustrate relative differences in the same order of magnitude. (B) Low-intensity (1 mW/cm^2) irradiation does not decrease the extent of degradation in vinyl sulfone-crosslinked hydrogels containing 4 wt% LAP. The y-axis is log10 scaled to demonstrate the timescale across which order-of-magnitude changes occur with varied intensity. Shaded region = light on. Black lines in both panels correspond to the 10 mW/cm^2 control.

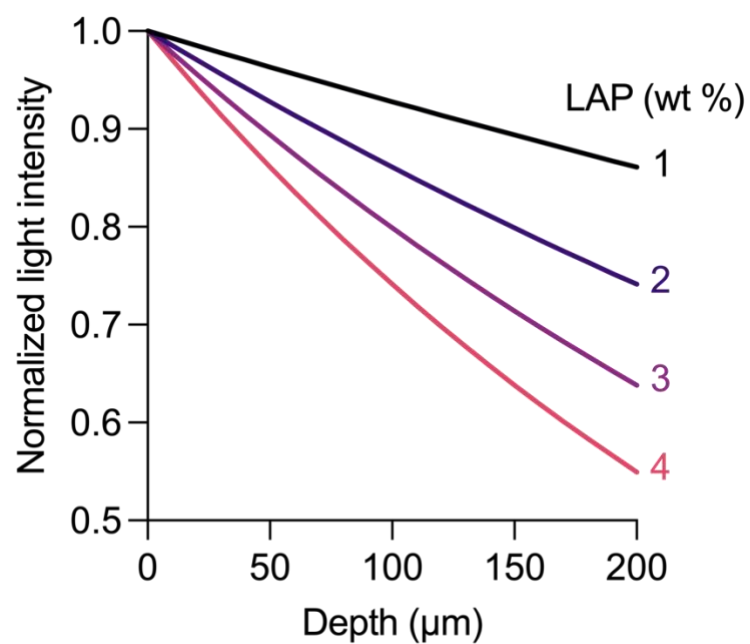


Fig. S8 | Estimated attenuation (according to Beer-Lambert law and a known LAP absorbance of $218 \text{ M}^{-1} \text{ cm}^{-1}$ at 365 nm) through 200 μm -thick hydrogels containing LAP (1-4 wt%). Optical thickness is typically defined as $\geq 20\%$ attenuation, meaning that samples containing 2-4 wt% LAP are not optically thin.

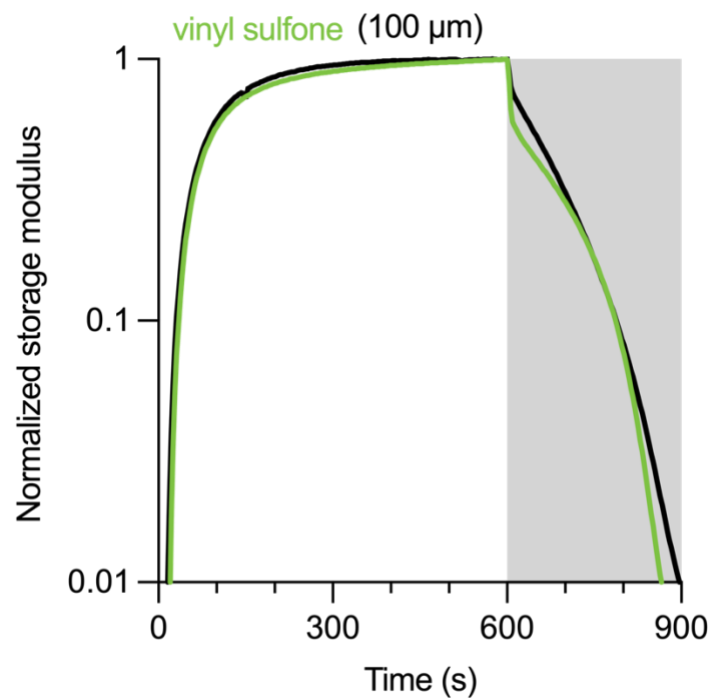


Fig. S9 | Photodegradation of thiol-vinyl sulfone hydrogels containing 4 wt% LAP at varied thickness. A 100 μm -thick hydrogel (black line) shows a very similar degradation profile to the 200 μm -thick reference gels used in this study (green line), suggesting that optical density does not preclude photodegradation (i.e., even $\sim 40\%$ attenuation provides sufficient light intensity to facilitate relatively rapid photodegradation). Shaded region = light on, 365 nm, 10 mW/cm².

