

*Supplementary Information for*  
**Time-Dependent Covalent Network Formation in Extrudable Hydrogels**

Dylan G. Karis<sup>a</sup> and Alshakim Nelson<sup>a</sup>

<sup>a</sup>Department of Chemistry, University of Washington, Seattle, Washington 98105, USA

**Table of Contents**

<b>Figure S1.</b> <sup>1</sup> H NMR spectrum of F127-BUM (500 MHz, 293 K, CDCl <sub>3</sub> ).....	3
<b>Figure S2.</b> GPC trace of F127-BUM in CHCl <sub>3</sub> with 0.1 wt/v% TEA as stabilizer. ....	4
<b>Figure S3.</b> Photorheological experiment on 30 wt% F127-BUM hydrogel with varying equivalents of EDT after 1 day of equilibration. ....	5
<b>Figure S4.</b> Photorheological experiment on 30 wt% F127-BUM hydrogel with varying equivalents of EDT after 3 days of equilibration.....	5
<b>Figure S5.</b> Photorheological experiment on 30 wt% F127-BUM hydrogel with varying equivalents of EDT after 14 days of equilibration. ....	6
<b>Figure S6.</b> Molecular weight between cross-links control with mercaptoethanol.....	6
<b>Figure S7.</b> Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 0.5 equivalents of EDT measured over the course of 14 days.....	7
<b>Figure S8.</b> Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 1 equivalent of EDT measured over the course of 14 days.....	7
<b>Figure S9.</b> Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 1.5 equivalents of EDT measured over the course of 14 days.....	8
<b>Figure S10.</b> Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 2 equivalents of EDT measured over the course of 14 days.....	8
<b>Figure S11.</b> Viscous flow controls. ....	9
<b>Figure S12.</b> Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 1.5 equivalents of EDT without LAP photoinitiator measured over the course of 7 days. ....	9
<b>Figure S13.</b> Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 3 equivalents of mercaptoethanol measured over the course of 7 days.....	10
<b>Figure S14.</b> Hydrogel tube extrusion setup using coaxial nozzle.....	10
<b>Figure S15.</b> Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT immediately after EDT addition.....	11
<b>Figure S16.</b> Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT 1 day after EDT addition. ....	11
<b>Figure S17.</b> Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT 3 days after EDT addition.....	12
<b>Figure S18.</b> Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT 7 days after EDT addition.....	12
<b>Figure S19.</b> Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT 14 days after EDT addition.....	13

### Supplementary Experimental Details

Gel permeation chromatography was performed using a Waters chromatograph equipped with two 10  $\mu\text{m}$  Malvern columns (300 mm X 7.8 mm) connected in series with increasing pore size (1000, 10000 Å), using chloroform as the eluent, and calibrated with poly(ethylene glycol) standards (102 to 40000 g/mol). Relative molecular weights were measured in chloroform using poly(ethylene glycol) standards and a refractive index detector (flow rate: 1 mL/min).

### Supplementary Table

Table S1. Summary of all data obtained for 30 wt% F127-BUM with varying equivalents of EDT over 14 days of equilibration

Dithiol equiv.	Day	$G_N^0$ (kg/mol)	$M_c$ (kg/mol) <sup>a</sup>	Y (MPa) <sup>b</sup>	E (MPa) <sup>b</sup>	Max Elongation at break (mm/mm)	Max Comp. Stress (MPa) <sup>c</sup>	Deg. of Swelling (%)	Gel Fraction (%)
0	0	347 $\pm$ 6	7.2 $\pm$ 0.1	1.0 $\pm$ 0.1	1.1 $\pm$ 0.1	0.55 $\pm$ 0.08	5 $\pm$ 1	391 $\pm$ 1	97.1 $\pm$ 0.1
0.5	0	337.8 $\pm$ 0.6	7.43 $\pm$ 0.01	-	-	-	-	445.2 $\pm$ 0.6	99.0 $\pm$ 0.2
	1	330 $\pm$ 10	7.5 $\pm$ 0.3	-	-	-	-	455.5 $\pm$ 0.9	98.0 $\pm$ 0.4
	3	329 $\pm$ 5	7.6 $\pm$ 0.1	0.78 $\pm$ 0.07	0.98 $\pm$ 0.03	2.0 $\pm$ 0.2	4.6 $\pm$ 0.9	452 $\pm$ 2	96.8 $\pm$ 0.4
	7	259 $\pm$ 1	9.68 $\pm$ 0.05	-	-	-	-	482.2 $\pm$ 0.9	98.1 $\pm$ 0.3
	14	266 $\pm$ 3	9.4 $\pm$ 0.1	-	-	-	-	-	-
1	0	292 $\pm$ 5	8.6 $\pm$ 0.3	-	-	-	-	467 $\pm$ 4	98.5 $\pm$ 0.5
	1	269 $\pm$ 3	9.3 $\pm$ 0.1	-	-	-	-	503.4 $\pm$ 8	97.6 $\pm$ 0.1
	3	249 $\pm$ 3	10.1 $\pm$ 0.1	0.54 $\pm$ 0.04	0.654 $\pm$ 0.006	3.2 $\pm$ 0.5	2.8 $\pm$ 0.2	533 $\pm$ 3	95.9 $\pm$ 0.3
	7	175 $\pm$ 3	14.3 $\pm$ 0.2	-	-	-	-	557 $\pm$ 3	97.0 $\pm$ 0.4
	14	230 $\pm$ 10	10.8 $\pm$ 0.5	-	-	-	-	-	-
1.5	0	266.0 $\pm$ 0.6	9.44 $\pm$ 0.02	-	-	-	-	502 $\pm$ 1	96.7 $\pm$ 0.3
	1	218 $\pm$ 3	11.5 $\pm$ 0.2	-	-	-	-	551 $\pm$ 1	96.0 $\pm$ 0.2
	3	172 $\pm$ 4	14.6 $\pm$ 0.4	0.25 $\pm$ 0.03	0.26 $\pm$ 0.03	8 $\pm$ 1	1.1 $\pm$ 0.1	682 $\pm$ 8	92.4 $\pm$ 0.5
	7	139 $\pm$ 5	18.1 $\pm$ 0.6	-	-	-	-	1000 $\pm$ 14	90.2 $\pm$ 0.5
	14	148 $\pm$ 5	17.0 $\pm$ 0.6	-	-	-	-	-	-
2	0	245 $\pm$ 4	10.3 $\pm$ 0.2	-	-	-	-	518 $\pm$ 2	96.5 $\pm$ 0.1
	1	191 $\pm$ 4	13.2 $\pm$ 0.2	-	-	-	-	623 $\pm$ 2	94.5 $\pm$ 0.1
	3	124 $\pm$ 6	20 $\pm$ 1	0.04 $\pm$ 0.01	0.039 $\pm$ 0.004	24.9 $\pm$ 0.9	0.44 $\pm$ 0.06	693 $\pm$ 7	83.8 $\pm$ 0.3
	7	55 $\pm$ 1	45 $\pm$ 1	-	-	-	-	2600 $\pm$ 100	70. $\pm$ 2
	14	62 $\pm$ 2	41 $\pm$ 1	-	-	-	-	-	-

