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Supporting Information for
Getting Control of Hydrogel Networks with Cross-Linkable Monomers

Pamela G. Cohn[1*], Sahar Qavi[2], Jasmine Cubuk[1], Mihir Jani[1], Mohamed Lamine Megdad[1], Dhvani Shah[1], Cara Cattafi[1], Panchatapa Baul[1], Shanthi Rajaraman[1], and Reza Foudazi[2*]

[1]Chemistry Program, Stockton University, Galloway, NJ 08205; [2]Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003.

Experimental

General

Nuclear Magnetic Resonance (NMR) spectra were recorded on a 400 MHz Bruker Ascend NMR magnet at 24 °C. Chemical shifts are reported in parts per million (ppm) with reference to Dimethyl sulfoxide (*d^6*-DMSO) and water (D_2O) or chloroform ($CDCl_3$) and deuterated methanol (CD_3OD) as the solvent. Multiplicities are abbreviated as followed: singlet (s), doublet (d), triplet (t), multiplet (m). Thin Layer Chromatography was done on a 3 by 1inch MF254 silica plate, pH 5, with an alumina backing. The eluent used was made of 90% dichloromethane with 10% ethanol. All solids were dissolved in 50% dichloromethane / methanol, methanol, dichloromethane, ethanol or dichloromethane/ethanol. Centrifugation used to separate materials. Beckman Coulter Avanti J-265 XP at 19°C run at JS745 at 2000 rpm for 5 minutes. The compounds were centrifuged with four mini 50 mL centrifuge tubes. Infrared Spectroscopy (IR) spectra were recorded on a NicoletiS5 using an Id5 ATR diamond. The bands are recorded in wavenumbers (cm^{-1}). Freeze-drying of the materials was done on a LABCOND Freezezone 6 plus Lyophilize Machine. Chiller was set to -60°C. Vacuum set to high with mBAR ~0.42 mBAR. Freezer's lowest temp chilled to -87°C.

Differential scanning calorimetry analysis was performed on gels using a Q20 TA instrument. After loading the sample into the calorimeter, the temperature the pans were cooled to -50 ºC and heated at 5 ºC/ min.

Frequency Sweep rheological measurements were performed on the gels using a TA Discovery HR-3 rheometer with an objective with cross-hatch geometry.

The compressive stress–strain measurements were performed on hydrogels swollen with DI water by using a Shimadzu universal testing machine (AGS-X Series) at a crosshead speed of 1 mm/min. The cylindrical gel samples were 20 mm in diameter and 10 mm in thickness.

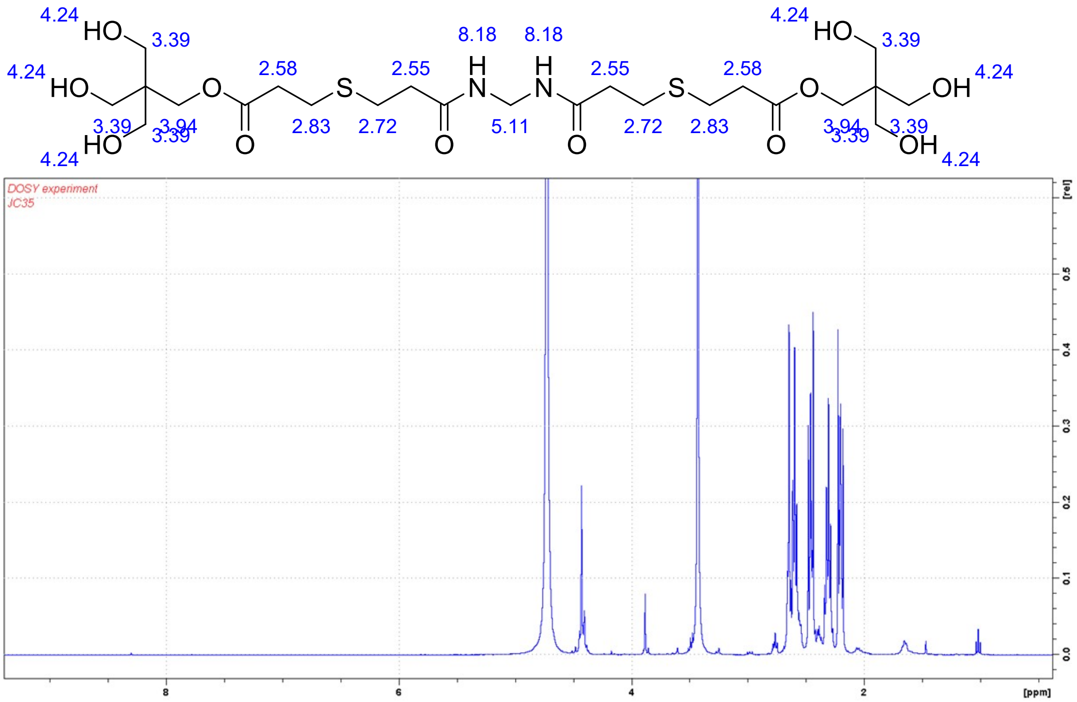
All reagents (N,N'-methylenebis(acrylamide), pentaerythritol(tetrakis(3-mercaptopropionate), 4,4'-azobis(4-cyanovaleric acid) were purchased from Sigma Aldrich Chemical Company. All solvents for reactions, purification, and spectroscopic analyses (absolute ethanol, dichloromethane, methanol) were purchased from ThermoFisher Scientific.