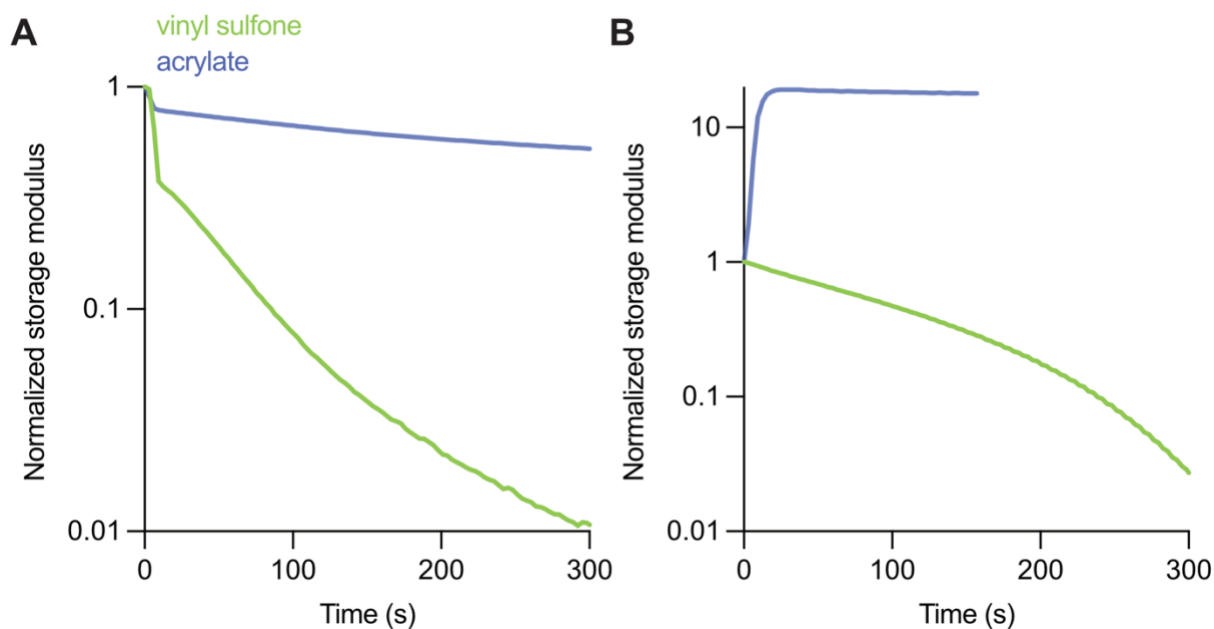


Fig. S10 | Responses to photoinitiated radicals in off-stoichiometry thiol-Michael hydrogels. (A) hydrogels containing excess thiol (2:1 thiol:alkene) and 4 wt% LAP show similar behavior to on-stoichiometry hydrogels, with increased degradation in vinyl sulfone versus acrylate gels, (B) hydrogels containing excess alkene (1:2 thiol:alkene) and 4 wt% LAP show differential responses to radicals, with softening in vinyl sulfone gels and stiffening in acrylate gels due to increased susceptibility to homopolymerization of the unreacted alkene. Light on at 0 seconds, 365 nm, 10 mW/cm².

