Electronic Supplementary Information (ESI)

Hyperbranched polymer hydrogels with large stimuli-responsive changes in storage moduli and peroxide-induced healing

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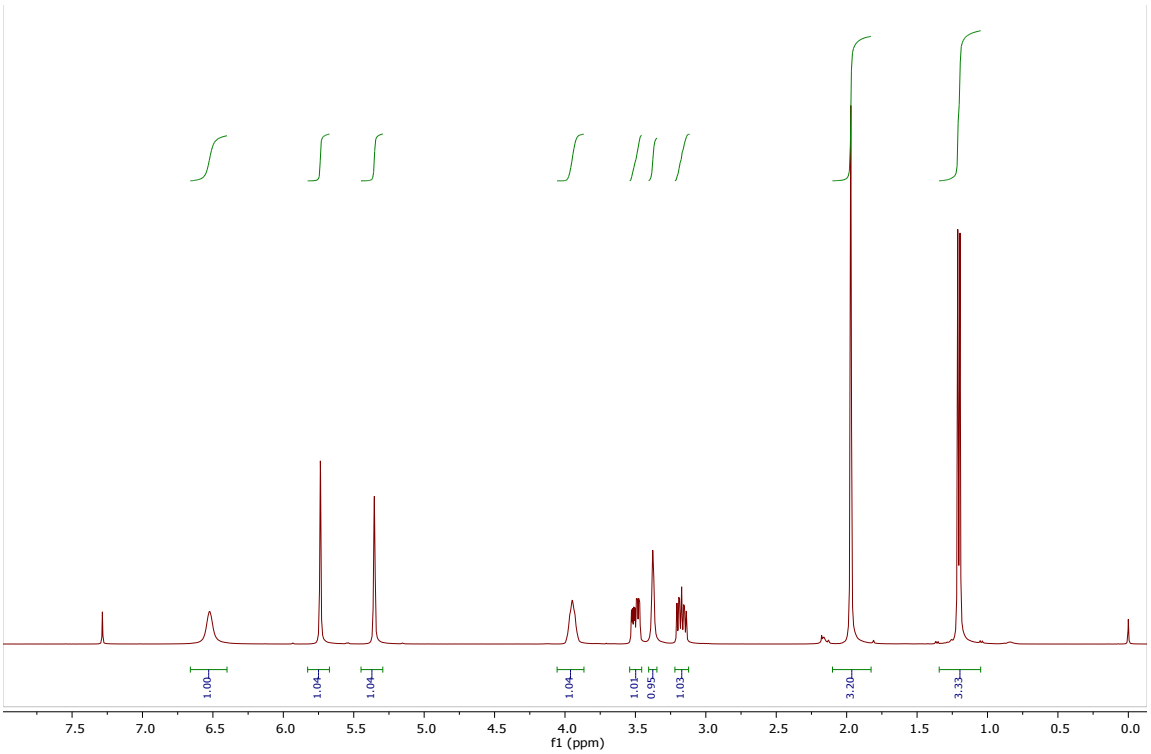

Figure S1. ^{1}H NMR spectrum of 2-hydroxypropyl methacrylate (HPMA).

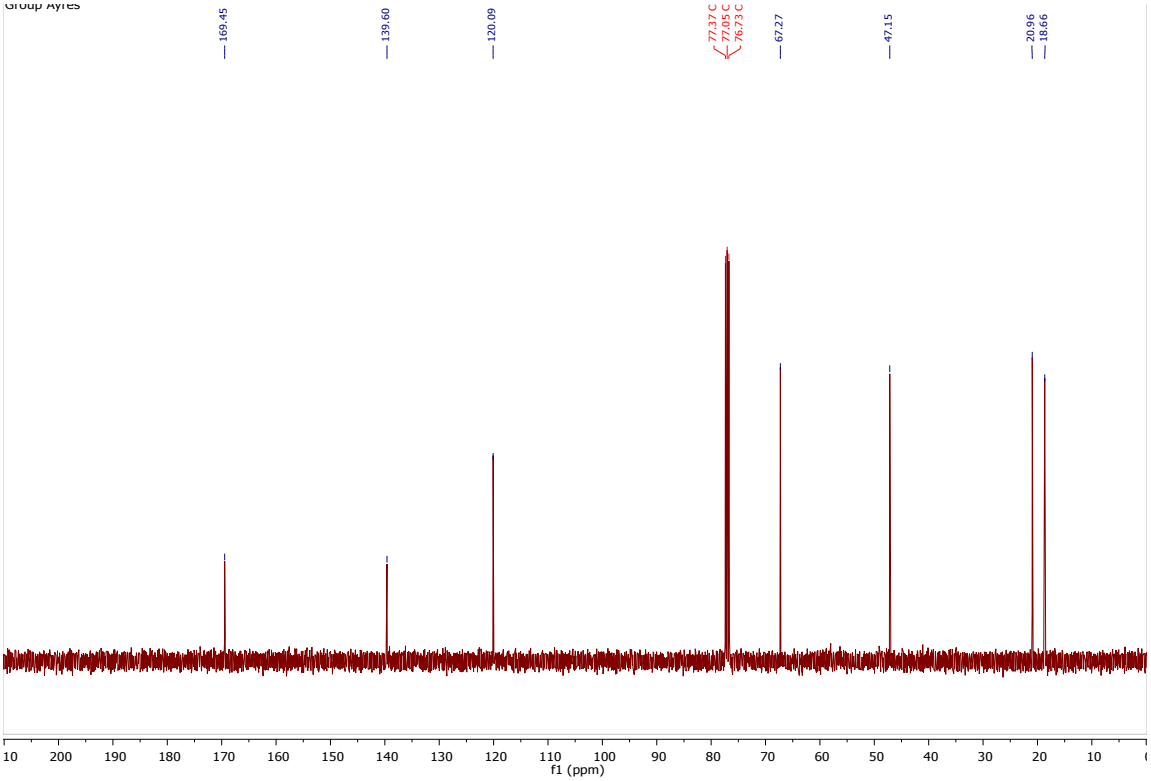

Figure S2. ^{13}C NMR spectrum of HPMA.

