Supporting Information

Reaction Environment Effect on the Kinetics of Radical Thiol-Ene Polymerizations in the Presence of Amines and Thiolate Anions

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1 Experimental methods and materials

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Burker Avance-III 400 spectrometer.

Materials. Trimethylol propane diallyl ether (DAE, 90%), tri(ethylene glycol) divinyl ether (DVE, 98%), 1,3-divinyltetramethyldisiloxane (DVSi, 97%), 1,4-diazabicyclo[2.2.2]octane (DABCO, ≥99%), aniline (≥99.5%), diallylamine (99%), 1,6-hexanedithiol (96%), 1-butanol (99.8%), 1-hexanol (anhydrous, ≥99%), 4-arm poly(ethylene glycol) M_n 10,000 g/mol, and 4-arm poly(ethylene glycol) norbornene terminate (PEG4NB) M_n 10,000 g/mol were purchased from Sigma-Aldrich. 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU, ≥99%) was purchased from Chem-Impex International. Triethylamine (TEA, 99%), sodium phosphate monobasic monohydrate (≥98%), sodium phosphate dibasic heptahydrate (≥98%), ethanol anhydrous (100%), N,N-dimethyl formamide anhydrous (DMF, ≥99.9%), dimethyl sulfoxide (DMSO, ≥99.9%), n-hexanes (95%), and ethylene glycol diacetate (EGDAc, 99%) were purchased from Fisher Scientific. Ethylene glycol bis(3-mercaptopropionate) (EGBMP, >98%) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, >98%) were purchased from TCI Chemicals. Methanol anhydrous (99.8%) and isopropanol anhydrous (99.8%) were purchased from Thermo Fisher Scientific. Tetrahydrofuran anhydrous (THF, 99%, stabilized with 250-300ppm butylated hydroxytoluene) was purchased from Alfa Aesar. Dichloromethane (DCM, 99.9%) was purchased from Acros Organics. 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure D-2959, 98%) was purchased from BASF. Poly(ethylene glycol) M_n 4,600 g/mol was purchased from JenKem Technology. All materials were used without further purification.

FTIR kinetic studies. Reaction formulations were laminated between NaCl plates (International Crystal Laboratories) separated by a 0.051 mm plastic spacer. Thiol (~2570 cm^{-1}, S—H stretch) and alkene (~3050 cm^{-1} C=C—H stretch and ~1650 C=C stretch) conversions were monitored in real-time in the mid IR (Nicolet Magna-IR 750 series II FTIR spectrometer) at a collection rate of 2 scans per second and a resolution of 2 cm^{-1}. Samples were then irradiated with 365-nm light with variable intensity (Thorlabs DC4104 4-channel LED driver equipped with a Thorlabs M365L2-C5, 80 mW collimated LED as the irradiation source). Irradiation intensities were measured with a Thorlabs PM100D radiometer.

Thiol-ene hydrogel polymerization studies. PEG4NB or PEG4AE was dissolved in deionized water with PEG2MP or PEG2MA (at a 1:2 molar ratio, 10 wt% PEG in water) along with Irgacure D-2959 photoinitator (0.5 wt% with respect to the mass of PEG in solution). Solutions were then aliquoted in 100 μL portions into microcentrifuge tubes and then lyophilized to yield a white powder. Lyophilized samples were then reconstituted in 90 μL of buffer solution varying in pH from 4.4 to 10.5. Buffers were prepared by mixing aqueous solutions of sodium phosphate monobasic (0.5 M) and sodium phosphate dibasic (0.5 M) at varying ratios to achieve desire pH. Buffer solutions with a pH greater than 9.2 were prepared by the dropwise addition of aqueous 1 M NaOH to a solution of 0.5 M sodium phosphate dibasic until the desired pH was achieved. pH was measured using a Thermo Scientific Orion Star A211 pH benchtop meter.

Samples in buffer solution were then irradiated with 365-nm light at an intensity of 10 mW/cm^2 using a Thorlabs DC4104 4-channel LED driver equipped with a Thorlabs M365L2-C5, 80 mW collimated LED as the irradiation source and the samples rheological properties were monitored in real-time with a TA Instruments Ares-G2 rheometer (1Hz oscillation frequency, 5% strain, 4 points per second sampling rate).

Synthesis of tricyclodecane dimethanol di-(endo, exo-norbornene-2-ene-5-carboxylate) (DNB). DNB was synthesized as previously reported.[1] Dicylcopentadiene (10 g, 75.6 mmol) was thermally cracked by heating to 170 °C and cyclopentadiene was isolated via distillation. A three-necked round bottom flask containing tricyclodecane dimethanol diacrylate (6.0 g, 19.7 mmol) and 2000 ppm phenothiazine was purged with nitrogen and heated to 80 °C. Using an addition funnel, a 20% molar excess of freshly cracked cyclo-pentadiene was added dropwise. The reaction mixture was stirred for 5 h and then excess cyclopentadiene was removed via vacuum. The product was then purified by flash chromatography (20 vol% ethyl acetate in hexanes). Yield (7.1 g, 82%). Due to the presence of three fused cyclic structures with variable configurational and conformational isomers, full assignments of peaks were not able to be performed for the ^{13}C NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.23-5.92 (m, 4H), 4.07-3.73 (m, 4H), 3.23 (s, 1H), 3.08-2.90 (m, 4H), 2.59-1.34 (m, 20H), 1.30 (m, 2H), 0.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.38 (C=O), 174.92 (C=O), 138.05 (C=C), 137.80 (C=C), 135.78 (C=C), 132.46 (C=C), 68.69-67.54 (**C**H_2–O), 49.69-24.35 (alkyl carbons).

Synthesis of poly(ethylene glycol)-bis(3-mercaptopropionate) (PEG2MP) and poly(ethylene glycol)-bis(2-mercaptoacetate) (PEG2MA). To a flame dried 500 mL round bottom flask, poly(ethylene glycol) M_n =4,600 g/mol (5.0 g, 1.09 mmol) was dissolved in 150 mL of toluene at 90 °C. Sodium sulfate anhydrous (5.0 g) and 20 mmol of either 3-mercaptopropionic acid or 2-mercaptoacetic acid were added to the reaction mixture. The reaction was stirred overnight at 90 °C and then was precipitated into 500 mL of ice-cold diethyl ether. The precipitate was isolated by filtration and then dissolved into 300 mL of deionized water. The aqueous phase was washed with ethyl acetate (2 x 100 mL) and then product was extracted into DCM (3 x 100 mL). The DCM phase was then washed with water and then dried with sodium sulfate. The DCM was then removed under vacuum to afford the

thiol functionalized product as a free flowing white powder. **PEG2MP.** Yield (4.2 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) 3.65 (m, O-C**H$_2$**-C**H$_2$**-O), 2.82-2.75 (m, 4H), 2.70 (td, 4H). **PEG2MA.** Yield (4.5 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) 3.66 (m, O-C**H$_2$**-C**H$_2$**-O), 3.32 (s, 2H), 3.30 (s, 2H).