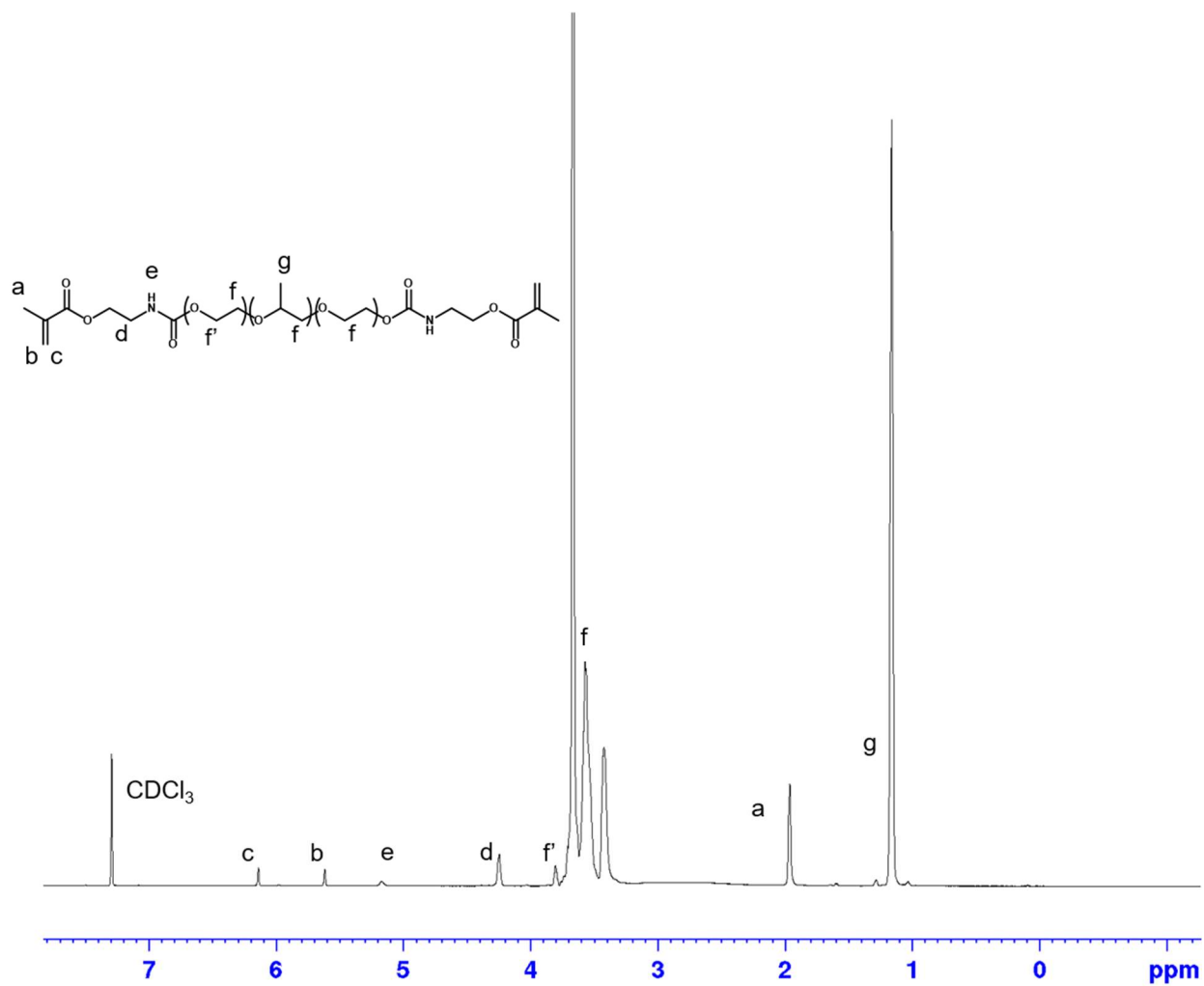
<sup>a</sup> Calculated using equation (1)