Representative Synthesis of Poly(MBA-*co*-PTK):

2:1, thiol:ene:
Absolute ethanol (50 mL) was degassed in a 100 mL round bottom flask (RBF) with nitrogen for 1 h. N, N'-methylenebis(acrylamide)(MBA), (1.000 g, 6.48 mmol) and 4,4'-Azobis (4-cyanovaleric acid)(0.05 g, 0.178 mmol) were placed in a 100 mL round bottom flask with a magnetic stir bar. The system was purged with argon gas for 5 min. Pentaerythritol tetrakis(3-mercaptopropionate) (PTK) (2.47 mL, 6.46 mmol) was

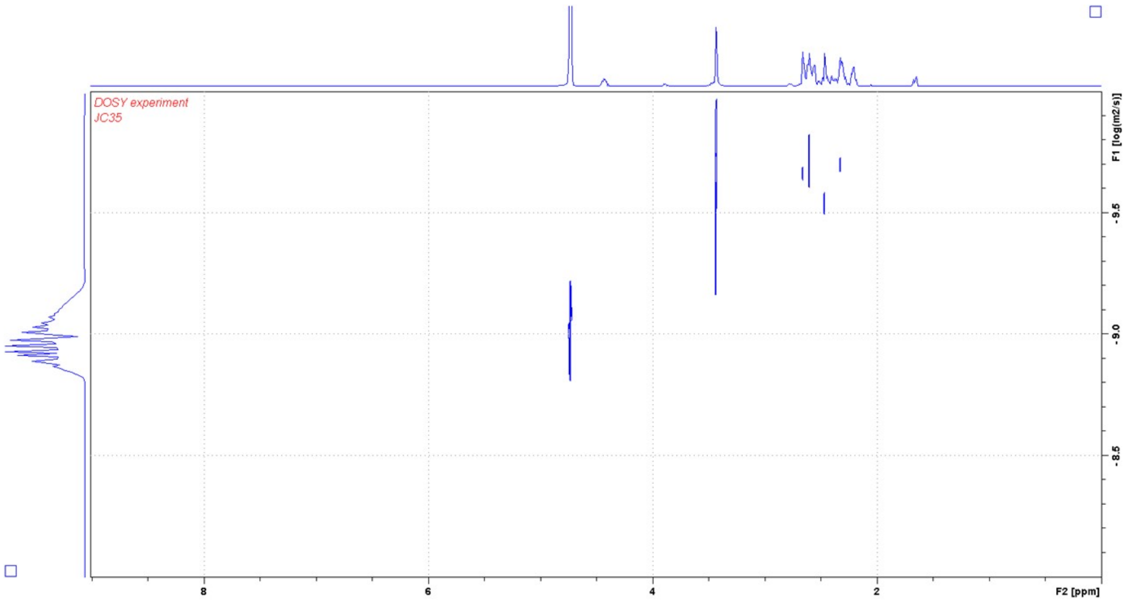
added via syringe. Degassed ethanol (10 mL) was also added via syringe, and the resulting solution was heated to 70 °C and stirred for 16 h. The resulting rubber-like copolymer poly(MBA-*co*-PTK)) was triturated with ethanol (100 mL), stirred and sonicated and vacuum filtered. The product gelled and was triturated with absolute ethanol, followed by deionized water. The gel was freeze-dried and characterized via thermal analysis, swelling measurements, and rheo-mechanical testing.