Synthesis of poly(ethylene glycol)-tetra-allylether (PEG4AE). Sodium hydride (20 mg, 0.83 mmol) was added to a solution of 4-arm poly(ethylene glycol) M_n 10,000 g/mol (500 mg, 0.05 mmol) in anhydrous THF (5 mL). The mixture was stirred for 1 h at room temperature under argon. Then a solution of allyl bromide (108 mg, 0.9 mmol) in THF (0.1 mL) was added dropwise, and the mixture was stirred for 2 h. The product was precipitated into 100 mL of ice-cold diethyl ether. The precipitate was isolated by filtration and then dissolved into 50 mL of deionize water. The aqueous phase was washed with ethyl acetate (2 x 20 mL) and then the product was extracted into DCM (3 x 30 mL). The DCM phase was then washed with water and then dried with sodium sulfate. The DCM was then removed under vacuum to afford the allyl ether functionalized product as a free flowing white powder. Yield (420 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) 5.94 (m, 4H), 5.25 (m, 8H), 4.05 (dt, 8H), 3.63 (m, O-C**H$_2$**-C**H$_2$**-O).

2 Bulk thiol-ene film polymerizations

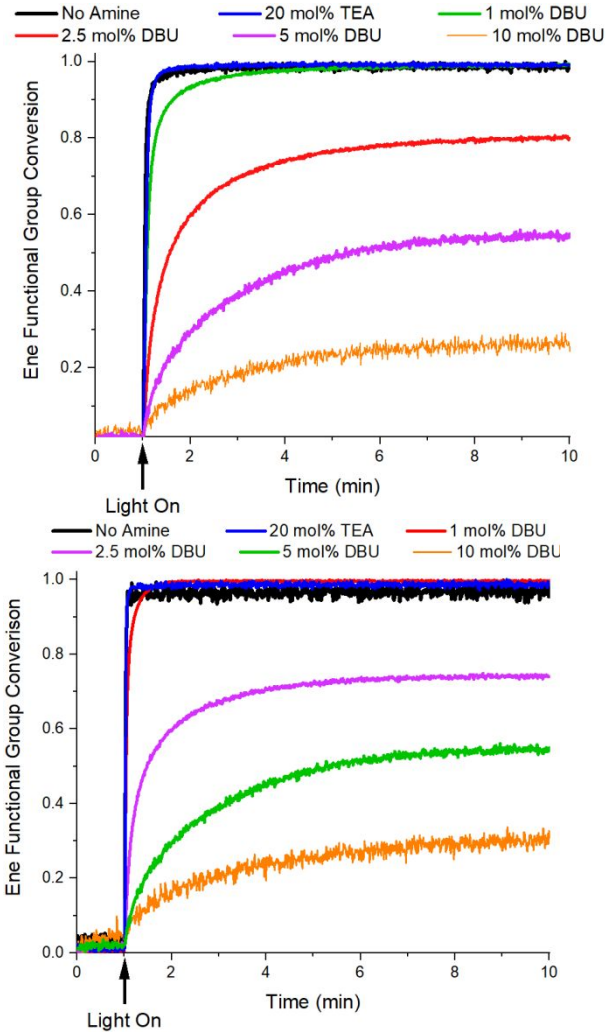

Figure S1. Ene conversion versus time for the solventless, thiol-ene polymerization of (left) PETMP-DAE and (right) PETMP-DVE in the presence of various amine additives. Reactions were formulated with 1:2 PETMP:diene, 0-20 mol% basic amine, and 2 mol% DMPA, where mol% is based off the moles of thiol functional groups. Reactions were irradiated with 10mW/cm^2 365nm light for 15 minutes or until the conversion was no longer changing with time. Conversions were monitored in situ via FTIR and irradiation was started at 1 minute.

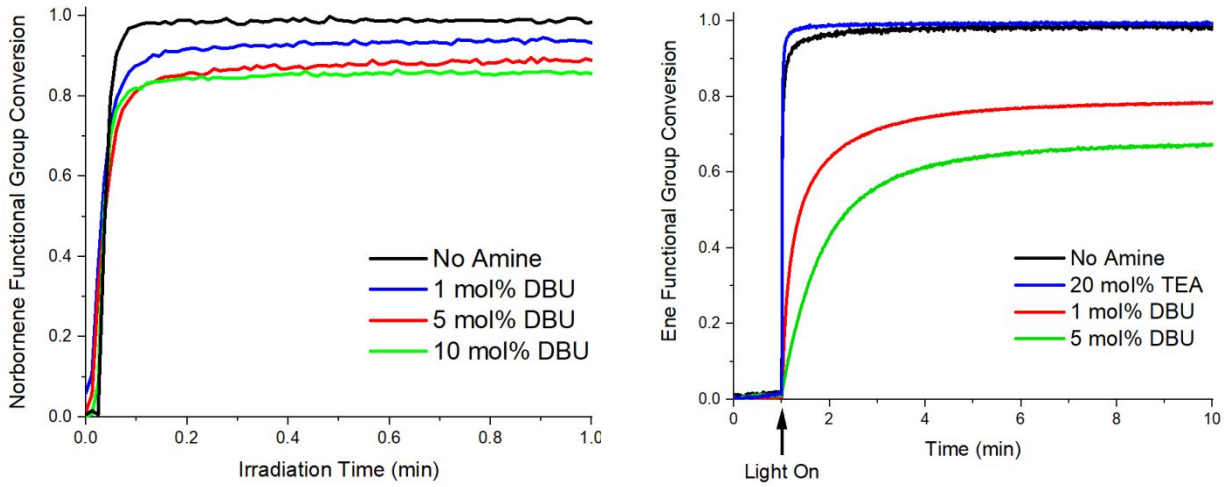

Figure S2. Ene conversion versus time for the solventless, thiol-ene polymerization of (left) PETMP-DNB and (right) PETMP-DVSi in the presence of various amine additives. Reactions were formulated with 1:2 PETMP:diene, 0-20 mol% basic amine, and 2 mol% DMPA, where mol% is based off the moles of thiol functional groups. Reactions were irradiated with 10mW/cm^2 365nm light for 15 minutes or until the conversion was no longer changing with time. Conversions were monitored in situ via FTIR and irradiation was started at 1 minute.