<sup>b</sup> Calculated as the linear region between 0 and 10% extension

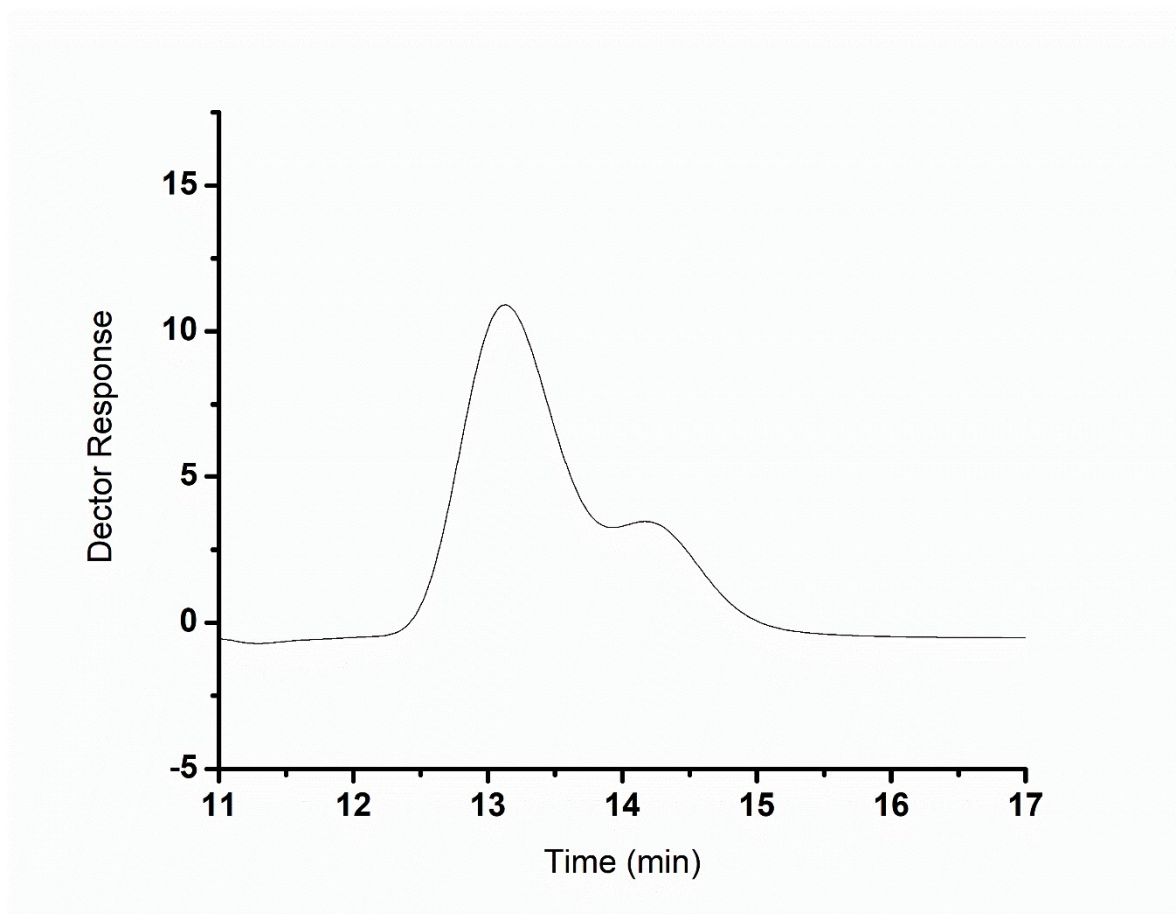
<sup>c</sup> Reported at 80% extension

All error given as standard deviation over 3 replicated tests

## Supplementary Figures

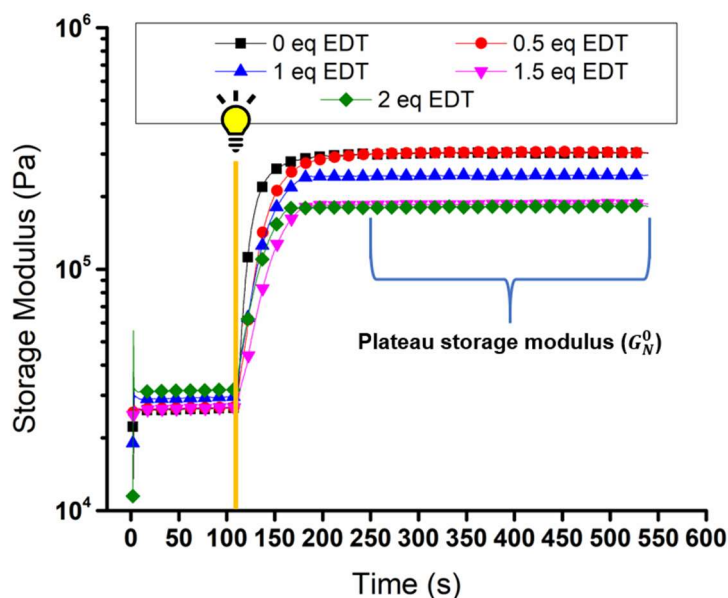


**Figure S1.**  $^1\text{H}$  NMR spectrum of F127-BUM (500 MHz, 293 K,  $\text{CDCl}_3$ )



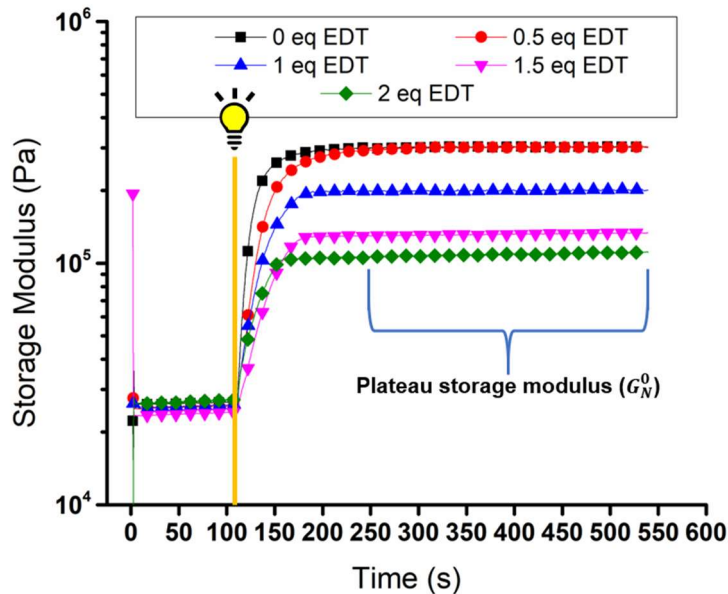
**Figure S2.** GPC trace of F127-BUM in  $\text{CHCl}_3$  with 0.1 wt/v% TEA as stabilizer.

