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Supporting Information for

A versatile synthetic extracellular matrix mimic via thiol-ene photopolymerization

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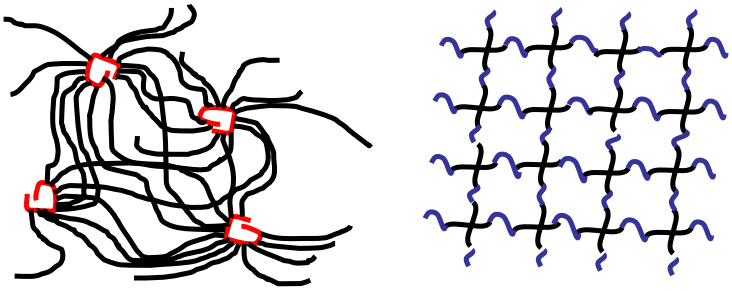

Figure S1. General network structure for radically polymerized chain growth PEG-diacrylate hydrogels (left with polyacrylate chains in red) and step-growth hydrogels (right with comonomers in blue).

$$p_c = \frac{1}{[r(f_{thiol}-1)(f_{ene}-1)]^{1/2}} \qquad \text{(Eqn. S1)}$$

The Flory-Stockmayer critical gel point equations relates the critical conversion for gelation, p_c, with respect to monomer functionality, f, and the stoichiometric ratio, r. For conditions under which $p_c>1$, gelation is precluded no matter what extent of conversion is reached.

Table S1. Results of polymerization of solutions of various stoichiometric ratios. Where the critical gel point conversion for a particular ratio remained below 1, gels formed. When greater than 1, no gel formed under the polymerization conditions. Additionally, the stoichiometrically balanced polymerization exhibited the highest modulus with those of lower stoichiometric ratios exhibited lower moduli.

Ratio norb:thiol	Stoichiometric ratio (r)	Critical gel point conversion (p_c)	Final shear elastic modulus of gel
1:1	1	0.58	2820±320
1:0.8	0.8	0.65	2010±330
0.8:1	0.8	0.65	1820±260
2:1	0.5	0.82	1210±420
1:2	0.5	0.82	739±220
4:1	0.25	1.15	no gel
1:4	0.25	1.15	no gel
100% norb	0	infinite	no gel
100% thiol	0	infinite	no gel

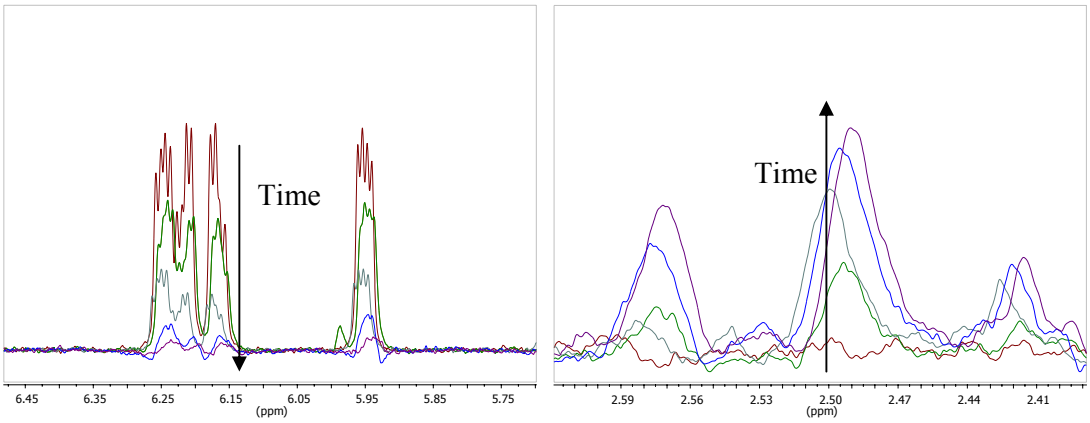

Figure S2. Spectral depletion of peaks associated with alkene protons on norbornene functional group (left) and simultaneous and proportional emergence of peaks associated with thioether α-protons (right).