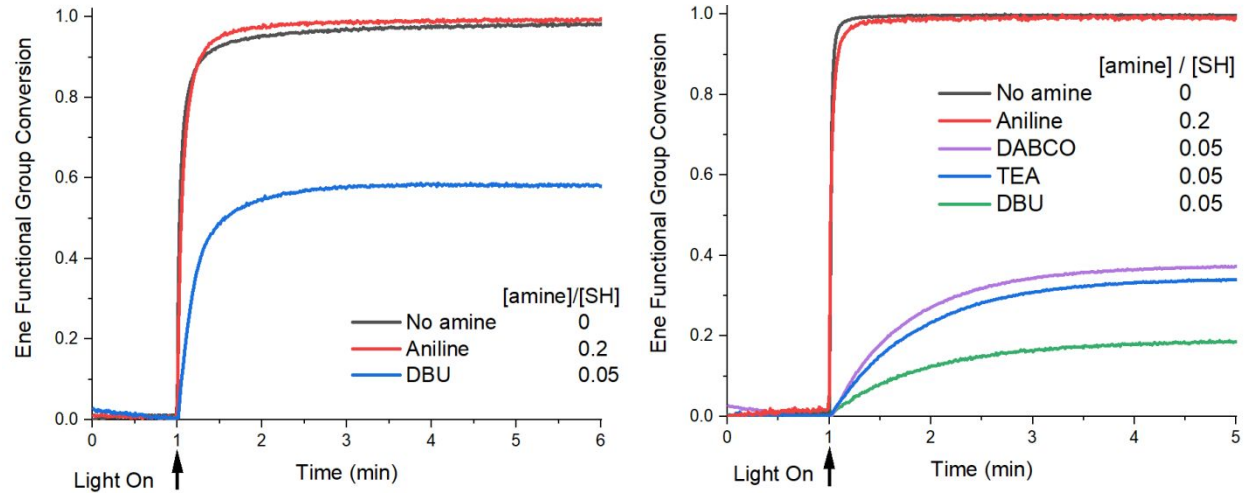

Figure S3. Ene conversion versus time for the solventless, thiol-ene polymerization of (left) PETMA-DAE and (right) PETMA-DVE in the presence of various amine additives. Reactions were formulated with 1:2 PETMA:diene, 0-20 mol% basic amine, and 2 mol% DMPA, where mol% is based off the moles of thiol functional groups. Reactions were irradiated with 10mW/cm^2 365nm light for 15 minutes or until the conversion was no longer changing with time. Conversions were monitored in situ via FTIR and irradiation was started at 1 minute.

Table S1. Kinetics of thiol-ene network polymerizations in the presence of amines

Thiol	Ene	Amine	[amine]/[SH]	R_0/R^a	Conversion (%)[b]
PETMP	DAE	--	--	1	100
		Aniline	0.2	1.03±0.04	100
		TEA	0.2	1.6±0.1	100
		DBU	0.01	2.7±0.1	100
		DBU	0.025	22±4	79±4
		DBU	0.05	78±8	54±2
		DBU	0.1	*d*	33±4
	DVE	--	--	1	100
		Aniline	0.2	1.3±0.4	100
		TEA	0.2	1.2±0.5	100
		DBU	0.01	2.4±0.7	100
		DBU	0.025	22±4	73±2
		DBU	0.05	120±10	54±3
		DBU	0.1	*c*	--
	DNB	--	--	1	100
		Aniline	0.2	1.1±0.2	100
		TEA	0.2	0.9±0.1	100
		DBU	0.01	1.3±0.1	96
		DBU	0.05	2.3±0.2	92
		DBU	0.1	2.5±0.2	87
		DBU	0.2	*c*	--
	DVSi	--	--	1	100
		Aniline	0.2	1.5±0.3	100
		TEA	0.2	1.7±0.3	100
		DBU	0.01	63±5	79±4
		DBU	0.05	110±30	64±6
		DBU	0.1	*c*	--
PETMA	DVE	--	--	1	100
		Aniline	0.2	1.1±0.3	100
		DABCO	0.05	*d*	39±4
		TEA	0.05	*d*	34±3
		DBU	0.05	*d*	21±6
	DAE	--	--	1	100
		Aniline	0.2	1.6±0.2	100
		DABCO	0.01	*c*	--
		TEA	0.01	*c*	--
		DBU	0.01	18±3	56±7
	DNB	--	--	1	100
		Aniline	0.2	1.3	100
		DABCO	0.01	*c*	--
		TEA	0.01	*c*	--
	DVSi	--	--	1	100
		Aniline	0.2	1.7±0.4	100
		DABCO	0.01	*c*	--
		TEA	0.01	*c*	--

Thiol-ene network polymerizations between a tetra-functional thiol and a diene, 1:1 [SH]:[C=C], were formulated with amine additives, and photoinitiator, 0.02:1 [DMPA]:[SH]. Formulations were irradiated with 365nm light, 10 mW/cm^2 for 15 minutes. [a] Ratio of the reaction rate with (R) and without (R_0) the presence of an amine additive. $R_{0,\ PETMP\text{-}DAE}$ = 74±3 mol L^{-1} min^{-1}, $R_{0,\ PETMP\text{-}DVE}$ = 170±10 mol L^{-1} min^{-1}, $R_{0,\ PETMP\text{-}DNB}$ = 190±20 mol L^{-1} min^{-1}, $R_{0,\ PETMP\text{-}DVSi}$ = 274±8 mol L^{-1} min^{-1}, $R_{0,\ PETMA\text{-}DAE}$ = 75±6 mol L^{-1} min^{-1}, $R_{0,\ PETMA\text{-}DVE}$ = 150±20 mol L^{-1} min^{-1}, $R_{0,\ PETMA\text{-}DNB}$ = 180±10 mol L^{-1} min^{-1}, $R_{0,\ PETMA\text{-}DVSi}$ = 210±10 mol L^{-1} min^{-1} [b] In situ conversions were monitored in real-time by FTIR. [c] Formulations phase-separated upon addition of the amine additive and could not be analyzed by FTIR. [d] Rates were not determined for samples that did not achieve 50% ene conversion.

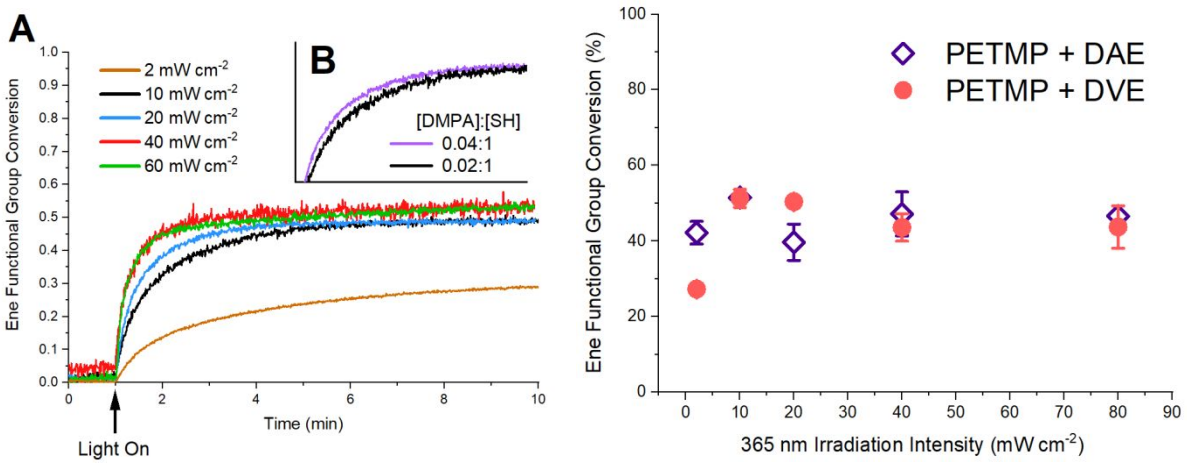

Figure S4. (A&B) Ene conversion versus time for the thiol-ene network polymerization of PETMP with DAE in the presence of DBU (0.05:1 [DBU]:[SH]). (A) Reactions were formulated with photoinitiator (0.02:1 [DMPA]:[SH]) and irradiated with 365 nm light with varying intensity. (B) Reactions were formulated with varying photoinitiator concentrations and irradiated with 10 mW/cm^2 365nm. All reactions were formulated without solvent and conversions were monitored in situ via FTIR. (C) Ene conversion versus 365nm light irradiation intensity for the thiol-ene polymerizations of PETMP with DAE and DVE, 1:2 PETMP:diene, formulated with DBU, 0.05:1 [DBU]:[SH]. Conversions were determined by ^{1}H NMR after formulations were irradiated for 15 minutes.