Smaller peak at higher retention time is due to diblock copolymers present in F127 batches from vendor.



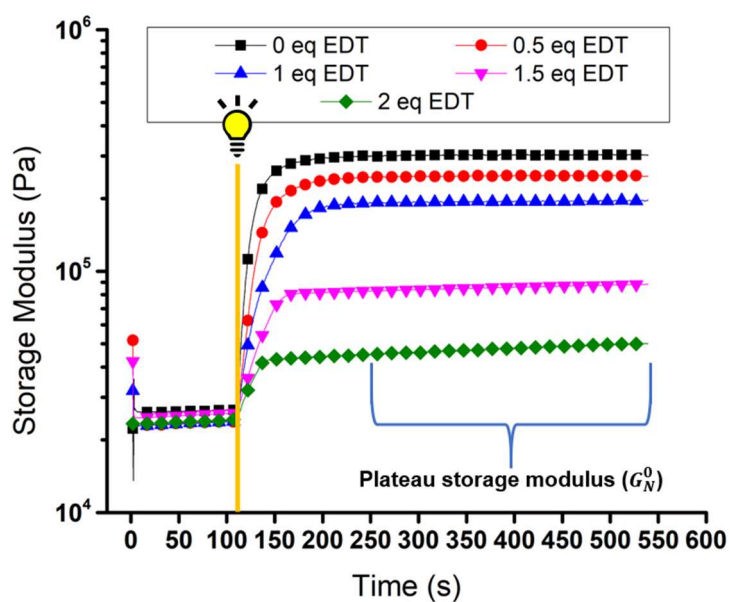
**Figure S3.** Photorheological experiment on 30 wt% F127-BUM hydrogel with varying equivalents of EDT after 1 day of equilibration.

At 120 s, the UV light is turned on and left on for the remainder of the experiment.



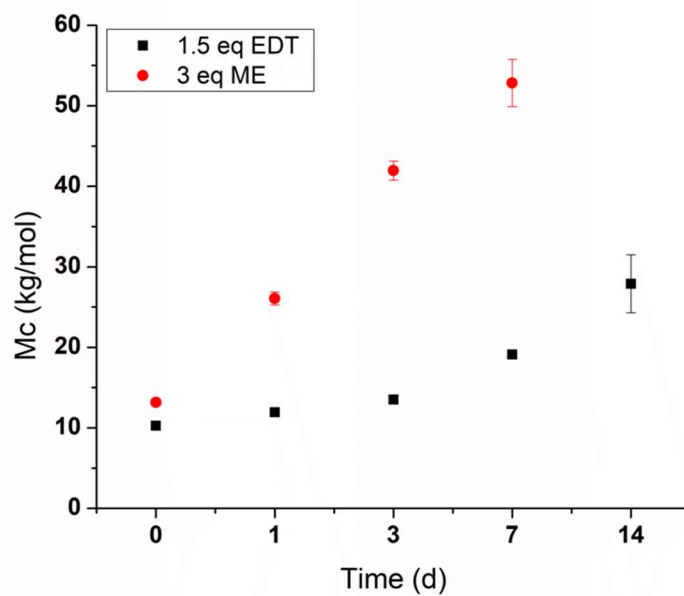
**Figure S4.** Photorheological experiment on 30 wt% F127-BUM hydrogel with varying equivalents of EDT after 3 days of equilibration.

