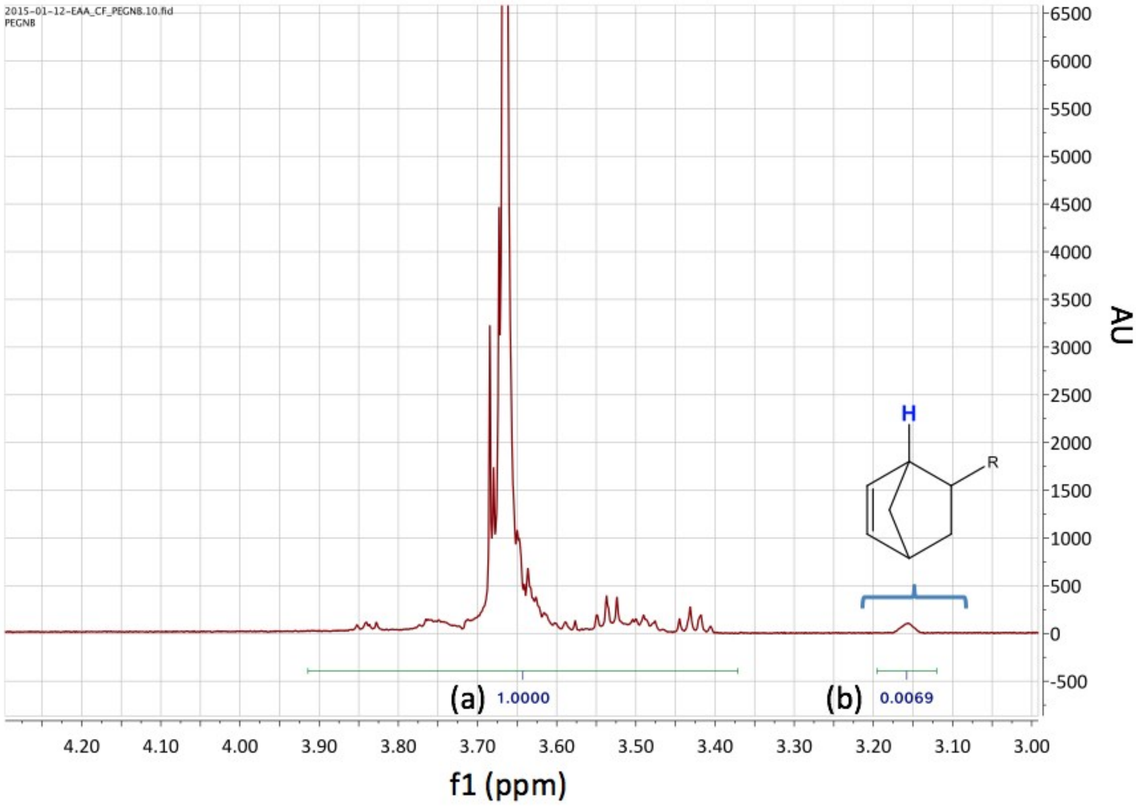
Soft Matter

Electronic Supplementary Information



ESI 1 Nuclear magnetic resonance spectrum of the conjugation product of norbornene (NB) to poly(ethylene glycol) amine (PEG), where (a) indicates the spectrum of the PEG backbone with resonance between ~3.4-3.85 ppm and (b) indicates the spectrum for the allylic proton closest to the NB bridged cyclic hydrocarbon group with resonance between ~3.1-3.2 ppm. A 99% conjugation percentage was found using the ratio of the two peak areas combined with the molecular weight of the PEG and NB molecules.