3. Thiol-ene polymerization of diallyl amine

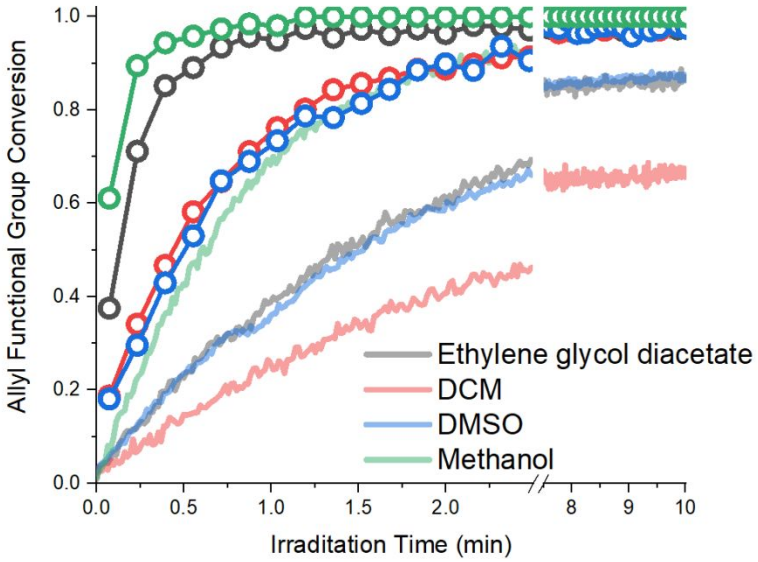

Figure S5. Allyl functional group conversion for the polymerization of diallylamine with EGBMP formulated with varying solvent environments. Reactions were formulated with (-O-) or without (—) 1 equivalent of acetic acid and with solvent ([SH] = 4.0 M) or solventless. All reactions were formulated with 0.01 equivalents of photoinitiator (DMPA) and irradiated with 365nm light (10 mW/cm^2) for 15 minutes. Conversions were monitored by FTIR.

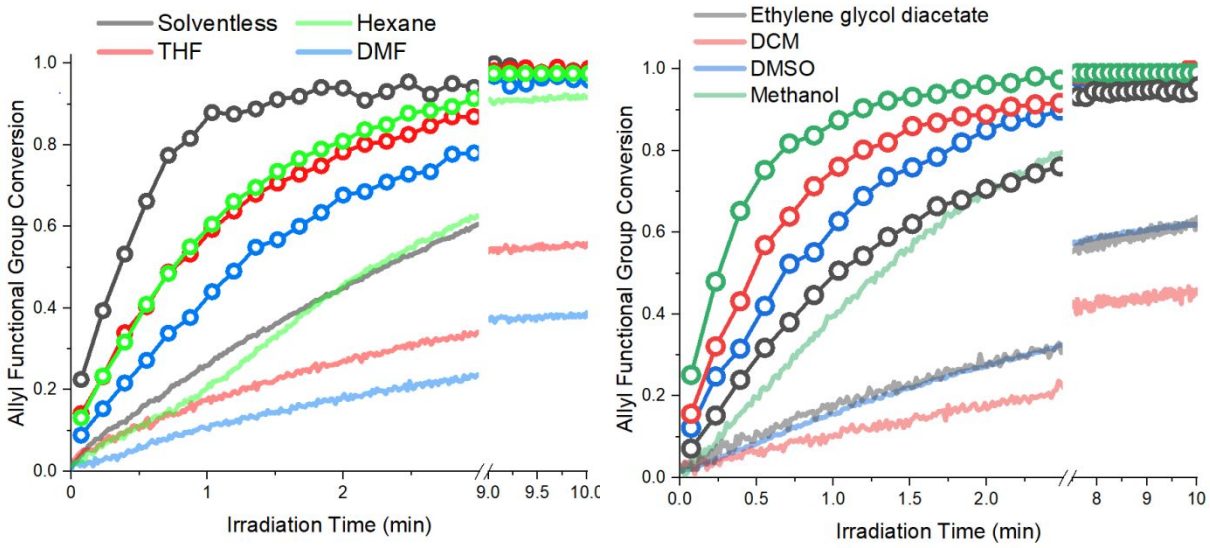

Figure S6. Allyl functional group conversion for the polymerization of diallylamine with HDT formulated with varying solvent environments. Reactions were formulated with (-O-) or without (—) 1 equivalent of acetic acid and with solvent ([SH] = 4.0 M) or solventless. All reactions were formulated with 0.01 equivalents of photoinitiator (DMPA) and irradiated with 365nm light (10 mW/cm^2) for 15 minutes. Conversions were monitored by FTIR.

Table S2: Kinetics of the photopolymerization of diallyl amine with EGBMP in various reaction environments.

Solvent	Solvent dielectric constant[a]	Relative solvent polarity[b]	Initial ene concentration (mol L^{-1})	Acetic acid concentration (mol L^{-1})	Rate of allyl functional group conversion (mol L^{-1} min^{-1})	Allyl functional group conversion after 10 min irradiation (%)
No Solvent	-	-	6.30	0	4.8 ± 0.3	100
No Solvent	-	-	5.33	2.66	9.9 ± 0.6	100
DMSO	47	0.44	4.00	0	1.6 ± 0.2	88 ± 3
DMSO	47	0.44	4.00	2.00	2.9 ± 0.1	100
DMF	38	0.39	4.00	0	0.6 ± 0.3	54 ± 7
DMF	38	0.39	4.00	2.00	2.8 ± 0.2	100
Methanol	33	0.76	4.00	0	3.2 ± 0.4	100
Methanol	33	0.76	4.00	2.00	18.0 ± 0.7	100
DCM	9.1	0.31	4.00	0	0.84 ± 0.09	69 ± 4
DCM	9.1	0.31	4.00	2.00	3.6 ± 0.5	100
THF	7.5	0.21	4.00	0	1.1 ± 0.1	74 ± 5
THF	7.5	0.21	4.00	2.00	4.3 ± 0.1	100
EGDAc	6	0.23	4.00	0	1.6 ± 0.4	89 ± 2
EGDAc	6	0.23	4.00	2.00	10 ± 0.8	100
Hexane	1.9	0.01	4.00	0	1.6 ± 0.3	88 ± 2
Hexane	1.9	0.01	4.00	2.00	2.0 ± 0.1	100

[a] Values were extracted from Vogel et al., *Textbook of Practical Organic Chemistry,* Longman Scientific & Technical, 5th ed., **1989.** [b] The values for relative polarity are normalized from measurements of solvent shifts of absorption spectra and were extracted from Christian Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Publishers, 3rd ed., **2003.**

Table S3: Kinetics of the photopolymerization of diallyl amine with hexane dithiol in various reaction environments.