At 120 s, the UV light is turned on and left on for the remainder of the experiment.



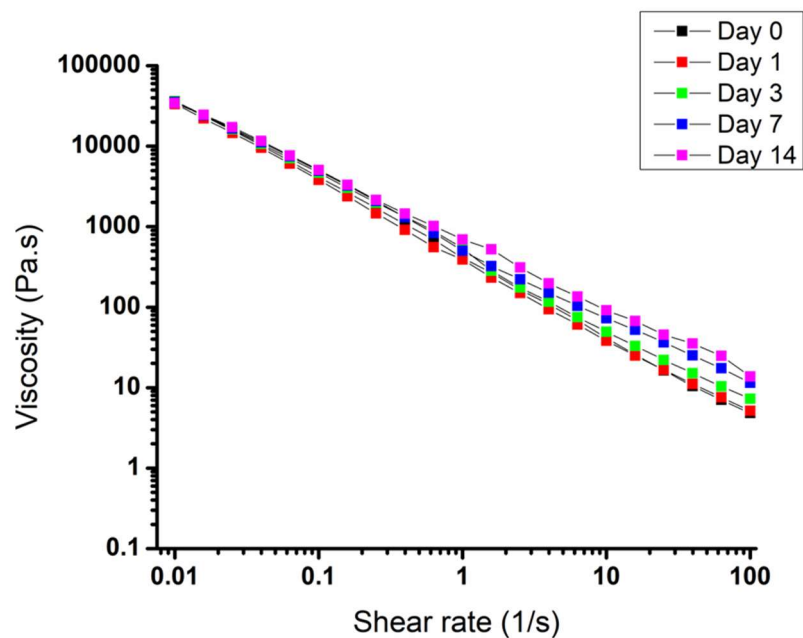
**Figure S5.** Photorheological experiment on 30 wt% F127-BUM hydrogel with varying equivalents of EDT after 14 days of equilibration.

At 120 s, the UV light is turned on and left on for the remainder of the experiment.