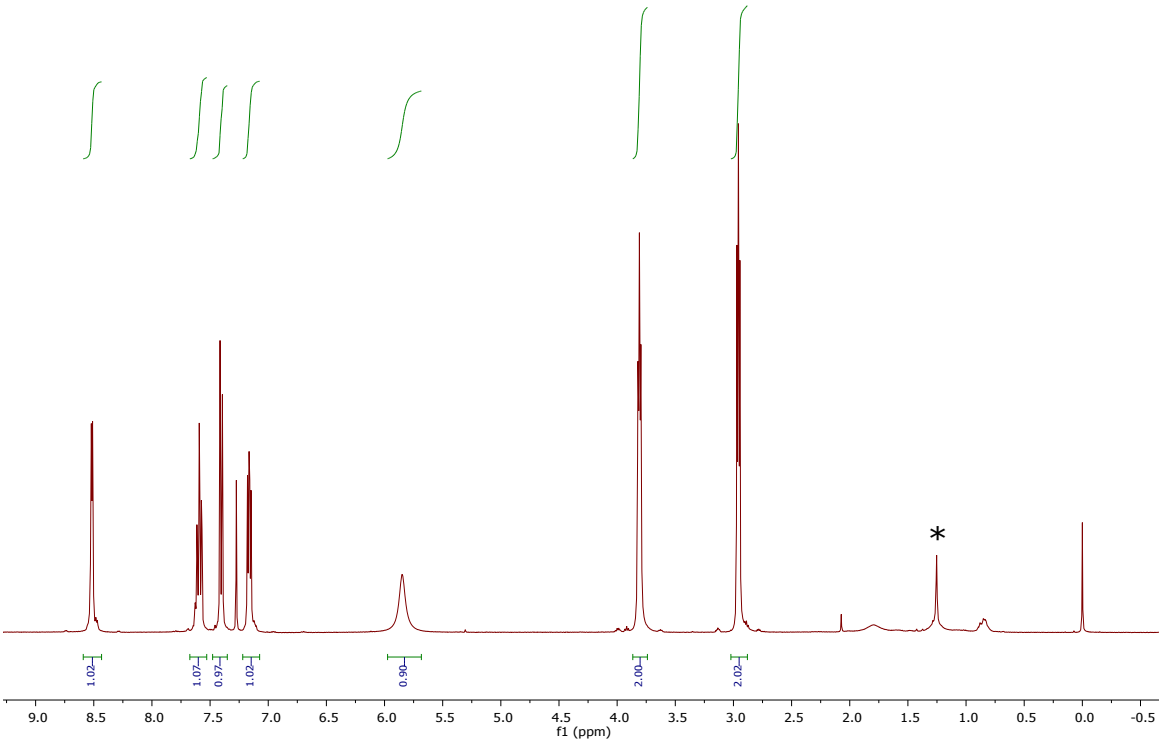

Figure S3. ^{1}H NMR spectrum of hydroxyethylpyridyl disulfide (HPDS). (* Solvent- Ethyl acetate)

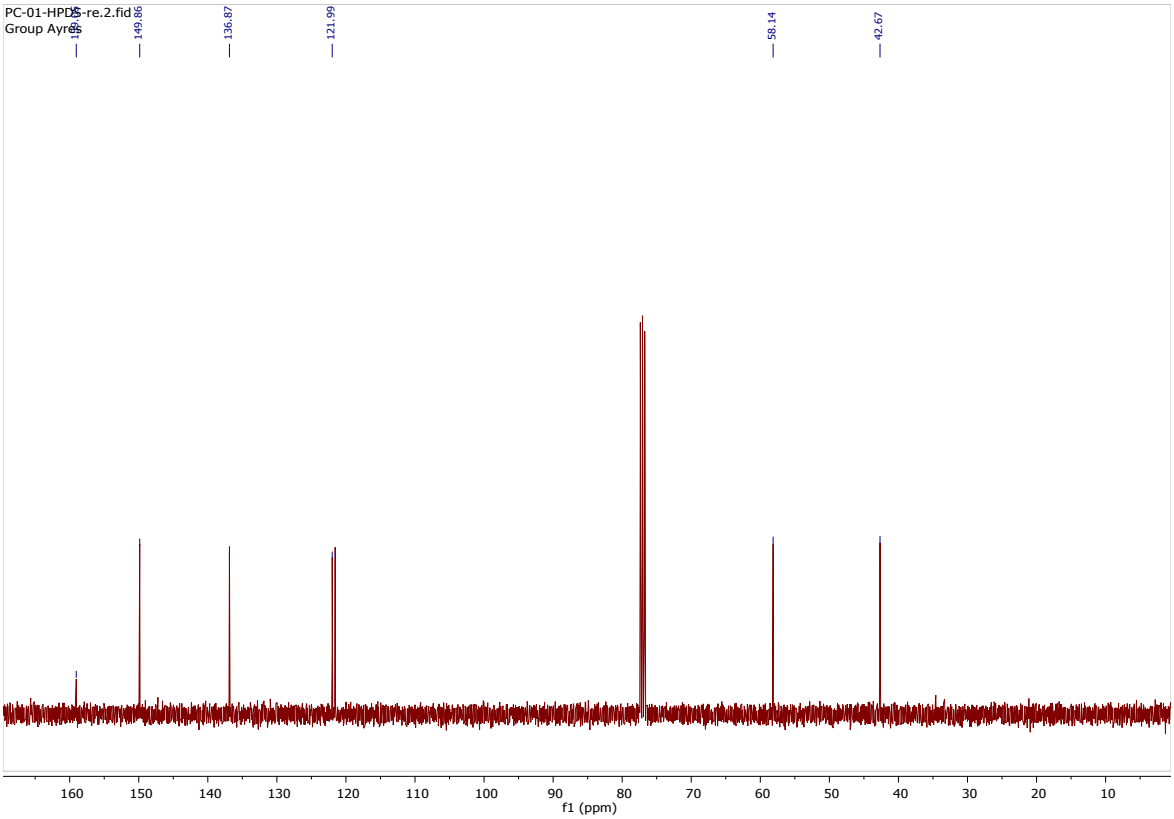

Figure S4. ^{13}C NMR spectrum of HPDS.