Solvent	Solvent dielectric constant[a]	Relative solvent polarity[b]	Initial SH concentration (mol L^{-1})	Acetic acid concentration (mol L^{-1})	Rate of allyl functional group conversion (mol L^{-1} min^{-1})	Allyl functional group conversion after 10 min irradiation (%)
No Solvent	-	-	7.23	0	1.6 ± 0.1	100
No Solvent	-	-	5.98	2.99	6.2 ± 0.2	100
DMSO	47	0.44	4.00	0	0.47 ± 0.11	62 ± 6
DMSO	47	0.44	4.00	2.00	2.4 ± 0.2	100
DMF	38	0.39	4.00	0	0.21 ± 0.09	51 ± 7
DMF	38	0.39	4.00	2.00	1.7 ± 0.4	100
Methanol	33	0.76	4.00	0	1.7 ± 0.2	100
Methanol	33	0.76	4.00	2.00	6.6 ± 0.3	100
DCM	9.1	0.31	4.00	0	0.27 ± 0.14	50 ± 5
DCM	9.1	0.31	4.00	2.00	4.0 ± 0.1	100
THF	7.5	0.21	4.00	0	0.42 ± 0.08	58 ± 6
THF	7.5	0.21	4.00	2.00	2.3 ± 0.4	100
EGDAc	6	0.23	4.00	0	0.54 ± 0.13	64 ± 6
EGDAc	6	0.23	4.00	2.00	2.1 ± 0.5	100
Hexane	1.9	0.01	4.00	0	0.84 ± 0.10	94 ± 3
Hexane	1.9	0.01	4.00	2.00	2.7 ± 0.3	100

[a] Values were extracted from Vogel et al., *Textbook of Practical Organic Chemistry,* Longman Scientific & Technical, 5th ed., **1989.** [b] The values for relative polarity are normalized from measurements of solvent shifts of absorption spectra and were extracted from Christian Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Publishers, 3rd ed., **2003.**

Table S4. Effect of polar protic solvents on the kinetics of the radical thiol-ene polymerization of diallylamine with EGBMP

Solvent	Solvent dielectric constant[a]	Initial ene concentration (mol L^{-1})	Concentration of OH functional groups (mol L^{-1})	Rate of allyl functional group conversion (mol L^{-1} min^{-1})	Allyl functional group conversion after 10 min irradiation (%)
No Solvent	-	6.30	0	4.8 ± 0.3	100
MeOH	33	4.00	9.02	3.2 ± 0.4	100
EtOH	24	4.00	6.27	3.5 ± 0.2	100
Isopropanol	18	4.00	4.77	2.5 ± 0.2	100
Butanol	18	4.00	4.00	3.6 ± 0.1	100
Hexanol	13	4.00	2.90	2.8 ± 0.4	100

[a] Values were extracted from Vogel et al., *Textbook of Practical Organic Chemistry,* Longman Scientific & Technical, 5th ed., **1989.**

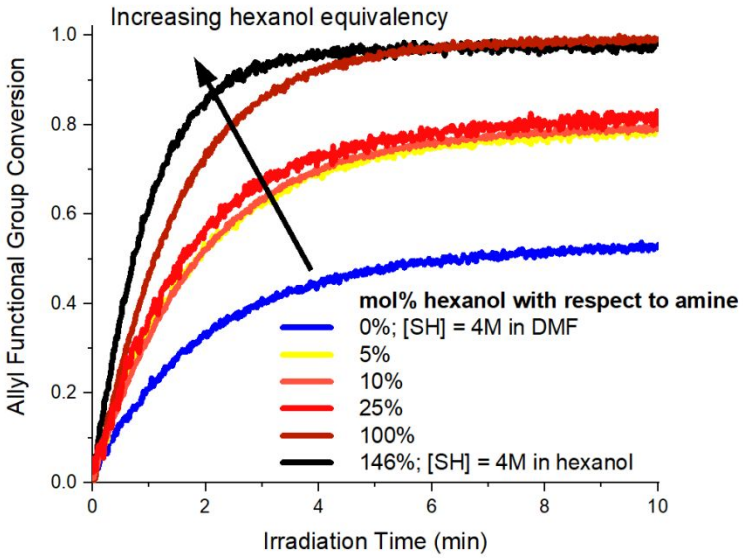

Figure S7. Allyl functional group conversion for the polymerization of diallylamine with EGBMP formulated with varying solvent environments. Reactions were formulated in a DMF/hexanol cosolvent system ([SH] = 4.0 M) with varying hexanol equivalency, with respect to diallylamine. All reactions were formulated with 0.01 equivalents of photoinitiator (DMPA) and irradiated with 365 nm light (10 mW/cm^2) for 15 minutes. Conversions were monitored by FTIR.

Table S5. Effect of OH to amine ratio on the kinetics of the radical thiol-ene polymerization of diallylamine with EGBMP

Cosolvent	[OH]/[NH]	Volume % alcohol in cosolvent system (%)	Rate of allyl functional group conversion (mol L^{-1} min^{-1})	Allyl functional group conversion after 10 min irradiation (%)
Methanol	0.05	1.1	0.95 ± 0.08	69 ± 3
Methanol	0.1	2.2	1.1 ± 0.3	73 ± 5
Methanol	0.25	5.5	1.1 ± 0.1	76 ± 3
Methanol	1.0	22	1.7 ± 0.1	85 ± 2
Methanol	2.0	44	1.7 ± 0.5	84 ± 4
Methanol	3.0	65	2.2 ± 0.3	100
Methanol	4.0	87	4.7 ± 0.6	100
Methanol	4.6	100	3.2 ± 0.4	100
Hexanol	0.05	3.5	1.2 ± 0.3	76 ± 4
Hexanol	0.10	6.9	1.3 ± 0.1	80 ± 6
Hexanol	0.25	17	1.6 ± 0.4	83 ± 6
Hexanol	1.0	68	2.1 ± 0.4	100
Hexanol	1.46	100	2.8 ± 0.4	100

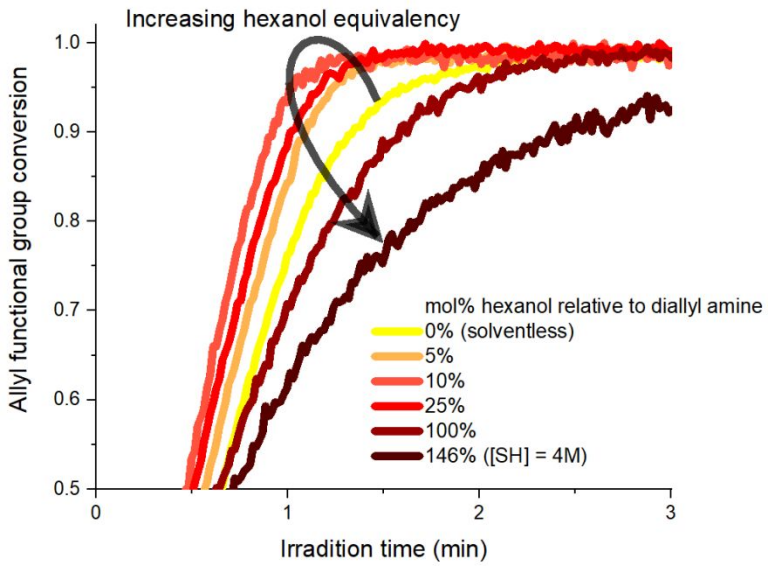

Figure S8. Allyl functional group conversion for the polymerization of diallylamine with EGBMP formulated with varying solvent environments. Reactions were formulated in a DMF/methanol cosolvent system ([SH] = 4.0 M) with varying methanol equivalency, with respect to diallylamine. All reactions were formulated with 0.01 equivalents of photoinitiator (DMPA) and irradiated with 365 nm light (10 mW/cm^2) for 15 minutes. Conversions were monitored by FTIR.