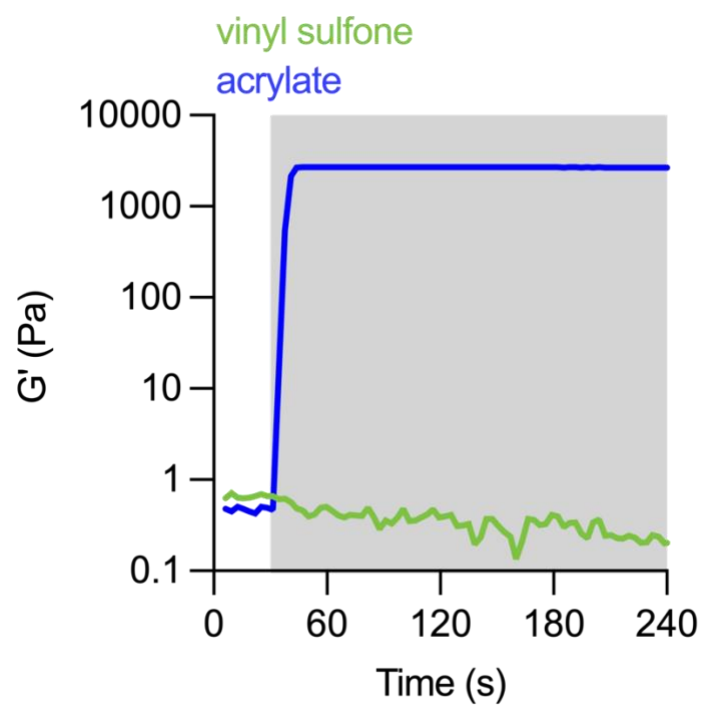


Fig. S11 | Homopolymerization of alkene macromers in the presence of 4 wt% LAP. Acrylates readily crosslink while vinyl sulfones show no gelation within 3.5 minutes of irradiation. Shaded region = light on, 365 nm, 10 mW/cm². Hydrogels were prepared in the same manner as thiol-Michael gels (10 mM alkene), excluding the thiol component.

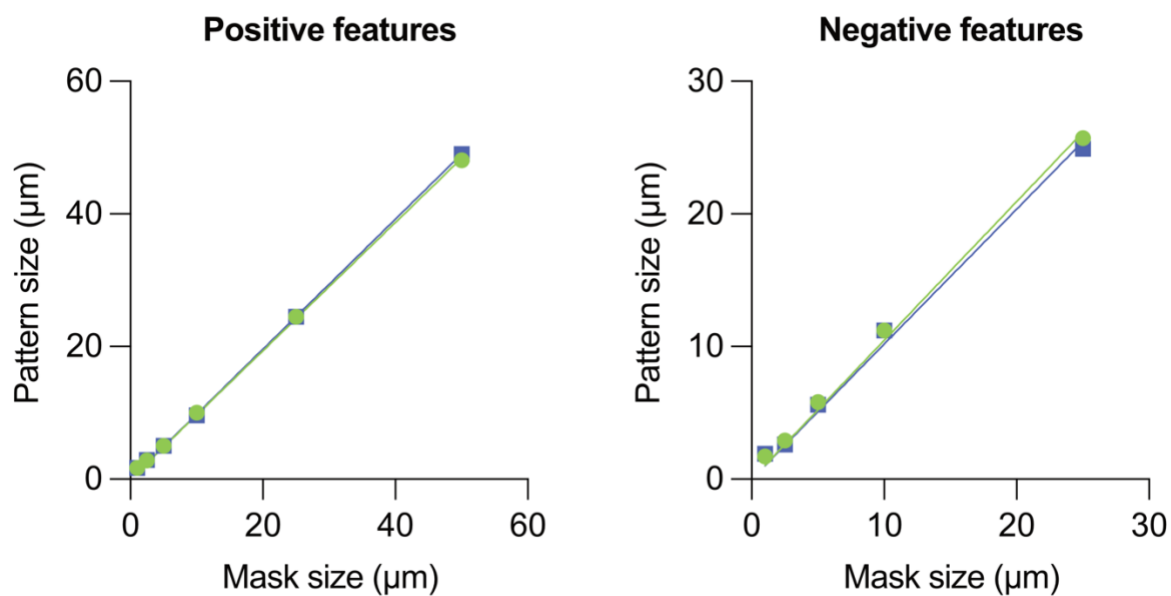


Fig. S12 | Quantified resolution of micron-scale photodegradation in vinyl sulfone (green) and acrylate (blue) thiol-Michael hydrogels. Both chemistries support high-fidelity patterning of positive and negative features, with $R^2 \geq 0.99$ for all linear fits.