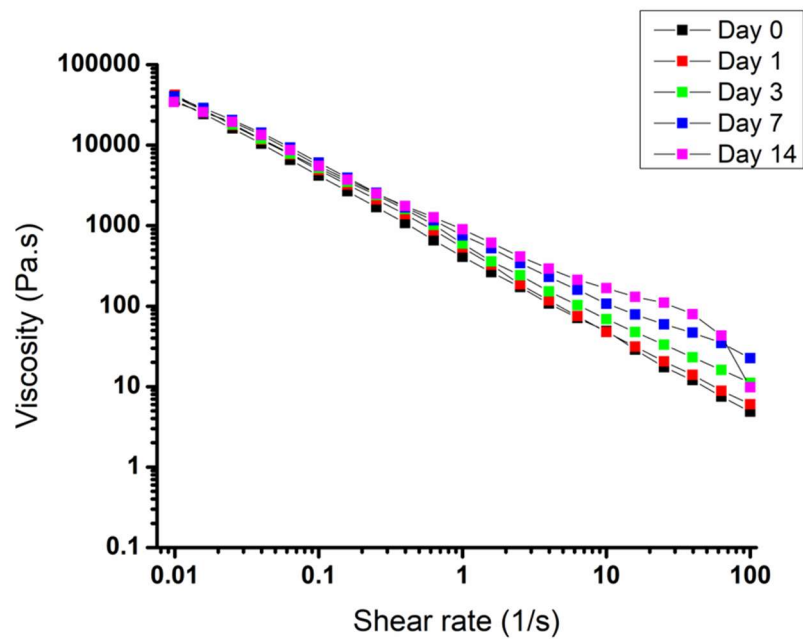


**Figure S6.** Molecular weight between cross-links control with mercaptoethanol.

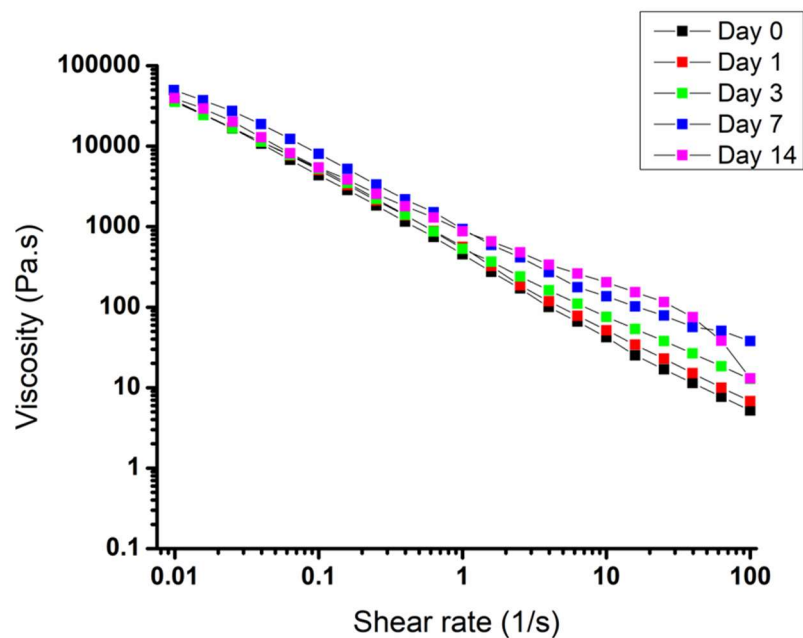
$M_c$  calculated from equation (1). Mercaptoethanol (ME) shows the effect of dead chain-ends on the  $M_c$  value as ME does not contribute to the hydrogel network.



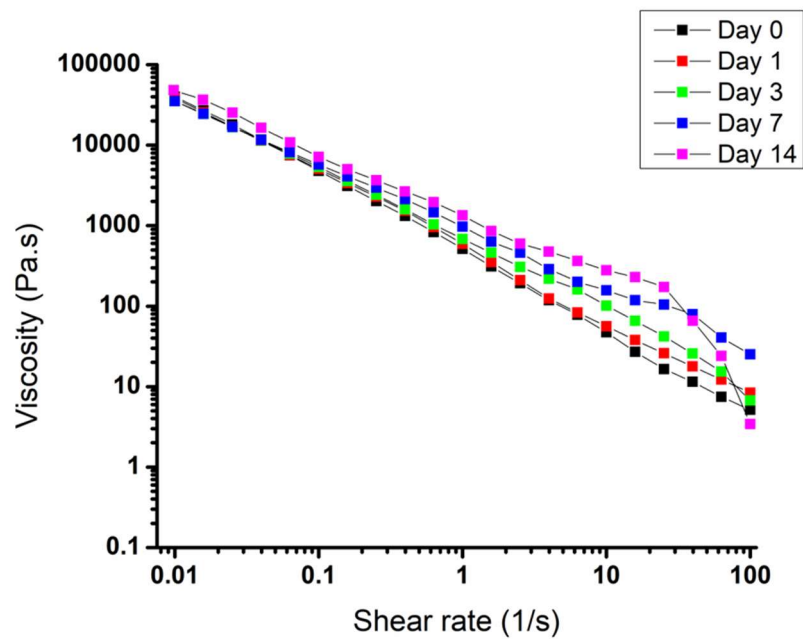
**Figure S7.** Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 0.5 equivalents of EDT measured over the course of 14 days.



**Figure S8.** Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 1 equivalent of EDT measured over the course of 14 days.

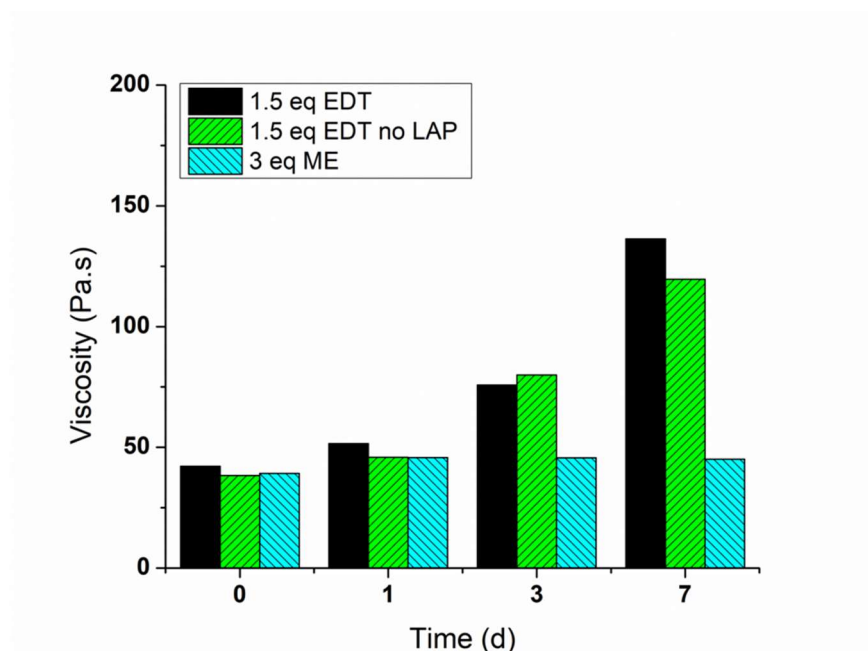


**Figure S9.** Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 1.5 equivalents of EDT measured over the course of 14 days.