Table S6. Effect of hexanol on the kinetics of the radical thiol-ene polymerization of diallylamine with EGBMP

[OH]/[NH]	Initial [SH] (mol L^{-1})	Rate of allyl functional group conversion (mol L^{-1} min^{-1})	Apparent rate constant, k_P (L mol^{-1} min^{-1})	Allyl functional group conversion after 10 min irradiation (%)
0	6.30	1.6 ± 0.1	0.082 ± 0.005	100
0.05	6.18	5.3 ± 0.7	0.28 ± 0.04	100
0.10	6.07	6.6 ± 0.4	0.37 ± 0.02	100
0.25	5.74	5.8 ± 0.5	0.35 ± 0.03	100
1.0	4.53	3.5 ± 0.4	0.35 ± 0.04	100
1.46	4.00	2.8 ± 0.4	0.36 ± 0.05	100

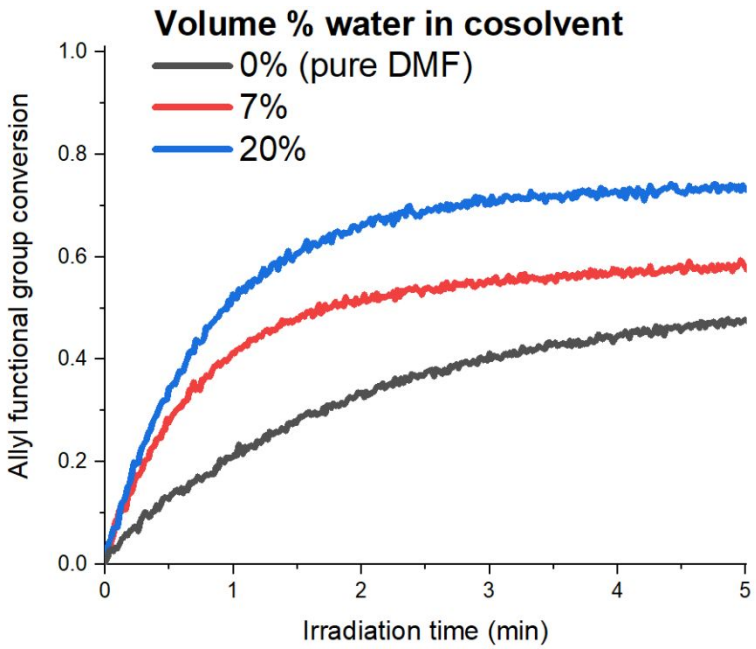

Figure S9. Allyl functional group conversion for the polymerization of diallylamine with EGBMP formulated with varying solvent environments.

4 pH effects on thiol-ene hydrogel polymerizations

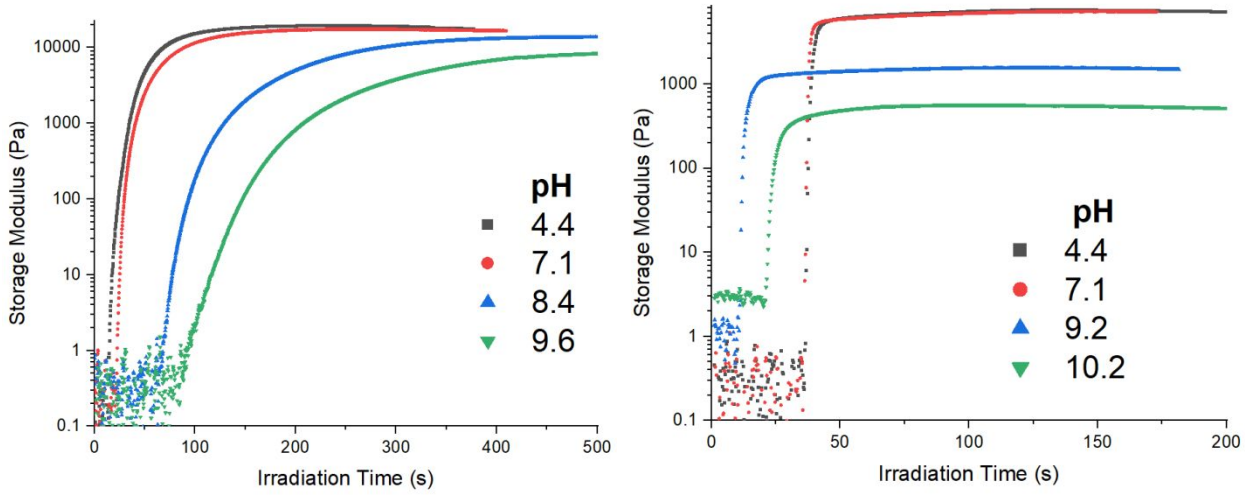

Figure S10. Effect of reaction buffer pH on the evolution of the storage modulus in the hydrogel polymerizations of (left) PEG2MP with PEG4AE and (right) PEG2MP with PEG4NB.

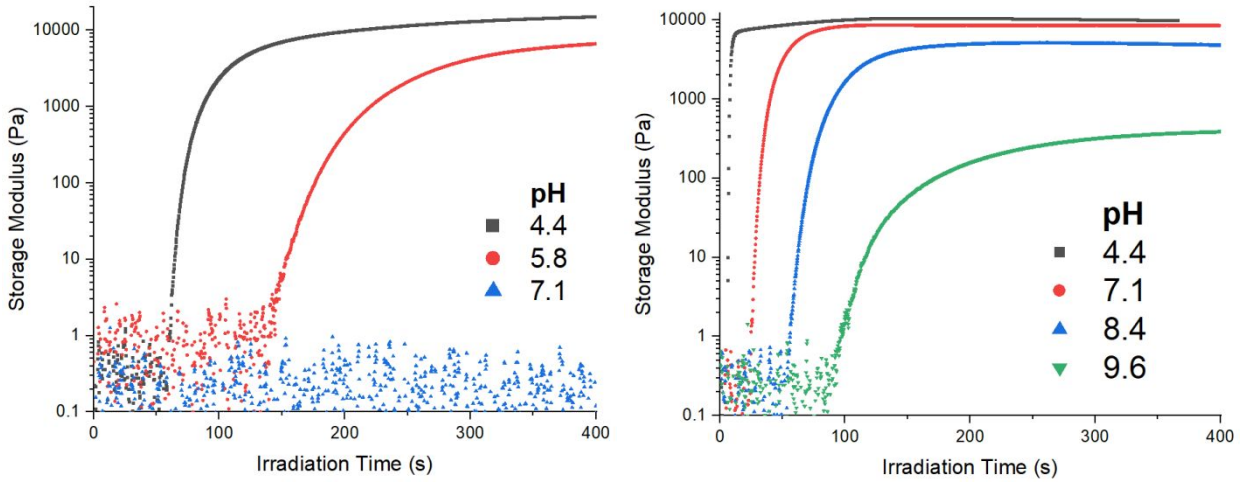

Figure S11. Effect of reaction buffer pH on the evolution of the storage modulus in the hydrogel polymerizations of (left) PEG2MA with PEG4AE and (right) PEG2MA with PEG4NB.