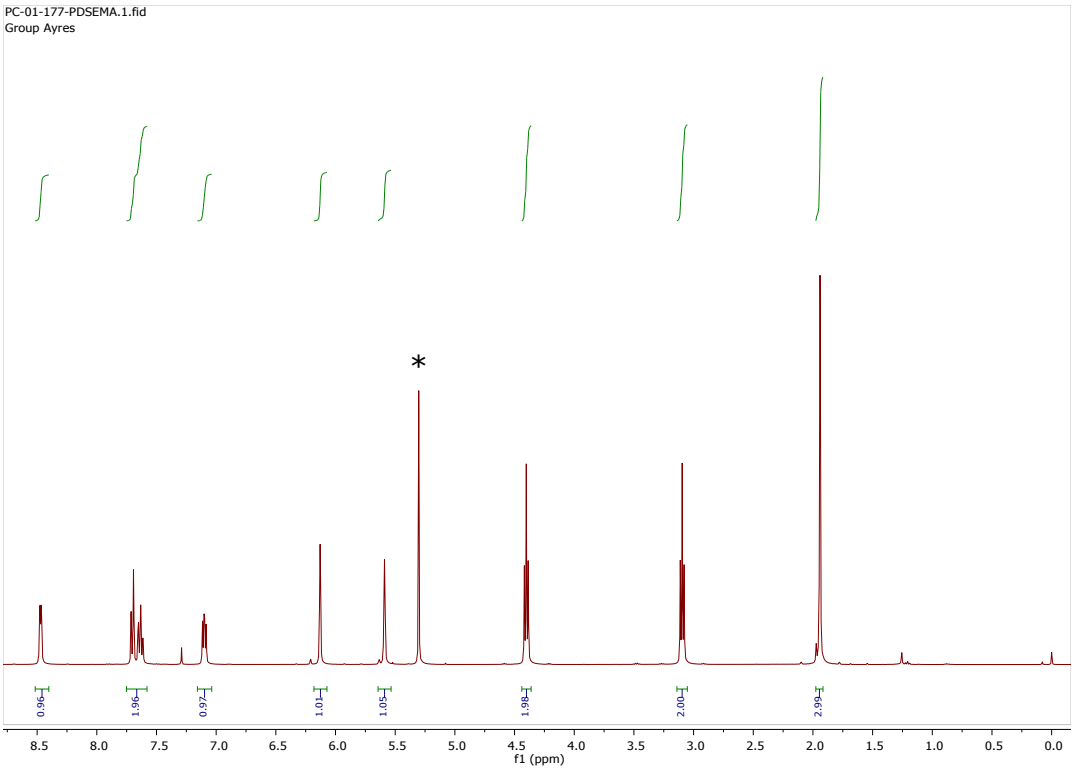

Figure S5. ^{1}H NMR spectrum of pyridyl disulfide ethylmethacrylate (PDSEMA). (* indicates the dichloromethane solvent)

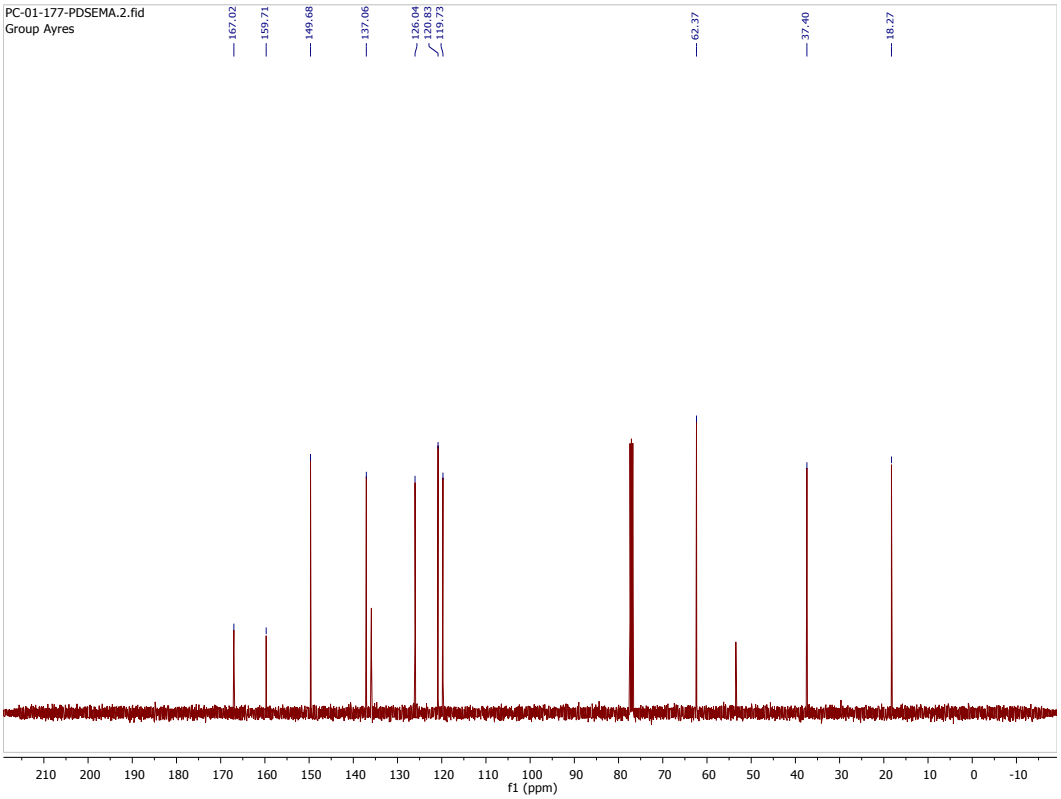

Figure S6. ^{13}C NMR spectrum of PDSEMA.

