

Supporting Information

Combined, Independent Small Molecule Release and Shape Memory via Nanogel-Coated Thiourethane Polymer Networks

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Nanogel Synthesis

Poly(ethylene glycol) methacrylate ($M_n=360$) and tetraethylene glycol dimethacrylate were combined in a round-bottom flask in a 70:30 molar ratio. 2-mercaptoethanol was added at 15 mol% relative to the total monomer content, and AIBN was added at 1.0 wt% relative to the total monomer content. The reaction mixture was dissolved in methyl ethyl ketone at 6x volumetric excess to bring the total monomer concentration to 13 wt%. Polyfluor 570 (methacryloxyethyl thiocarbonyl rhodamine B) was added at 0.1 wt% relative to the total monomer content. The reaction mixture was purged with nitrogen at room temperature while stirring for 30 minutes and transferred to a 75 °C oil bath with reflux condenser. After 6 h the flask was removed from the oil bath and exposed to air to stop the polymerization. Allyl isocyanate was then added at 15 mol% relative to total -OH group content along with ~10 mg dibutyltin dilaurate, and the reaction mixture was stirred at room temperature for 16 h. Solvent was then removed under reduced pressure, and the crude product was dissolved in methanol and dialyzed against methanol for 48 h (3500 molecular weight cutoff). The purified nanogels were dried under reduced pressure. Hydrodynamic radius of 4.14 nm and Mark-Houwink alpha parameter of 0.271 were determined via triple detection gel permeation chromatography, and indicate that the isolated product has a globular, particulate morphology.

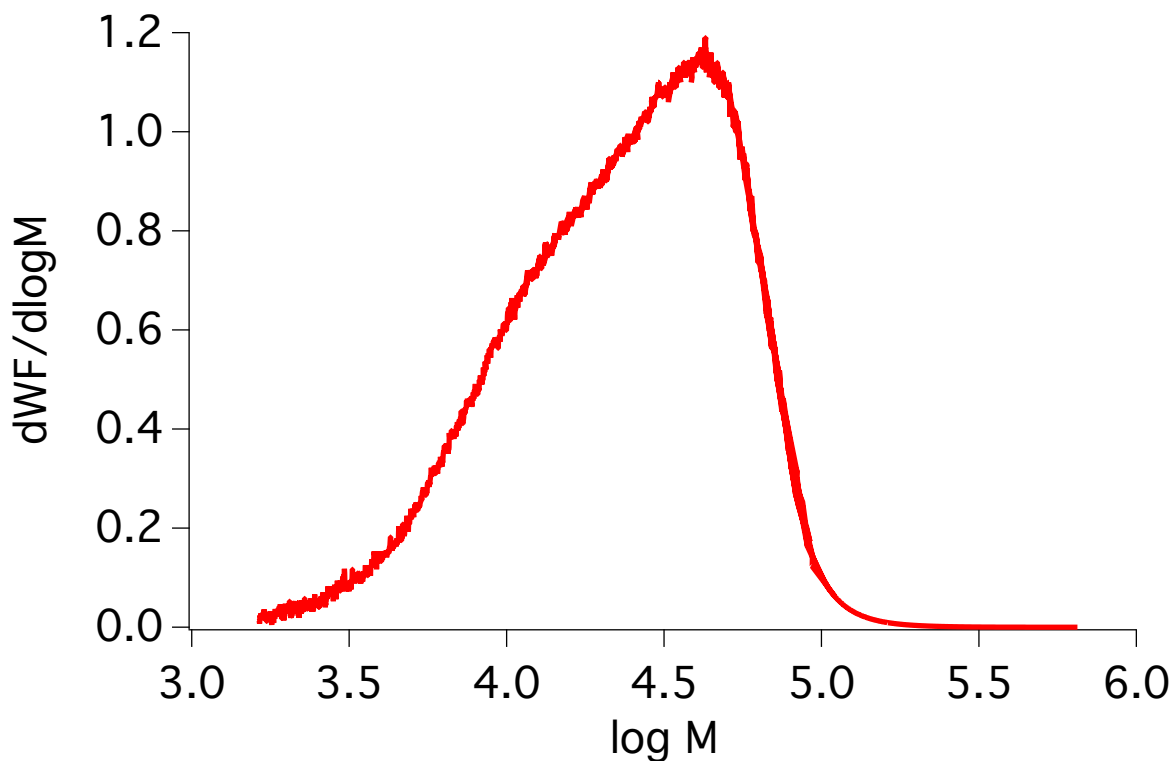


Figure S1. Nanogel differential weight fraction vs. log molecular weight as determined from triple-detection GPC in THF.