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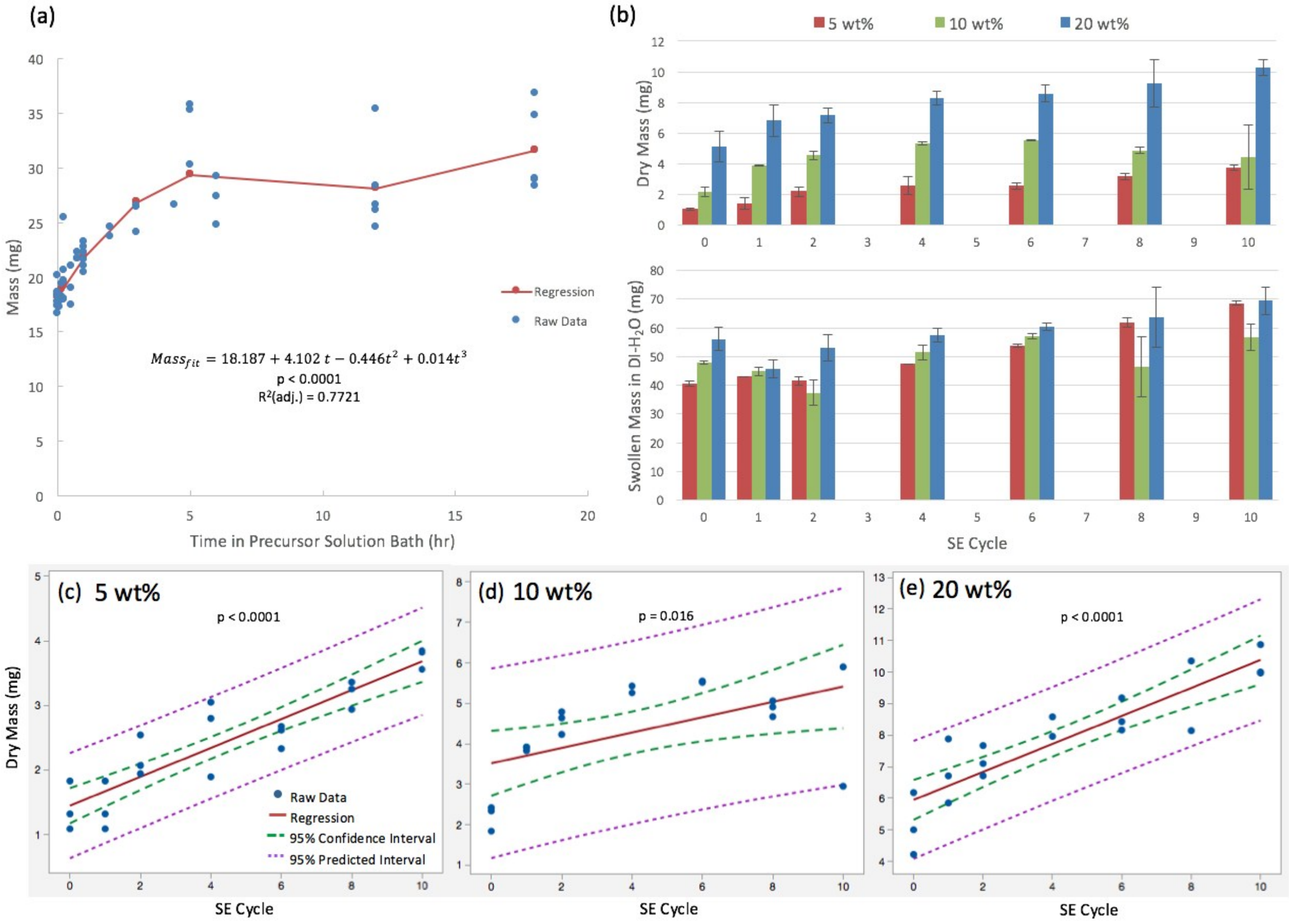

ESI 2 (a) Swollen mass as a function of time in precursor solution bath and the polynomial regression analysis, shown as solid line in red ($p<0.0001$) (b) Bar graphs illustrating increased dry and swollen masses as a function of SE cycle with standard deviation indicated. (c-d) Regression fits with 95% confidence interval, demonstrating statistically significant increase in dry polymer mass as a function of SE cycle.