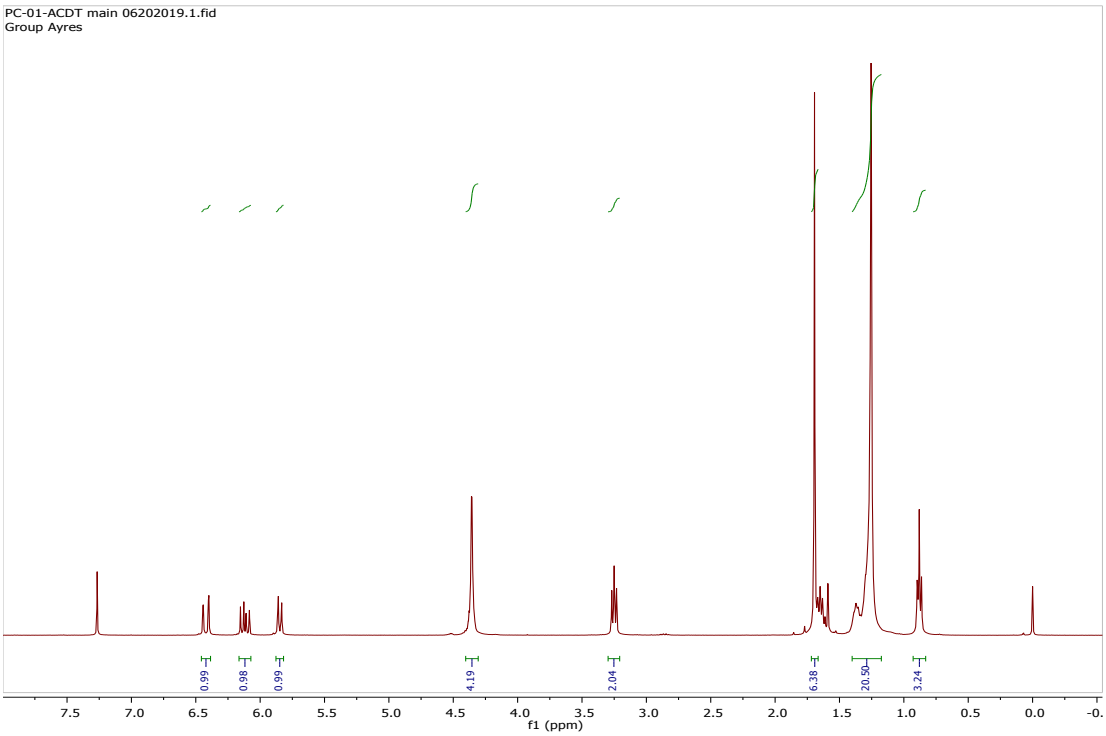

Figure S7. ^{1}H NMR spectrum of 2-((2-(((Dodecylthio)carbonothioyl)thio)-2-methylpropanoyl)oxy)ethyl Acrylate (ACDT).

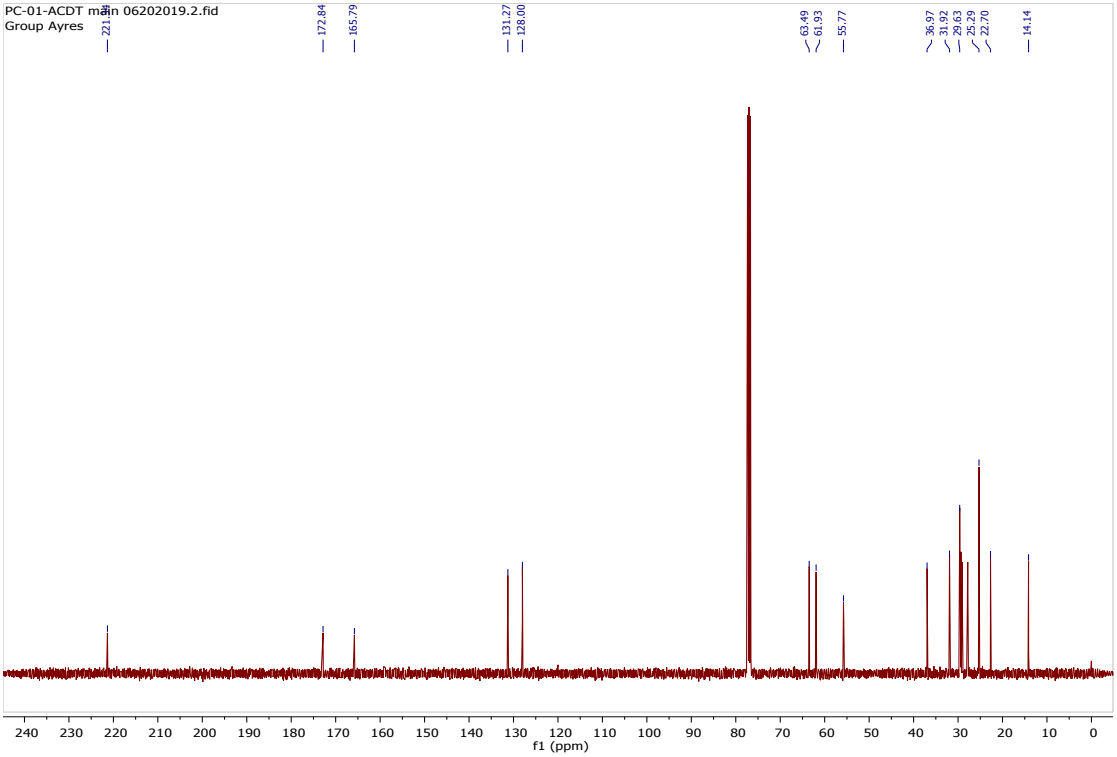

Figure S8. ^{13}C NMR spectrum of ACDT.

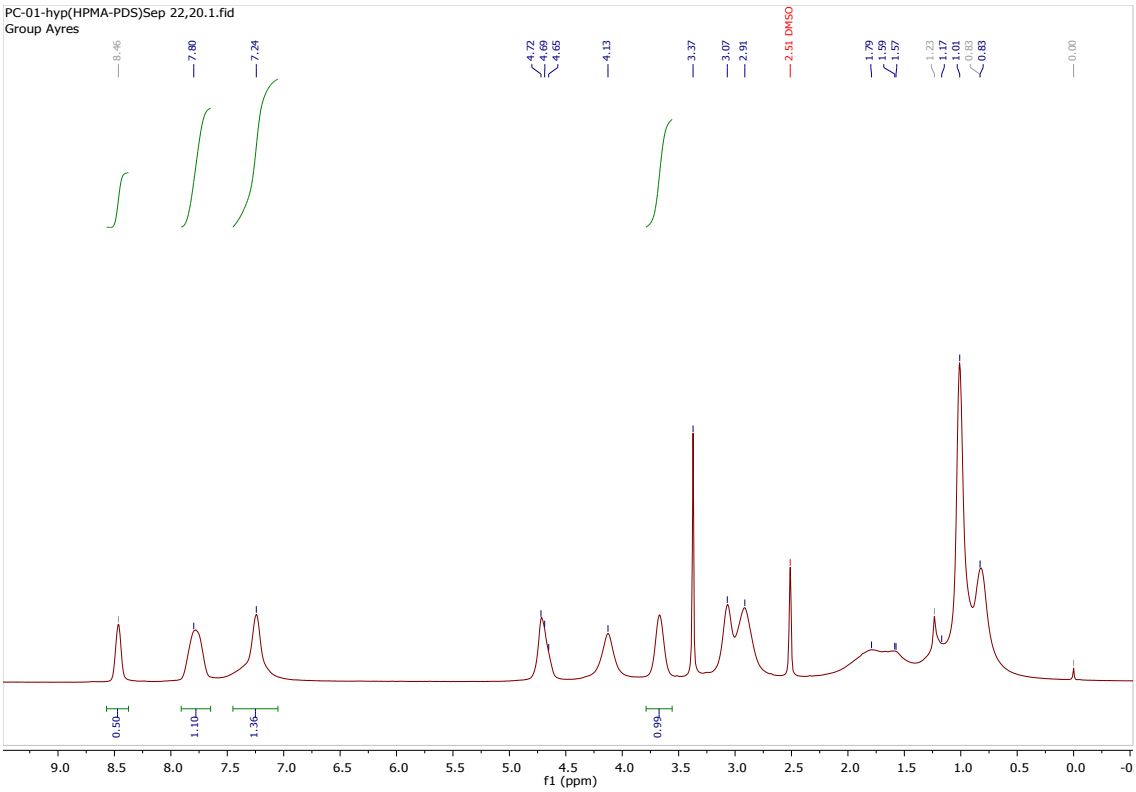

Figure S9. ^{1}H NMR spectrum of hb-poly(HPMA$_{84}$-*stat*-PDSEMA$_{24}$).