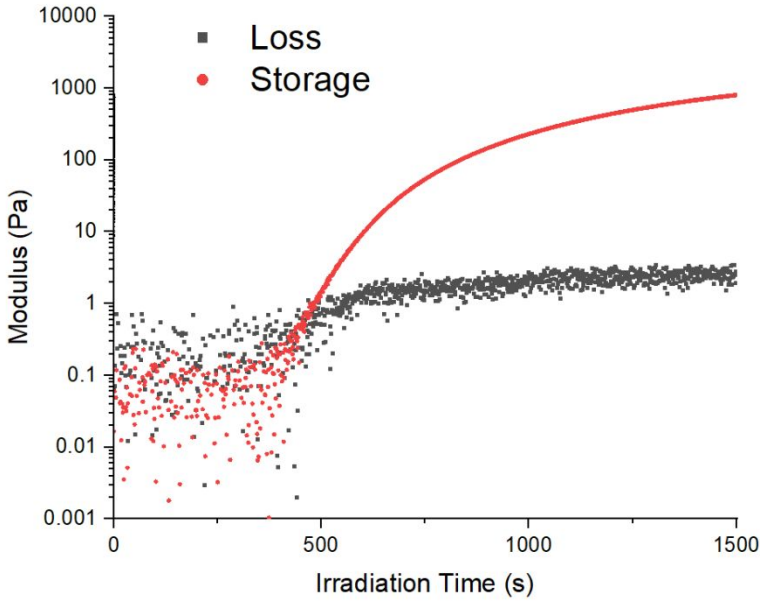

Figure S12. Real time rheological properties of the homopolymerization of PEG4AE. Reaction was formulated with 10 wt.% PEG4AE in 2.0 M sodium phosphate monobasic aqueous solution pH 4.4 and 0.5 wt.% photoinitiator Irgacure 2959. Reaction was irradiated with 365 nm light (10 mW/cm^2) for 1500 seconds.

References

1) J. A. Carioscia, L. Schneider, C. O'Brien, R. Ely, C. Feeser, N. Cramer, C. N. Bowman., *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 5686-5696.

5 NMRs of synthesized compounds

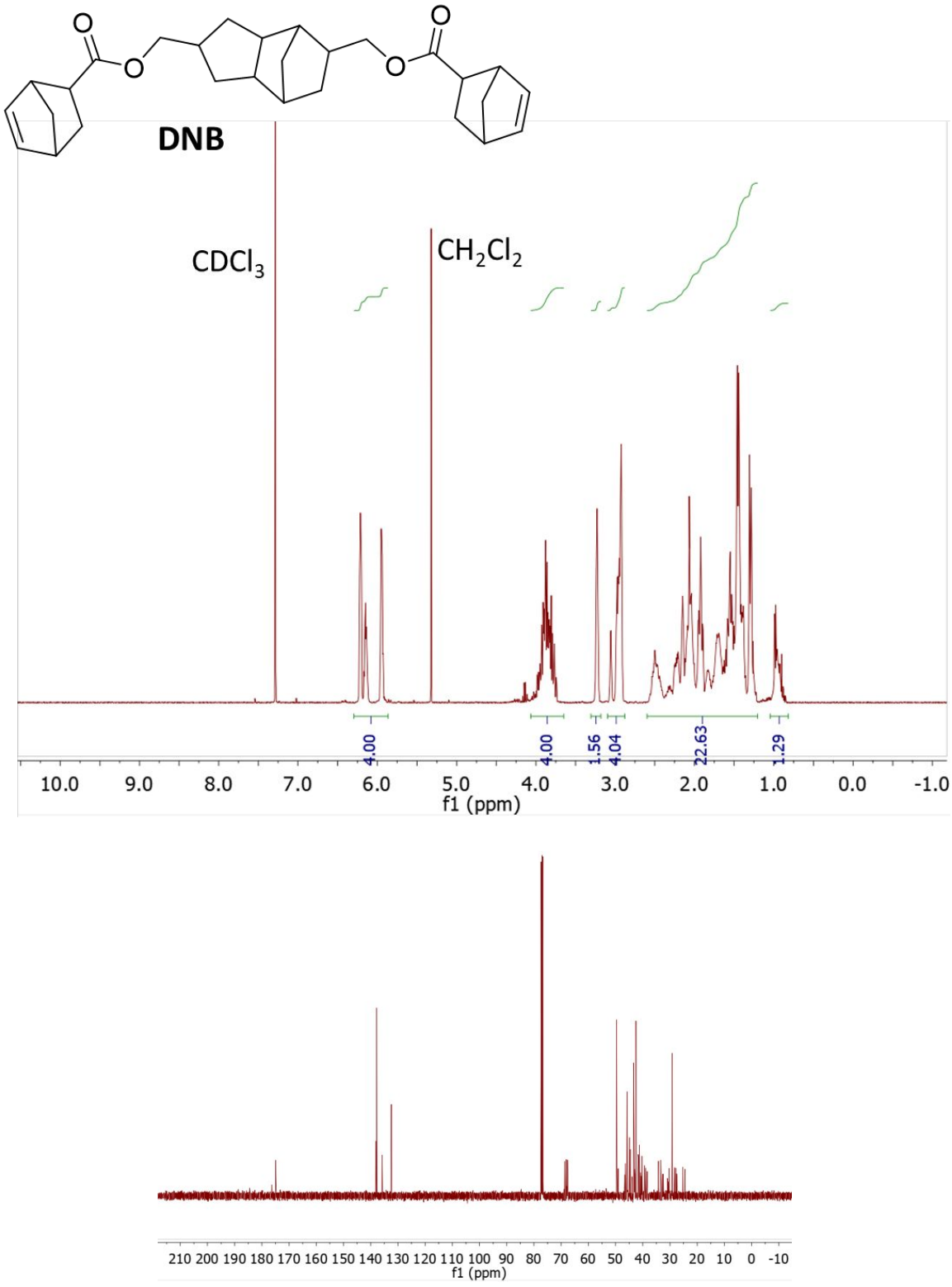

Figure S13. (Top) ^{1}H NMR and (bottom) ^{13}C NMR spectrums of DNB.