S1A: *JC35 (2:1, thiol:ene, D_2O, 400 MHz) NMR analysis:*
In the sample containing a 2:1 composition of thiol:ene groups, there is no presence of the vinyl end group in the spectrum. The spectrum would suggest the structure is comprised of the di-substituted thiol-ene adduct, which is consistent with the following hydrolysis product (with ChemDraw chemical shifts indicated in blue on the structure):

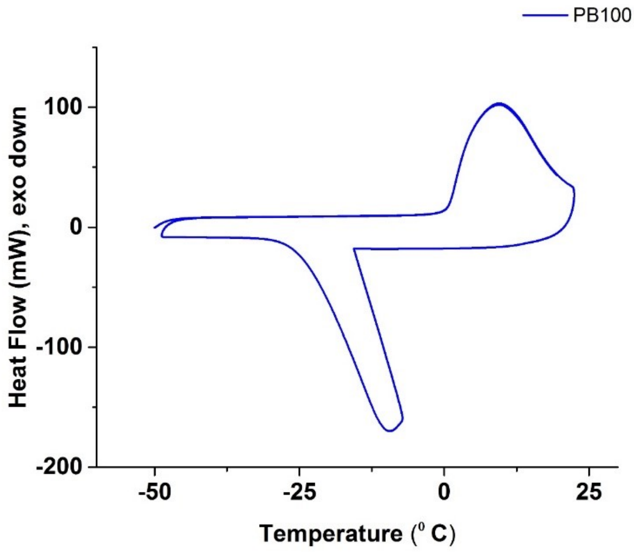


S1B: *DOSY NMR analysis of 2:1 (thiol:ene) gel in D_2O (400 MHz)*

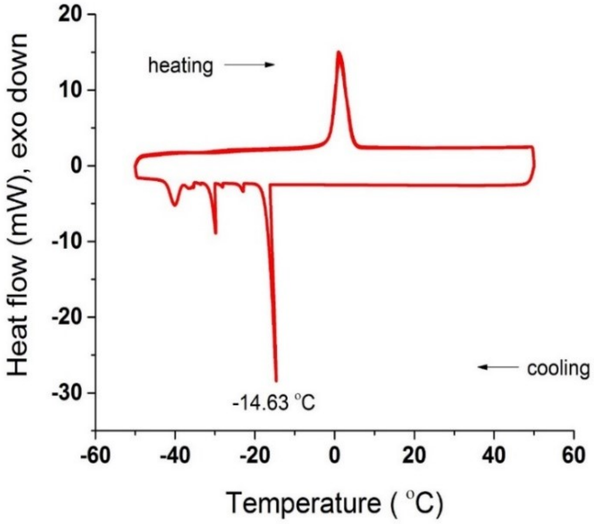
The DOSY NMR spectrum (at pH~10) shows one major diffusion coefficient at -9.7 (log(m^2/ s)) in addition to residual water.



Differential Scanning Calorimetry of Different Gel Compositions and their crystallization exotherms:
S2 A: 1:1, thiol:ene, DSC (scan rate 10 °C/ min)

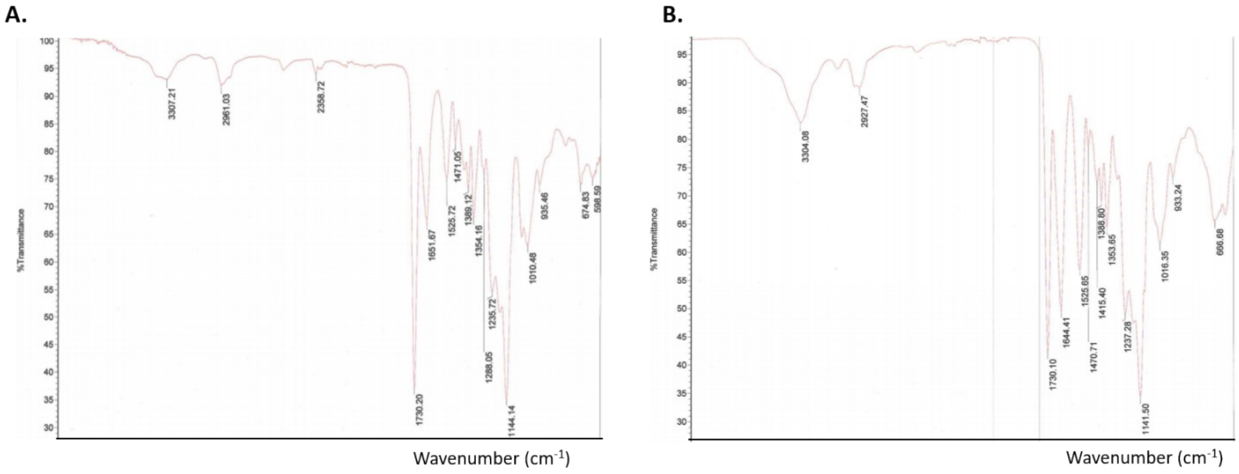


S2B: 4:1, thiol:ene, DSC (scan rate 10 °C/ min)