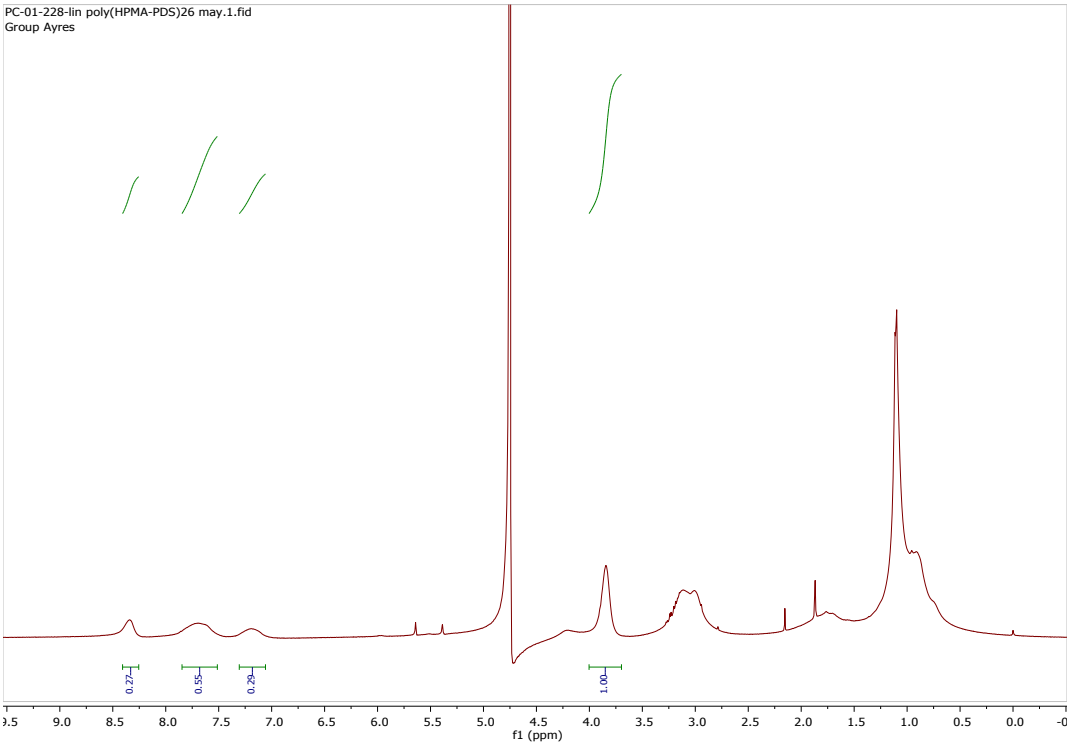

Figure S10. ^{1}H NMR spectrum of l-poly(HPMA$_{104}$-*stat*-PDSEMA$_{16}$).

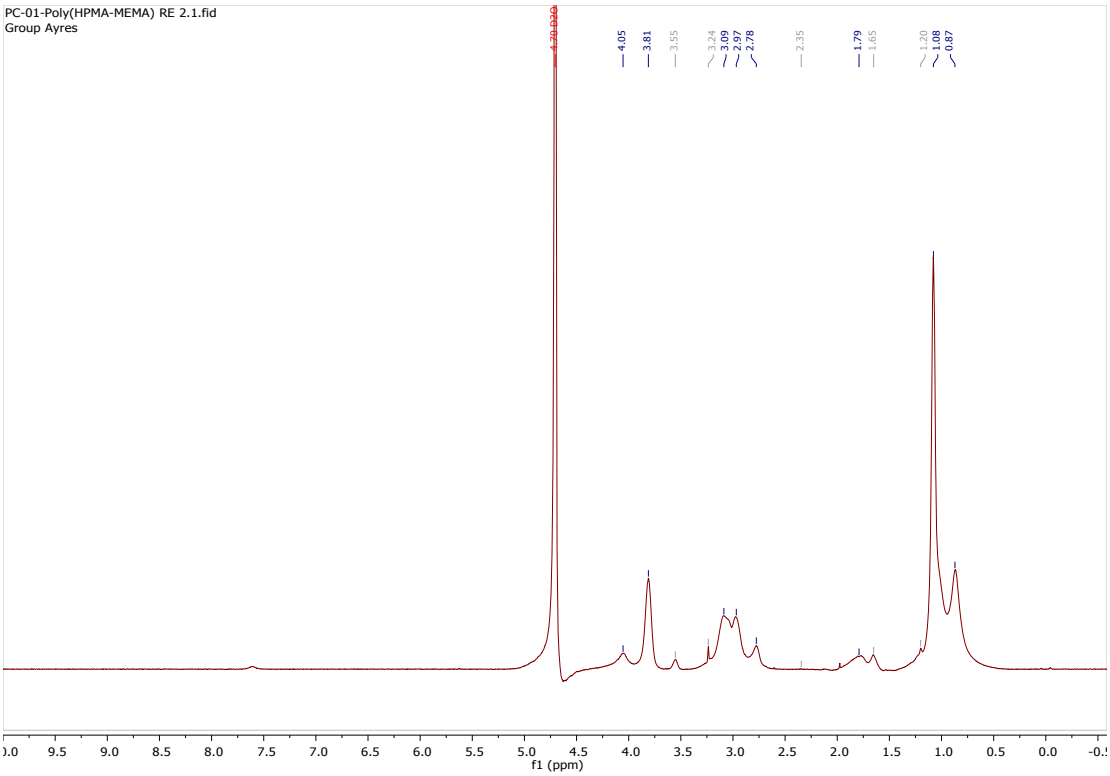

Figure S11. ^{1}H NMR spectrum of hb-poly(HPMA$_{84}$-*stat*-MEMA$_{24}$).