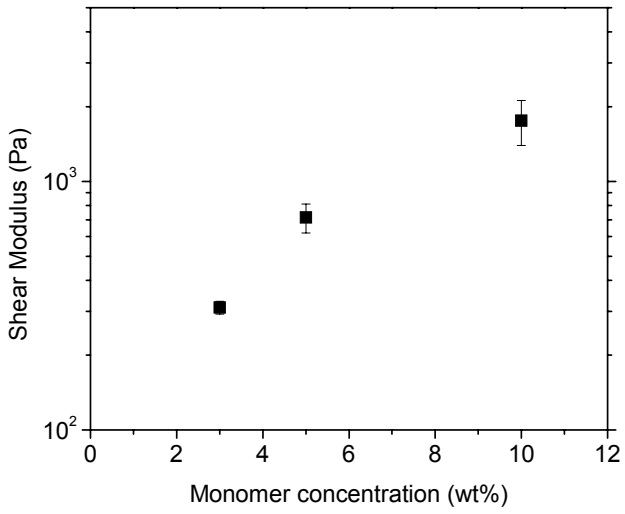

Figure S3. Shear elastic modulus for 3, 5, and 10 wt% gels.

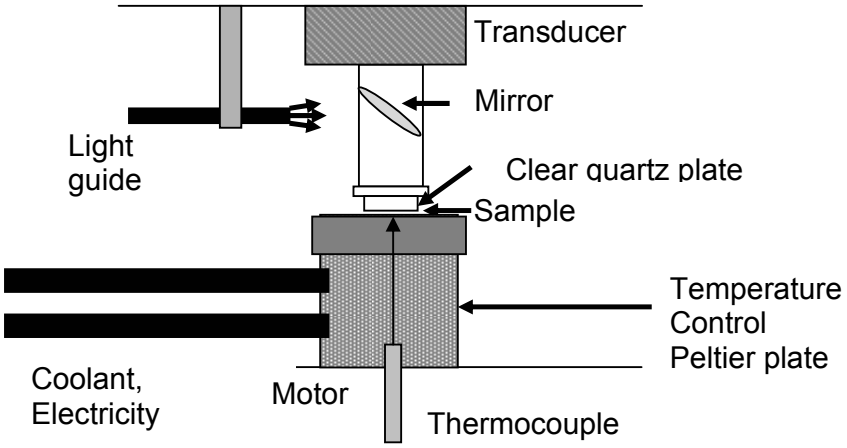

Figure S4. Schematic for photorheometer instrumentation setup. Light is directed by mirror to sample through transparent quartz plate. Motor is strain controlled. Transducer connected to upper plate and shaft. Temperature controlled by Peltier plate.

Table S2. Results from Tukey's pair-wise comparison of means with α=0.05. Here, the prefix ALA, LEU, and TRP refer to the gels crosslinked with the MMP-ALA, MMP-LEU, and MMP-TRP respectively. The numbers 0, 250, 500, and 1000 refer to the concentration, in mM, of cell adhesion ligand CRGDS present in each gel. Significant trends exist for both RGDS concentration and for crosslink degradation rate. In the table, YES indicates a significant difference and NO indicates no significant difference.

	ALA 0	**ALA 250**	**ALA 500**	**ALA 1000**	**LEU 0**	**LEU 250**	**LEU 500**	**LEU 1000**	**TRP 0**	**TRP 250**	**TRP 500**	**TRP 1000**
ALA 0		NO	NO	YES	NO				NO			
ALA 250			NO	YES		YES				YES		
ALA 500				YES			YES				YES	
ALA 1000								YES				YES
LEU 0						YES	YES	YES	NO			
LEU 250							YES	YES		YES		
LEU 500								NO			NO	
LEU 1000												YES
TRP 0										YES	YES	YES
TRP 250											NO	YES
TRP 500												YES
TRP 1000												