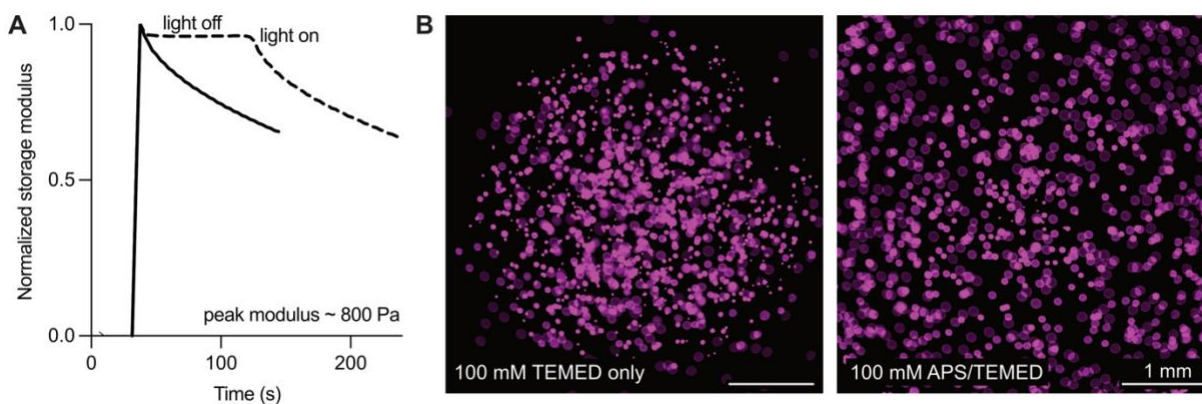


Fig. S13 | Radical-mediated thiol-ene polymerization and subsequent degradation of 4-arm 20 kDa PEG-norbornene and stoichiometric 2 kDa PEG-dithiol (6 wt% overall solids, 10 mM functional groups). (A) Photocrosslinking and photosoftening in the presence of 2 wt% LAP. Temporal control over softening response (dashed line) indicates that this behavior is not due to passive thermal relaxation. Light on at 30 seconds, 365 nm, 10 mW/cm². (B) TEMED alone does not result in bead release from a thiol-ene hydrogel after 40 minutes of equilibration (left), while the addition of equimolar APS results in hydrogel degradation and fluorescent bead release (right).

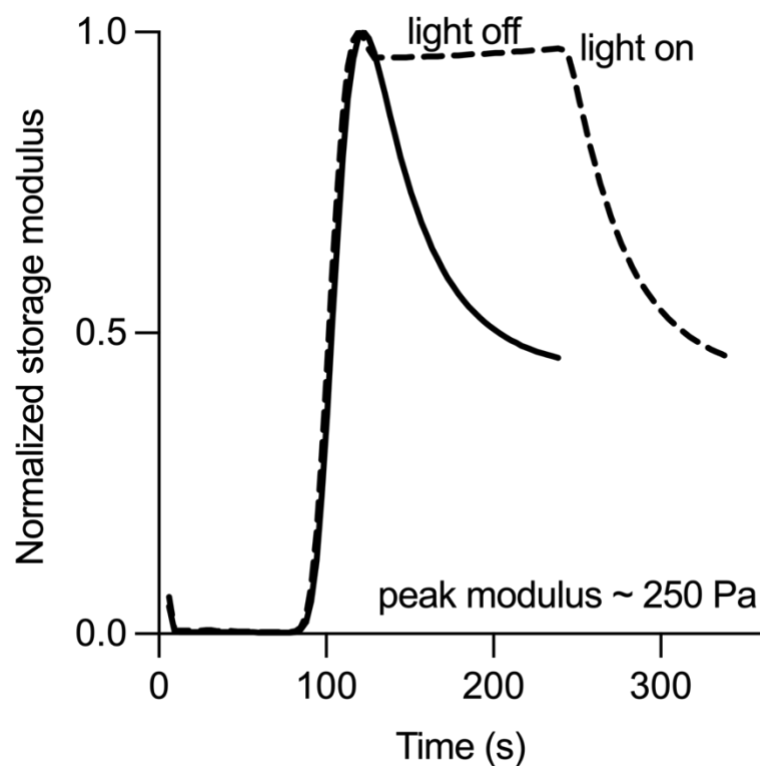


Fig. S14 | Radical-mediated homopolymerization and subsequent softening of 4-arm 20 kDa PEG-norbornene at 20 wt% (40 mM alkene) in the presence of 2 wt% LAP. Temporal control over softening response (dashed line) indicates that this behavior is not due to passive thermal relaxation. Light on at 30 seconds, 365 nm, 10 mW/cm².

Movie Captions

Movie S1 | APS/TEMED-based degradation of on-stoichiometry thiol-Michael hydrogels. 10 minute time-lapse of radical-mediated bead release from vinyl sulfone (left) and acrylate (right) hydrogels. Encapsulated beads are 1 μm FluoSpheres. Video dimensions are approximately 4.5 x 4.5 mm (i.e., gels are roughly 3 mm in diameter). On-stoichiometry formulations show similar responses, with both gels releasing beads upon addition of APS.

Movie S2 | APS/TEMED-based degradation of off-stoichiometry thiol-Michael hydrogels (1:2 thiol:alkene). 10 minute time-lapse of radical-mediated bead release from vinyl sulfone (left) and acrylate (right) hydrogels. Encapsulated beads are 1 μm FluoSpheres. Video dimensions are approximately 4.5 x 4.5 mm (i.e., gels are roughly 3 mm in diameter). Off-stoichiometry formulations show differential responses to radicals, with vinyl sulfones uniquely releasing beads upon addition of APS due to gel-stabilizing homopolymerization in the acrylate system.