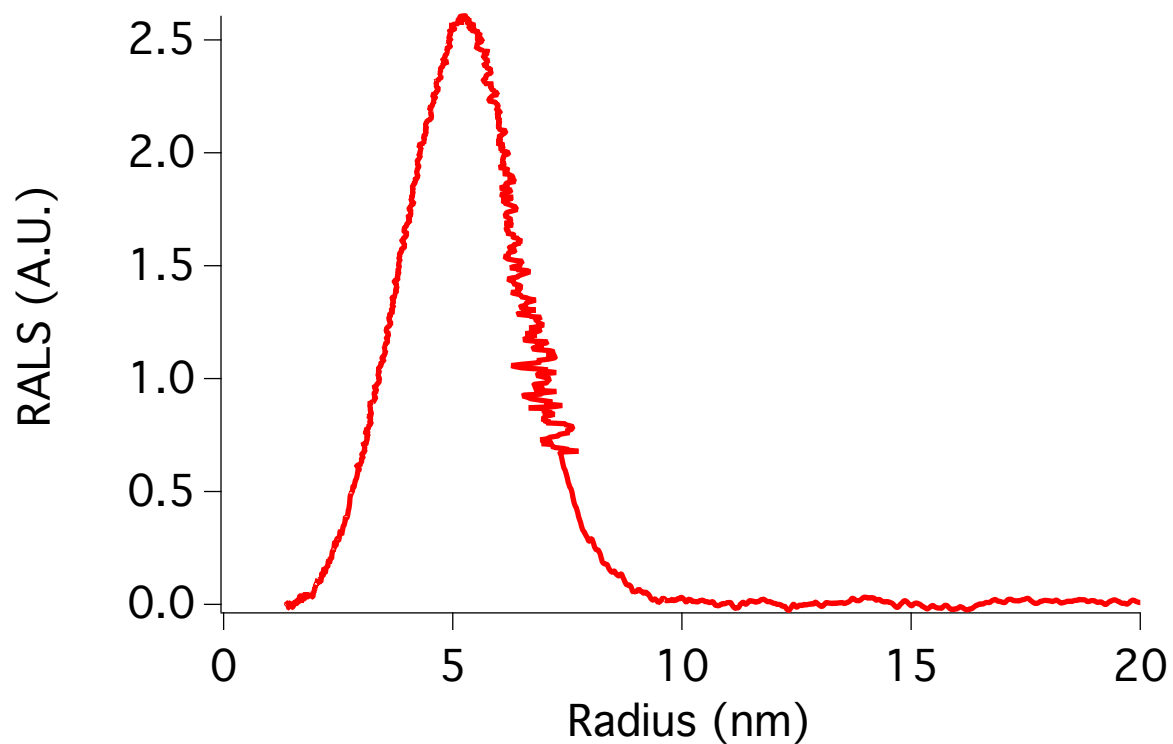


Figure S2. Nanogel right angle light scattering (RALS) detector response vs. radius as determined by triple-detection GPC with inline light scattering in THF.