S3: *Infrared Spectra for 2:1 Gel composition before and after swelling*

The infrared spectra of both wet and dry states for the 2:1, thiol:ene composition of gel were unremarkable. The presence of the free thiol groups is indicated by a small broad S-H stretch at ~2600 cm^{-1}. Additionally, the amidic carbonyl stretch at 1650 cm^{-1} (from MBA) and the ester carbonyl stretch (from PTK) at 1730 cm^{-1} suggest incorporation of both monomers in to the gel network. Upon the addition of water, the only noticeable change is the broadened O-H stretch at 3304 cm^{-1}, which is indicative of hydrogen bonding in the material.

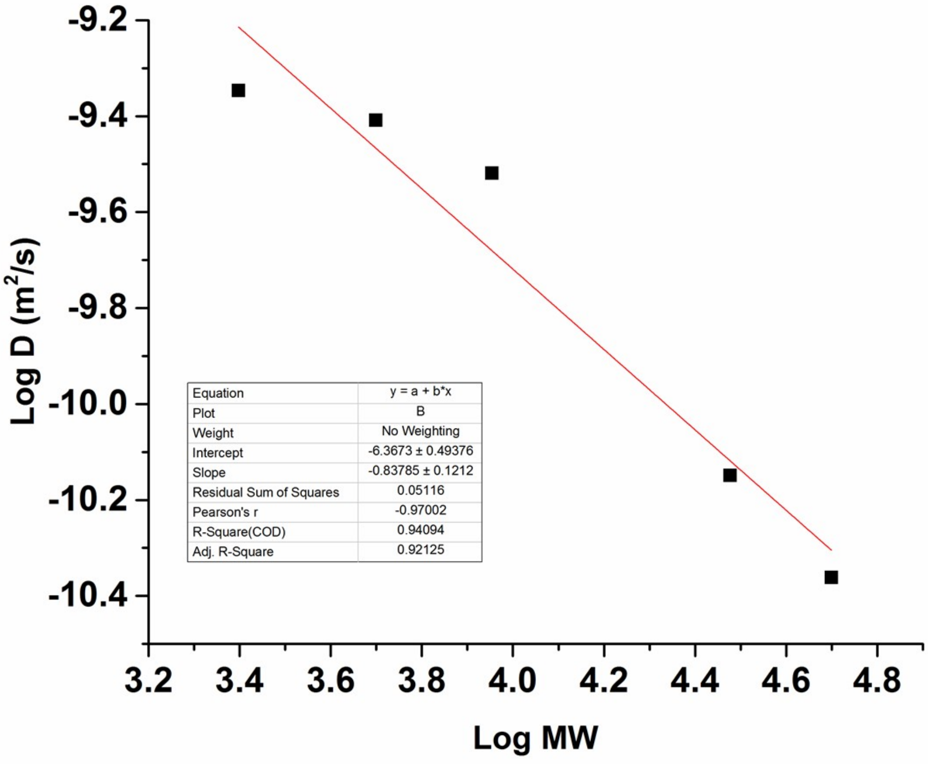


The infrared spectrum (neat) for the A) 2:1, thiol:ene, PTK: MBA, dry state for the gel; B) 2:1, thiol:ene, PTK: MBA, wet state after swelling in water for 24 h.

Table 1. Spectral Assignment for Hydrogel with 1:1, thiol: ene functionality.