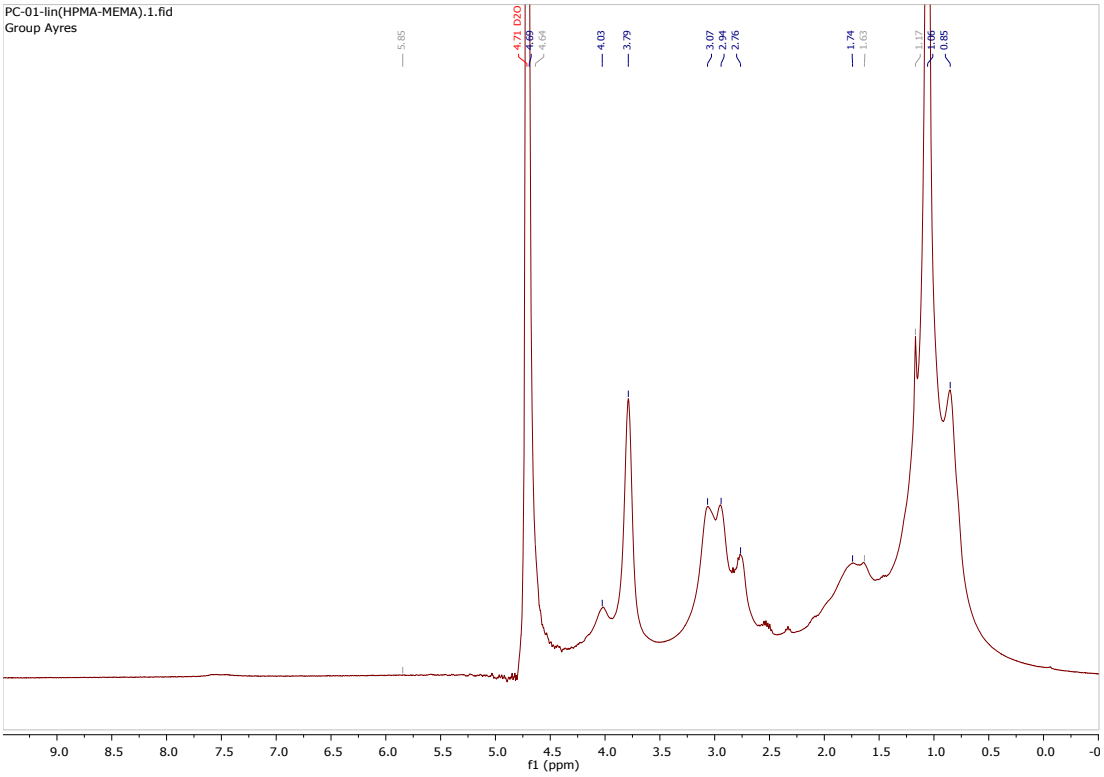

Figure S12. ^{1}H NMR spectrum of l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$).

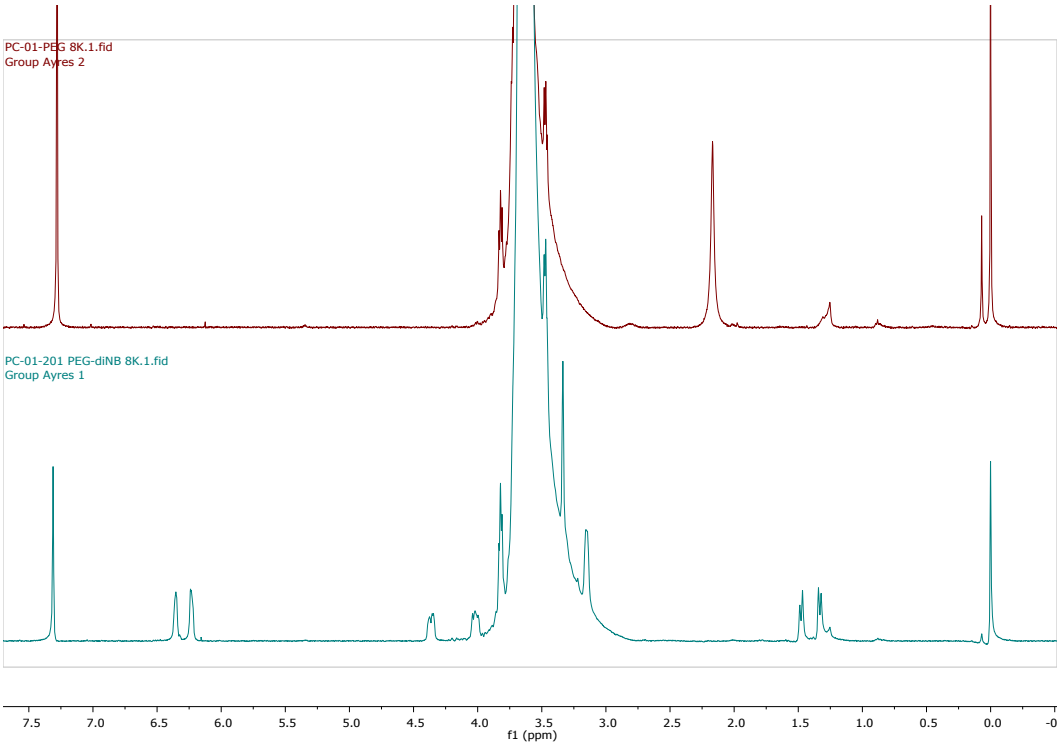

Figure S13. ^{1}H NMR spectrum of PEG (top figure) and Norbornene modified PEG (PEG-diNB) (bottom figure).

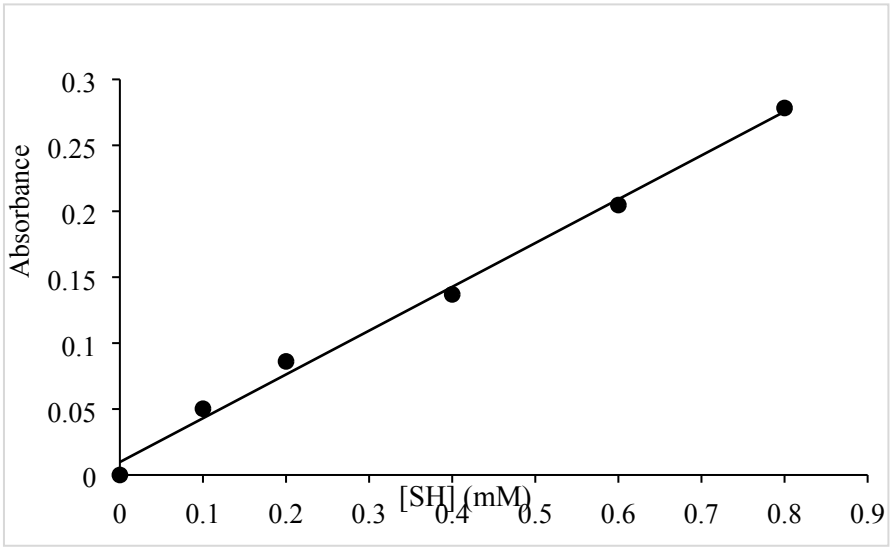

Figure S14. Standard calibration curve of Ellman's assay using DTT. For the assay, 200 µL of 2 mM (5,5- dithiobis[2nitrobenzoic acid]) (DTNB) solution, 290 µL of ultrapure water, 500 µL of 0.5 M tris buffer solution at pH 8, and 10 µL of a solution of 50 mg of copolymer dissolved in 1 mL of ultrapure water were mixed and left in the dark for ten minutes. Optical absorbance of the solution was measured at λ_{max} = 412 nm.