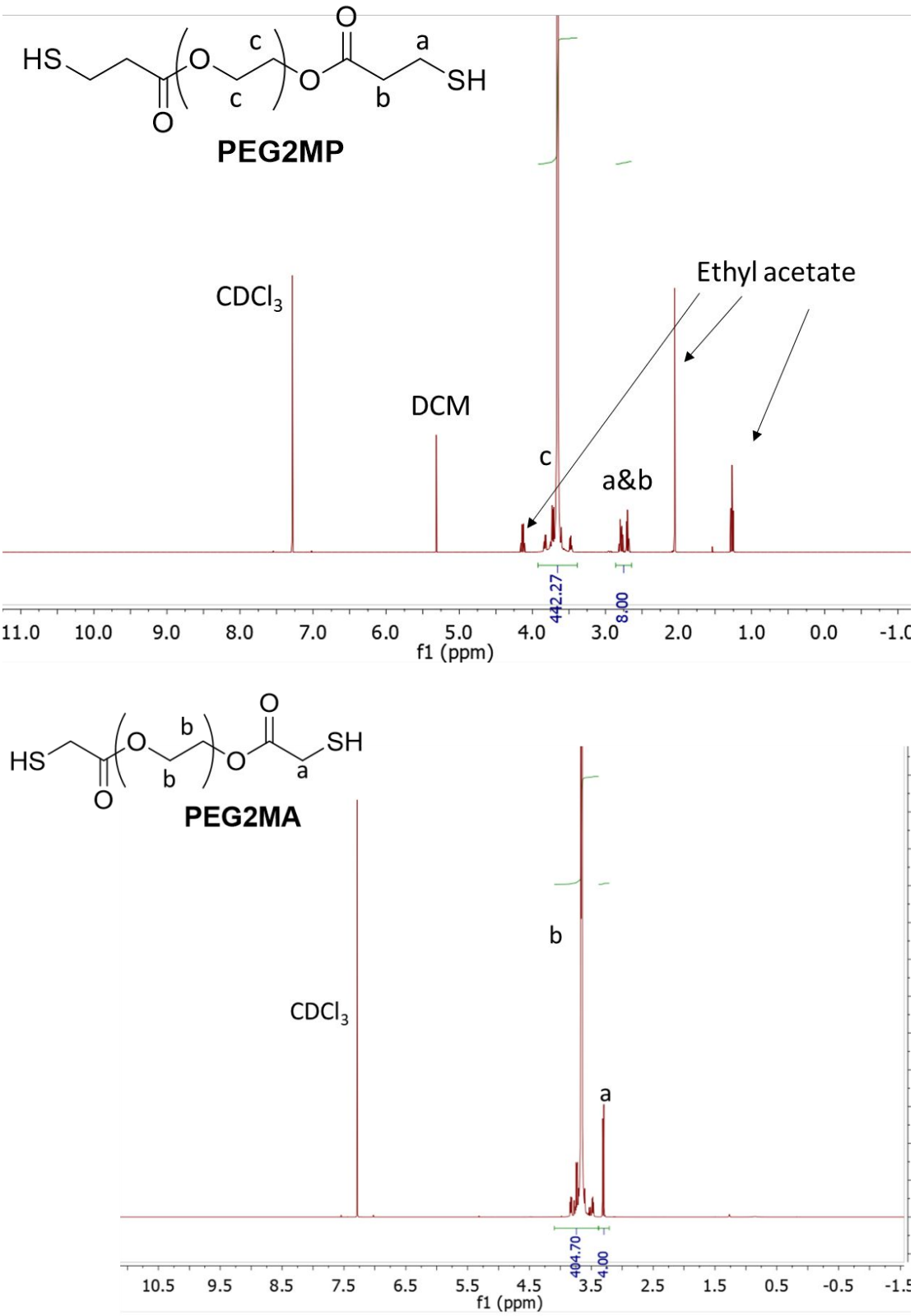

Figure S14. [1]H NMR spectrums of (top) PEG2MP and (bottom) PEG2MA.

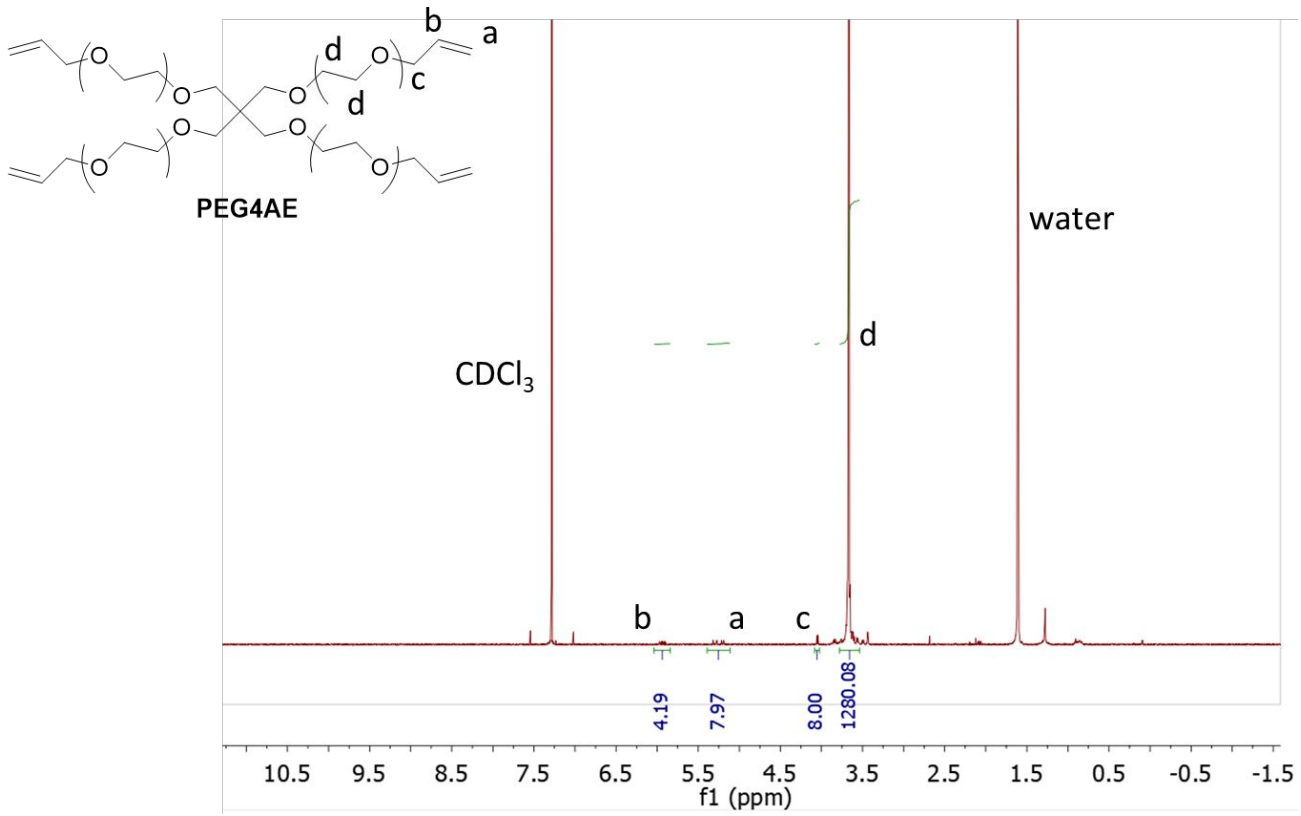

Figure S15. [1]HNMR spectrum of PEG4AE.