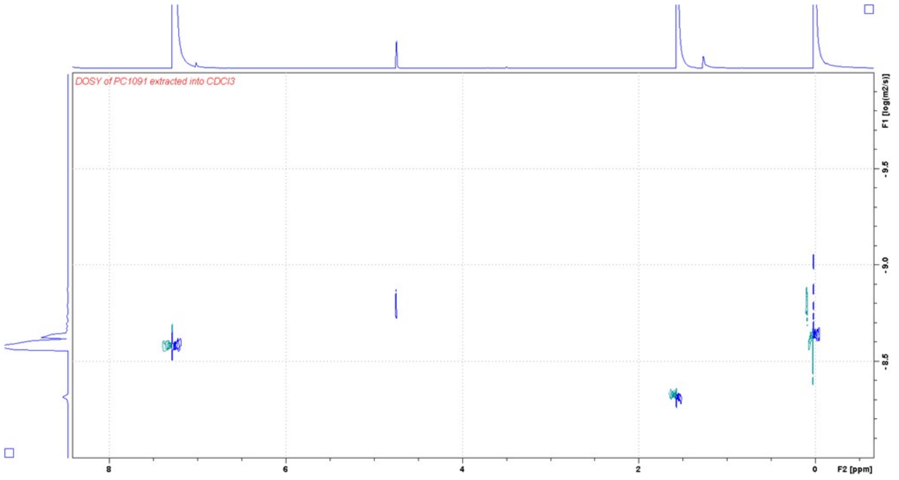
Signal	Chemical Shift (ppm)	Number Hydrogens	Multiplicity (J^3 in Hz)	Group
A	5.3183-5.9468	3	m	-C**H** (alkenyl, overlapping signals)
B	4.1772-4.2942	8	s	-C$\mathbf{H}_2$O-
C	3.2628-3.6832	18	s	(overlapping signals)
D	2.0761-2.3442	56	m	(overlapping signals)
E	1.8631	2	t (J = 6.8 Hz)	-C$\mathbf{H}_2$CH$_2$-
F	1.4666	2	t (J = 6.8 Hz)	-C$\mathbf{H}_2$CH$_2$-

S4A: *Standard Curve for DOSY NMR (CDCl$_3$, 400 MHz) for polystyrene standard compounds of MW (g/ mole) of 2500, 5000, 9000, 30000, 50000:*



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	-6.3673 ± 0.49376
Slope	-0.83785 ± 0.1212
Residual Sum of Squares	0.05116
Pearson's r	-0.97002
R-Square(COD)	0.94094
Adj. R-Square	0.92125

S4B: *DOSY NMR Spectrum of 1:1, thiol:ene gel after basic degradation and extraction into CDCl$_3$ (400 MHz):*



S5: *Rheological Measurements:*

All rheological measurements were performed with a Discovery Hybrid Rheometer (DHR3) from TA Instruments (New Castle, DE, USA). All experiments were carried out at constant temperature of 25 °C with a parallel plate geometry with a diameter of 40 mm and a gap between plates of 1 mm and using a solvent trap to avoid solvent evaporation. Dynamic frequency sweep was done at ω=0.1-1000 rad/s in the linear viscoelastic regime with constant strain of 1%.

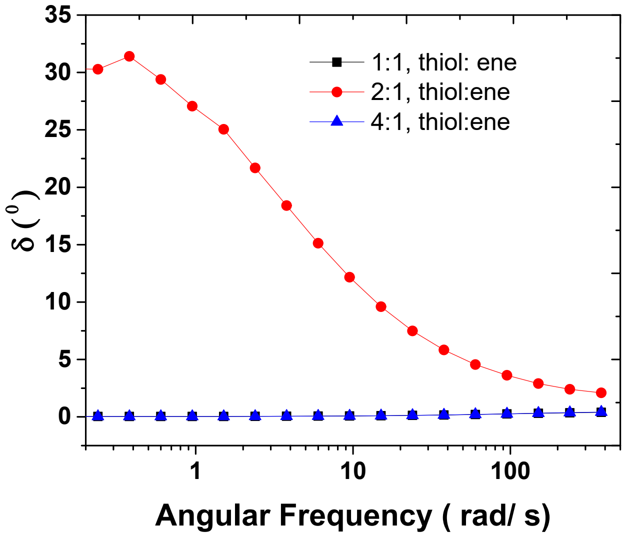
G=nRT , we know R=8.314 J/mol.K and T=25 °C=298.15 K

2:1, thiol: ene in chloroform ---> G=2×10^5 ---> n=80.68 ~ 81
2:1, thiol: ene in water---> G=10^4 ---> n=4.03 ~ 4

% of chemical crosslinks= 4/81×100= 4.94% ~ 5%
% of physical crosslinks= (81-4)/81×100= 95.06% ~ 95%

4:1, thiol: ene in chloroform ---> G=10^5 ---> n=40.34 ~ 40
4:1, thiol: ene in water---> G=5×10^3 ---> n=2.02 ~ 2

% of chemical crosslinks= 2/40×100 = 5%
% of physical crosslinks= (40-2)/40×100 = 95%



δ measurements from frequency sweep measurements for various thiol:ene gel compositions in water.

S6: *Kinetic Swelling Measurements for hydrogels:*

Swelling measurements based on mass uptake of water were taken on ~ 0.100 g samples of freeze-dried gels over time as they were immersed in deionized water at room temperature.