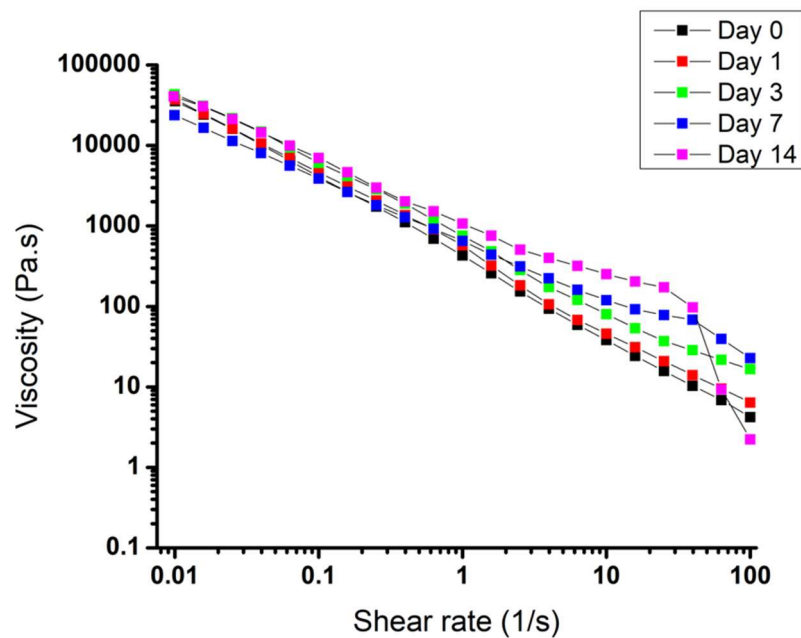
**Figure S10.** Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 2 equivalents of EDT measured over the course of 14 days.



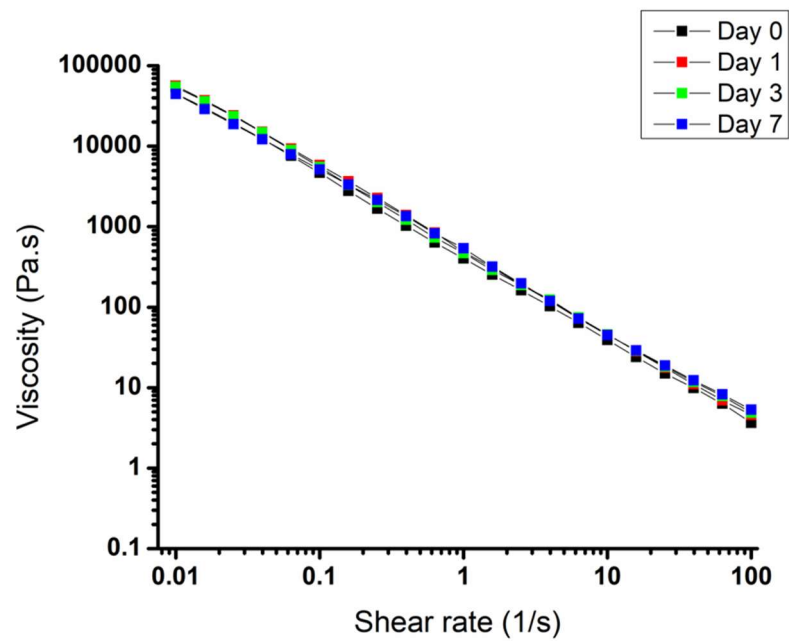


**Figure S11.** Viscous flow controls.

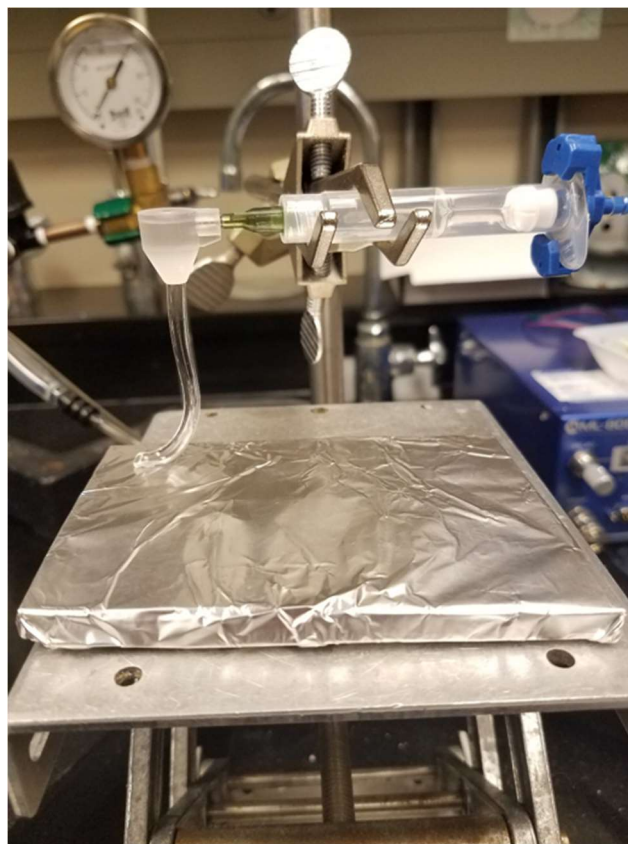
Measurements of 30 wt% F127-BUM taken at  $10 \text{ s}^{-1}$  and at  $21^\circ\text{C}$ . The photoinitiator LAP does not influence the viscosity change over time. Mercaptoethanol has no effect on the viscosity of the hydrogel.