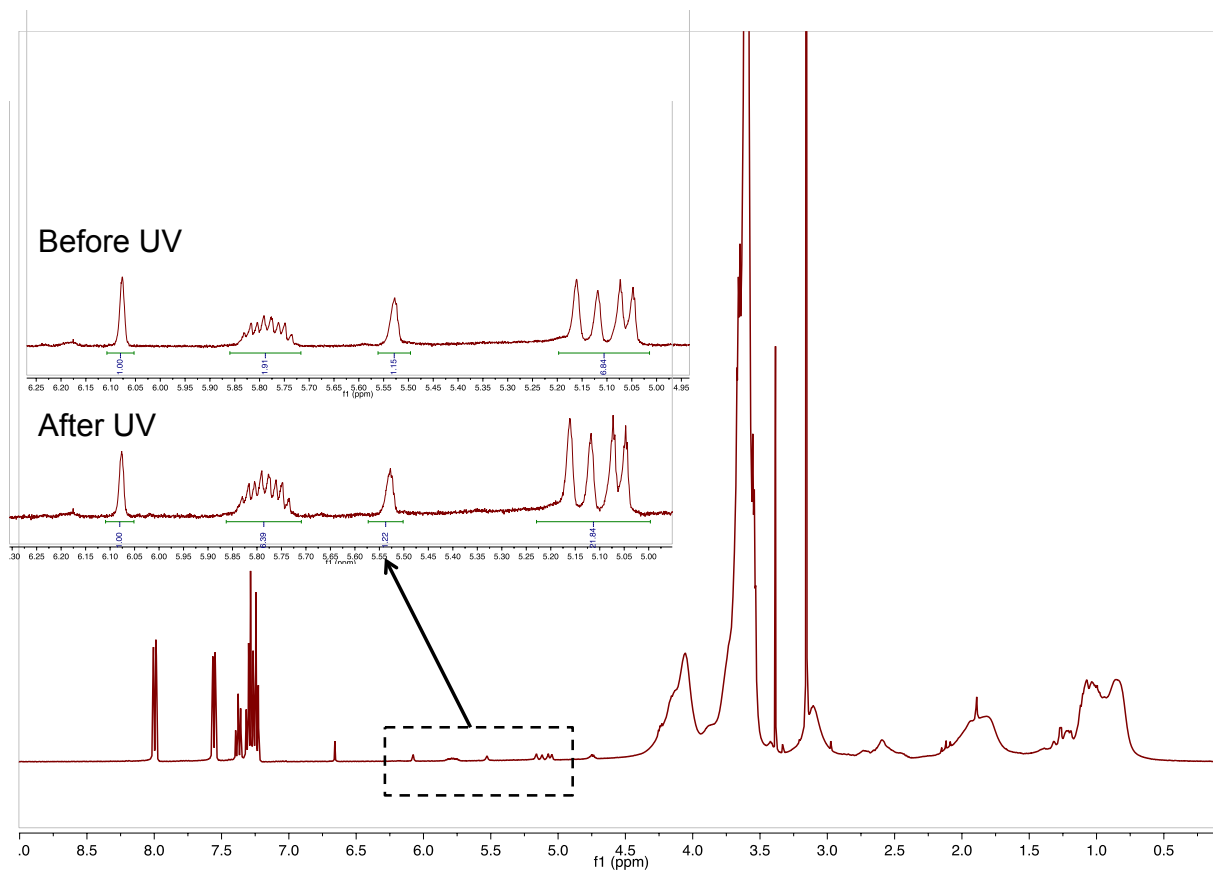


Figure S3. ^1H NMR spectrum of allyl and methacrylate-functional nanogels before and after UV irradiation in CDCl_3 with 1.0 wt% DMPA.

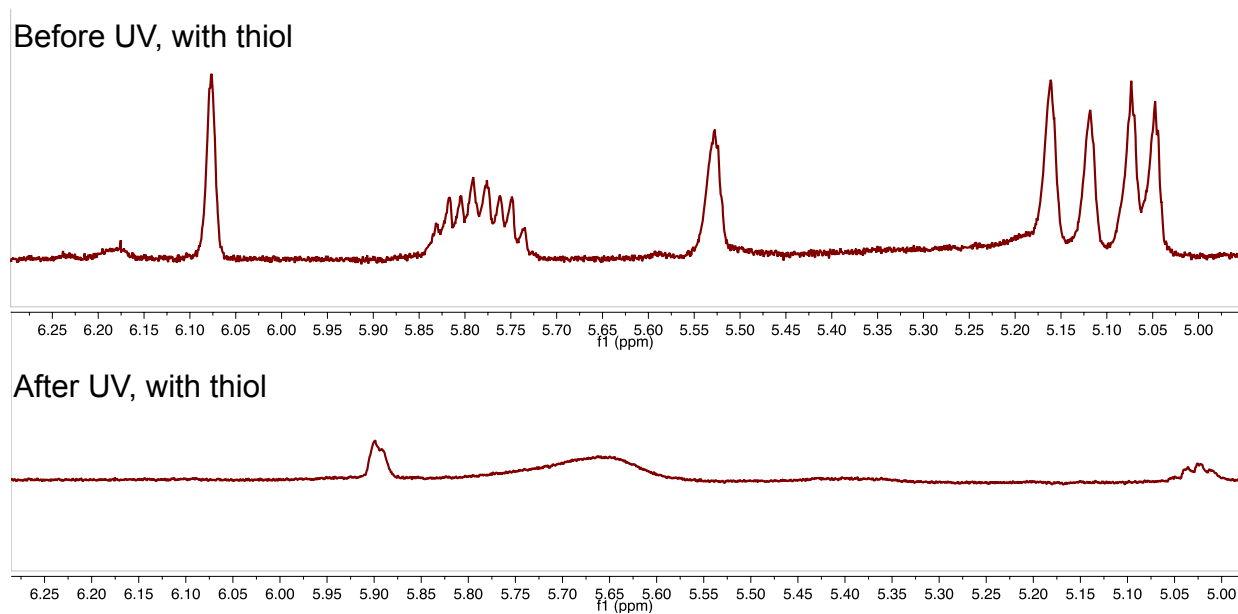


Figure S4. ^1H NMR spectrum of allyl and methacrylate-functional nanogels before and after UV irradiation in CDCl_3 with 1.0 wt% DMPA and 10 wt% mercaptoethanol.