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	Best-fit Polynomial Regression Analysis		
	Fit Equation	p-value	R^2(adj.)
5 wt%			
Compressive Modulus (*E*)	$E_{fit} = -2.8 + 36.0\ \mathrm{SE} - 6.3\ \mathrm{SE}^2 + 0.3\ \mathrm{SE}^3$	<0.0001	0.768
Toughness (*T*)	$\ln(T)_{fit} = 1.11 + 1.88\ \mathrm{SE} - 0.38\ \mathrm{SE}^2 + 0.02\ \mathrm{SE}^3$	0.0092	0.670
Volume Swelling Ratio (*Q*)	$Q_{fit} = 40.6 - 13.3\ \mathrm{SE} + 2.5\ \mathrm{SE}^2 - 0.1\ \mathrm{SE}^3$	<0.0001	0.811
Crosslink Density (ρ_x)	$\rho_{xfit} = -0.000526 + 0.0101\ \mathrm{SE} - 0.00172\ \mathrm{SE}^2 + 0.00009\ \mathrm{SE}^3$	0.0198	0.896
Linear Deformation (λ)	$\lambda_{fit} = 1.289 - 0.015\ \mathrm{SE} - 0.0016\ \mathrm{SE}^2 + 0.0002\ \mathrm{SE}^3$	<0.0001	0.864
Linear Deformation Ratio (λ_n)	$\lambda_{nfit} = 3.435 - 0.443\ \mathrm{SE} - 0.082\ \mathrm{SE}^2 + 0.005\ \mathrm{SE}^3$	<0.0001	0.790
10 wt%			
Compressive Modulus (*E*)	$\ln(E)_{fit} = 3.00 + 1.22\ \mathrm{SE} - 0.21\ \mathrm{SE}^2 + 0.01\ \mathrm{SE}^3$	<0.0001	0.931
Toughness (*T*)	$T_{fit} = 9.4 + 38.1\ \mathrm{SE} - 8.0\ \mathrm{SE}^2 + 0.5\ \mathrm{SE}^3$	<0.0001	0.759
Volume Swelling Ratio (*Q*)	$Q_{fit} = 21.2 - 8.4\ \mathrm{SE} + 1.5\ \mathrm{SE}^2 - 0.1\ \mathrm{SE}^3$	0.0006	0.636
Crosslink Density (ρ_x)	$\rho_{xfit} = 0.00436 + 0.0148\ \mathrm{SE} - 0.00208\ \mathrm{SE}^2 + 0.00009\ \mathrm{SE}^3$	0.0018	0.980
Linear Deformation (λ)	$\lambda_{fit} = 2.868 - 0.712\ \mathrm{SE} + 0.129\ \mathrm{SE}^2 + 0.006\ \mathrm{SE}^3$	0.042	0.300
Linear Deformation Ratio (λ_n)	$\lambda_{nfit} = 1.351 - 0.072\ \mathrm{SE} + 0.008\ \mathrm{SE}^2 - 0.006\ \mathrm{SE}^3$	<0.0001	0.864
20 wt%			
Compressive Modulus (*E*)	$E_{fit} = 107 + 152\ \mathrm{SE} - 30\ \mathrm{SE}^2 + 2\ \mathrm{SE}^3$	<0.0001	0.695
Toughness (*T*)	$\ln(T)_{fit} = 3.41 + 0.88\ \mathrm{SE} - 0.17\ \mathrm{SE}^2 + 0.01\ \mathrm{SE}^3$	<0.0001	0.695
Volume Swelling Ratio (*Q*)	$Q_{fit} = 10.9 - 2.79\ \mathrm{SE} + 0.56\ \mathrm{SE}^2 - 0.03\ \mathrm{SE}^3$	0.0011	0.628
Crosslink Density (ρ_x)	$\rho_{xfit} = 0.0242 + 0.0277\ \mathrm{SE} - 0.0051\ \mathrm{SE}^2 + 0.0003\ \mathrm{SE}^3$	0.0302	0.862
Linear Deformation (λ)	$\lambda_{fit} = 2.207 - 0.209\ \mathrm{SE} + 0.042\ \mathrm{SE}^2 - 0.002\ \mathrm{SE}^3$	0.0018	0.600
Linear Deformation Ratio (λ_n)	$\lambda_{nfit} = 1.408 - 0.081\ \mathrm{SE} - 0.0134\ \mathrm{SE}^2 - 0.0007\ \mathrm{SE}^3$	0.0167	0.425