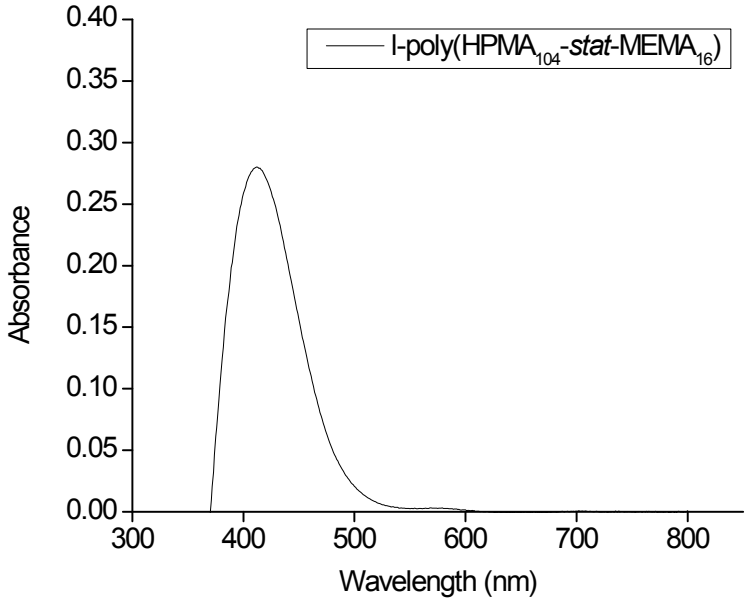

Figure S15. UV-VIS absorbance curve for l-poly($HPMA_{104}$-*stat*-$MEMA_{16}$).

Table S1. Storage moduli, swelling ratio, and gel fractions for the hb-Poly(HPMA-*stat*-MEMA)s prepared in this work taking 10 wt% solid content at different thiol to ene (T:E) ratios.

Polymer	T:E	% solids	G' (kPa)	Swelling ratio	Gel fraction (%)
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	1:1	10	4.2	15.30	94
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	2:1	10	5.8	15.18	93
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	3:1	10	7.6	15.02	92
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	4:1	10	10.2	14.83	90
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	5:1	10	13.1	13.90	89

Table S2. Storage moduli, swelling ratio, and gel fractions for the hb-Poly($HPMA_{84}$-*stat*-$MEMA_{24}$)s prepared in this work using 20 wt% solid content and 5 wt% solid content.

Polymer	T:E	% solids	G' (kPa)	Swelling ratio	Gel fraction (%)
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	1:1	20	6.82	14.85	93
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	2:1	20	8.91	14.61	90
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	3:1	20	11.05	14.43	86
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	4:1	20	13.09	13.82	85
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	5:1	20	16.3	13.14	82
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	1:1	5	1.6	16.82	93
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	2:1	5	1.8	16.70	92
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	3:1	5	1.9	16.61	91
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	4:1	5	2.1	16.41	90
hb-poly($HPMA_{84}$-*stat*-$MEMA_{24}$)	5:1	5	2.2	16.32	90

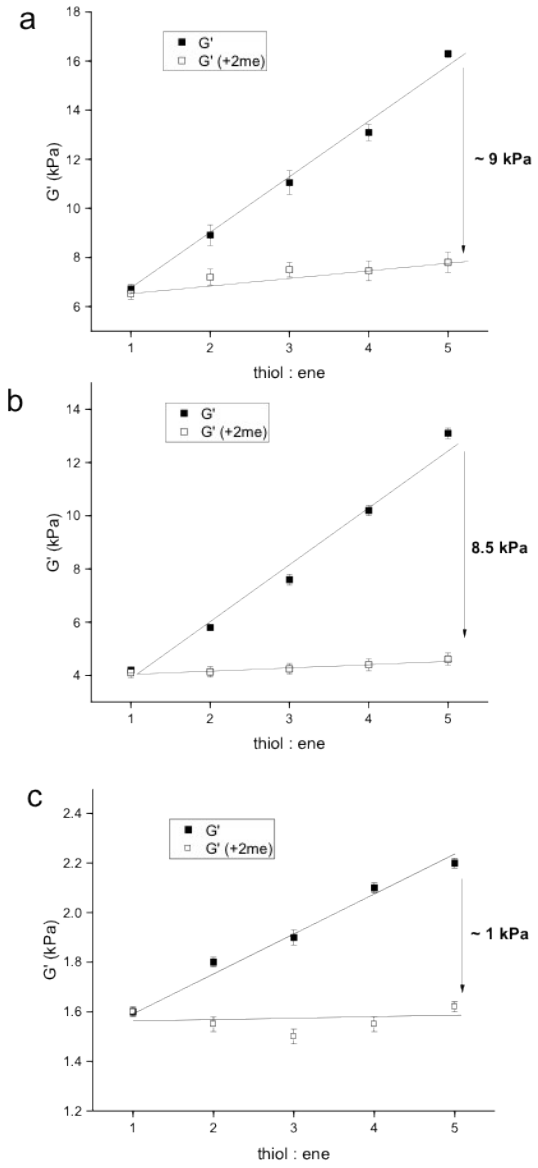

Figure S16. Storage moduli, G', of hydrogels synthesized using hb-poly(HPMA$_{84}$-*stat*-MEMA$_{24}$) using a) 20 wt %, b) 10 wt%, and c) 5 wt % solids with different thiol to ene ratios before (black squares) and after (white squares) softening with 2-mercaptoethanol.

Table S3. Storage moduli and thiol concentrations before and after adding 2-mercaptoethanol for gels made using the hb-Poly(HPMA-*stat*-MEMA)s prepared in this work using 10 wt% solid content at different thiol to ene (T:E) ratios.