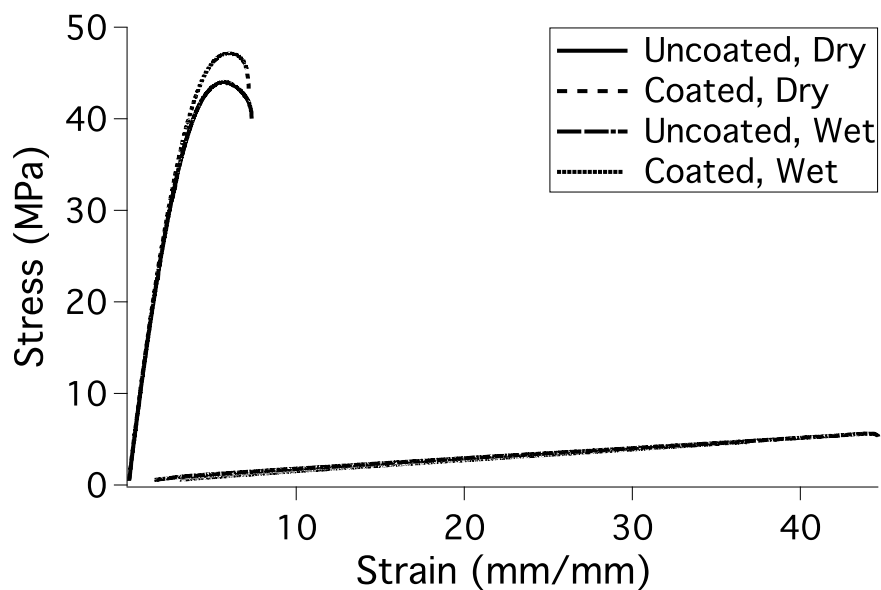


Figure S5. Representative stress-strain plots of the coated and uncoated SMP in the dry or water-equilibrated state.

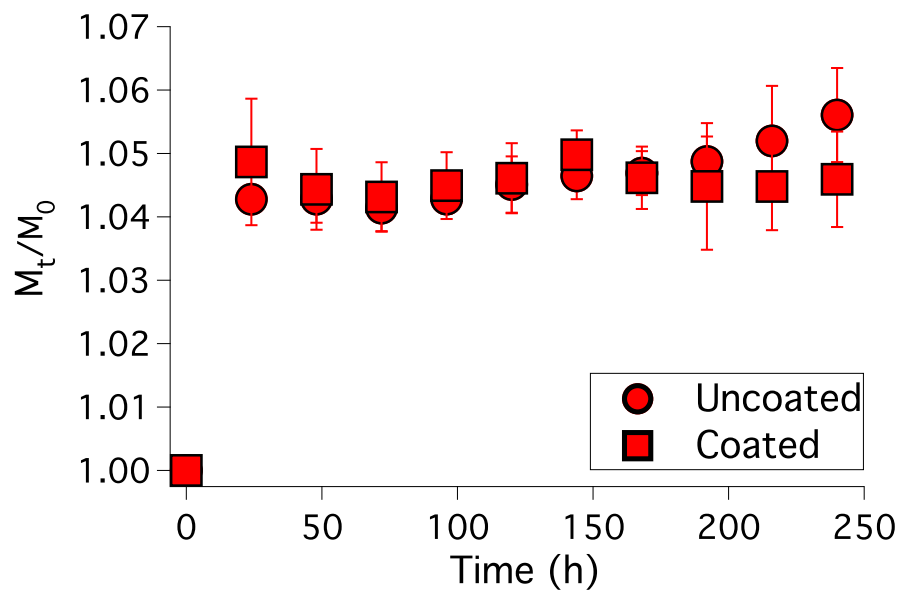


Figure S6. Ratio of the mass of a water-swollen SMP (M_t) to the mass of the dry SMP (M_0) for the uncoated and coated samples.