ESI 3 Polynomial regression analysis for all initial precursor formulations and hydrogel properties as functions of SE cycle are reported here along with their respective p and R^2(adjusted) values. For all models, we compared with linear and quadratic terms only models and for each response variable, a linear-quadratic-cubic model was most appropriate.

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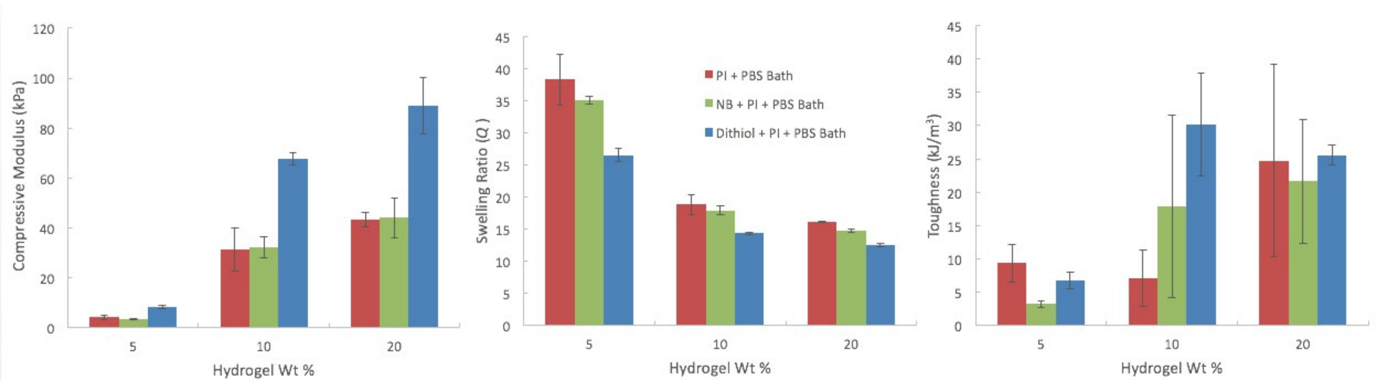
Precursor Solution Concentration	Bath with photoinitiator	Bath without photoinitiator	Compressive Modulus (kPa)	Volume Swelling Ratio (Q)
5 wt%	X		6.9 ± 0.1	19.4 ± 2.0
		X	6.7 ± 0.4	20.5 ± 1.0
10 wt%	X		18.8 ± 1.8	14.5 ± 3.4
		X	18.1 ± 2.4	15.6 ± 1.6
20 wt%	X		50.6 ± 3.1	12.1 ± 0.4
		X	49.8 ± 1.3	11.6 ± 1.2

ESI 4 Mechanical properties are not influence by the presence of photoinitiator. In a two-way ANOVA the main effect of wt% was significant ($p < 0.0001$). However, there was no significant main effect of photoinitiator status, and no significant interaction between wt% and photoinitiator status.



ESI 5 Mechanical properties of hydrogels after a single swelling and exposure cycle using precursor solution containing solely (red) photoinitiator and PBS; (green) PEG-NB, photoinitiator, and PBS; or (blue) PEG-dithiol, photoinitiator. The compressive modulus was unaffected by the presence of solely PEG-NB in the solution, while it doubled when the PEG-dithiol solution was in-swelled and polymerized ($p<0.0001$). For both PEG-NB and PEG-dithiol solution, the swelling ratio decreased with respect to the photoinitiator solution control ($p<0.05$). Hydrogel toughness was not uniformly affected by the presence of either solely PEG-NB or PEG-dithiol across the three formulations ($p>0.05$).