Polymer	T:E	% solids	Solvent (ml)	G' (kPa)	G' (+2me, kPa)	[SH] (added)	[SH] (+2me, mmol)	Theoretical [SH] (+2me, mmol)
hb-poly(HPMA$_{84}$-*stat*-MEMA$_{24}$)	1:1	10	1	4.1	4.0	0.021	0.001	-
hb-poly(HPMA$_{84}$-*stat*-MEMA$_{24}$)	2:1	10	1	5.8	4.2	0.036	0.015	0.018
hb-poly(HPMA$_{84}$-*stat*-MEMA$_{24}$)	3:1	10	1	7.6	4.4	0.048	0.030	0.032
hb-poly(HPMA$_{84}$-*stat*-MEMA$_{24}$)	4:1	10	1	10.2	4.4	0.056	0.041	0.042
hb-poly(HPMA$_{84}$-*stat*-MEMA$_{24}$)	5:1	10	1	13.1	4.5	0.064	0.048	0.051

Table S4. Storage moduli and thiol concentrations before and after adding 2-mercaptoethanol for gels made using the l-Poly(HPMA-*stat*-MEMA)s prepared in this work at different thiol to ene (T:E) ratios.

Polymer	T:E	% solids	Solvent (ml)	G' (kPa)	G' (+2me, kPa)	[SH] (added)	[SH] (+2me, mmol)	Theoretical [SH] (+2me, mmol)
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	1:1	11	1	3.1	3.0	0.021	0.001	-
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	2:1	12	1	4.3	3.1	0.036	0.016	0.018
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	3:1	12	1	5.6	3.3	0.048	0.029	0.032
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	4:1	12	1	7.2	3.3	0.056	0.040	0.042
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	5:1	13	1	8.1	3.7	0.064	0.049	0.051
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	1:1	10	1.11	3.0	2.8	0.021	0.002	-
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	2:1	10	1.16	4.2	3.2	0.036	0.015	0.018
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	3:1	10	1.22	5.4	3.4	0.048	0.028	0.032
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	4:1	10	1.24	6.7	3.5	0.056	0.039	0.042
l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$)	5:1	10	1.28	7.5	3.8	0.064	0.050	0.051

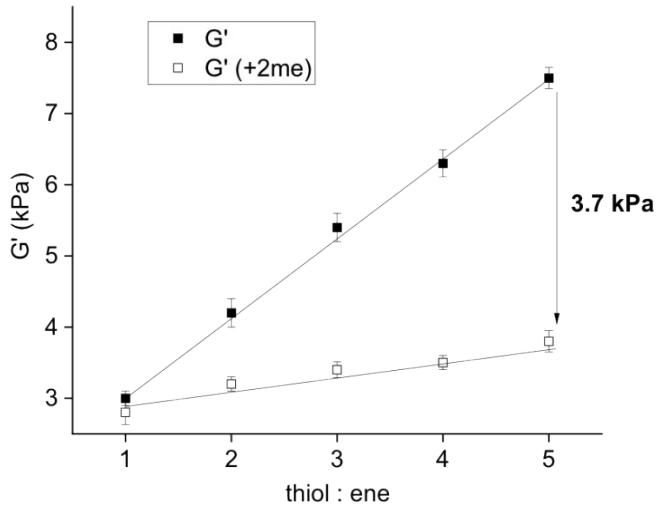

Figure S17. Storage moduli, G', of hydrogels synthesized using l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$) at the same thiol concentrations and weight percent solids to the hyperbranched polymers with different thiol to ene ratios before (black squares) and after (white squares) softening with 2-mercaptoethanol.

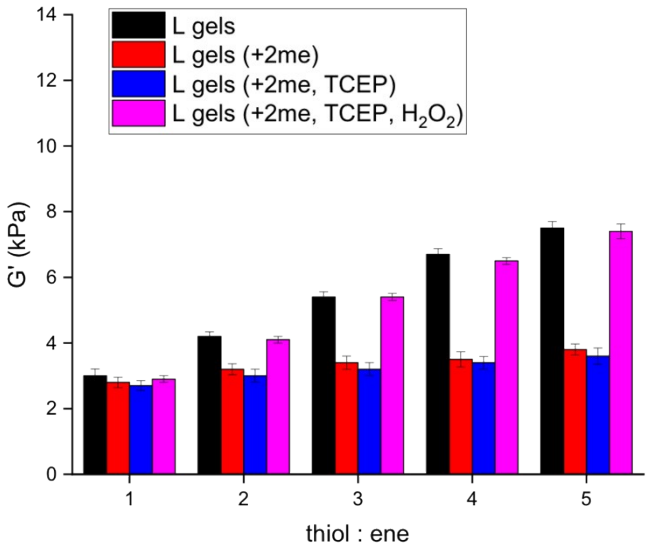

Figure S18. Storage moduli, G', before (black bar) and after softening of hydrogels (red bar) and then reducing with TCEP (blue bar) and after peroxide-induced healing of gels (pink bar) prepared using l-poly(HPMA$_{104}$-*stat*-MEMA$_{16}$) maintaining the same thiol concentration and weight percent solids as the hyperbranched polymers at that thiol to ene ratio.

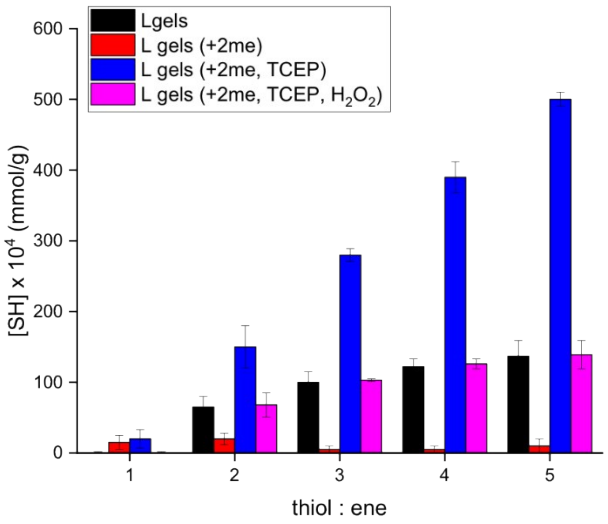

Figure S19. Thiol concentrations (x10^4 mmol/g) before (black bar) and after softening of hydrogels (red bar) and then reducing with TCEP (blue bar) and after peroxide-induced healing of gels (pink bar) prepared using l-poly($HPMA_{104}$-*stat*-$MEMA_{16}$) maintaining the same thiol concentration and weight percent solids as the hyperbranched polymers at that thiol to ene ratio.