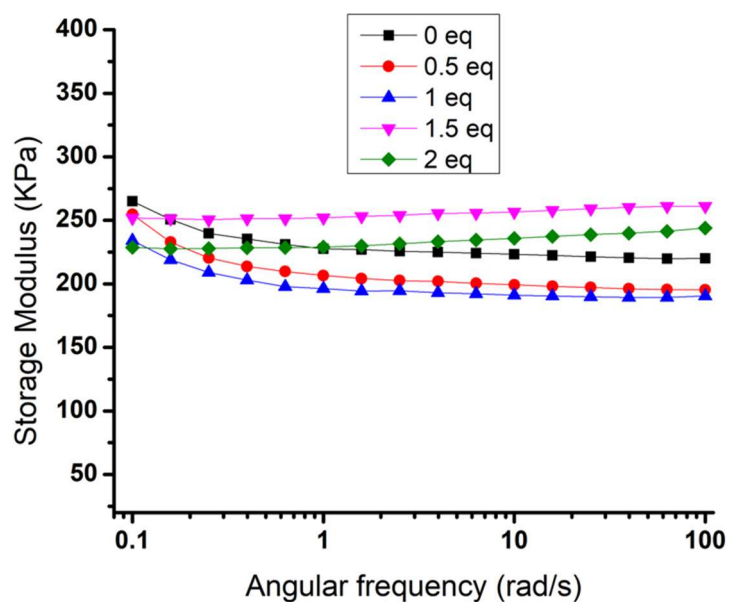
**Figure S12.** Viscous flow measurement of 30 wt% F127-BUM at  $21^\circ\text{C}$  with 1.5 equivalents of EDT without LAP photoinitiator measured over the course of 7 days.



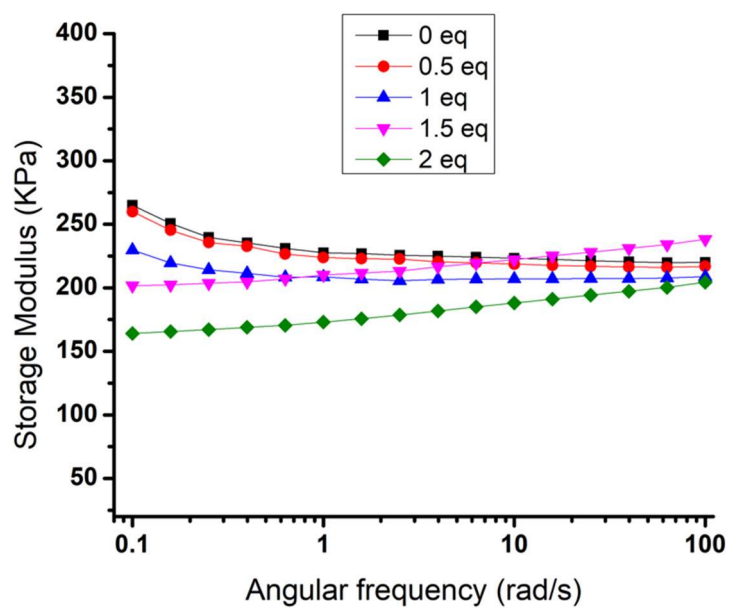
**Figure S13.** Viscous flow measurement of 30 wt% F127-BUM at 21 °C with 3 equivalents of mercaptoethanol measured over the course of 7 days.



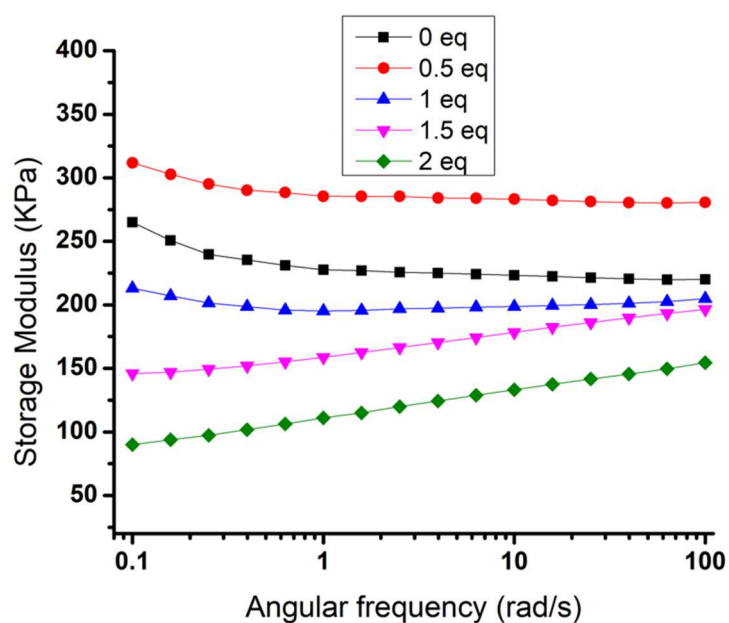
**Figure S14.** Hydrogel tube extrusion setup using coaxial nozzle



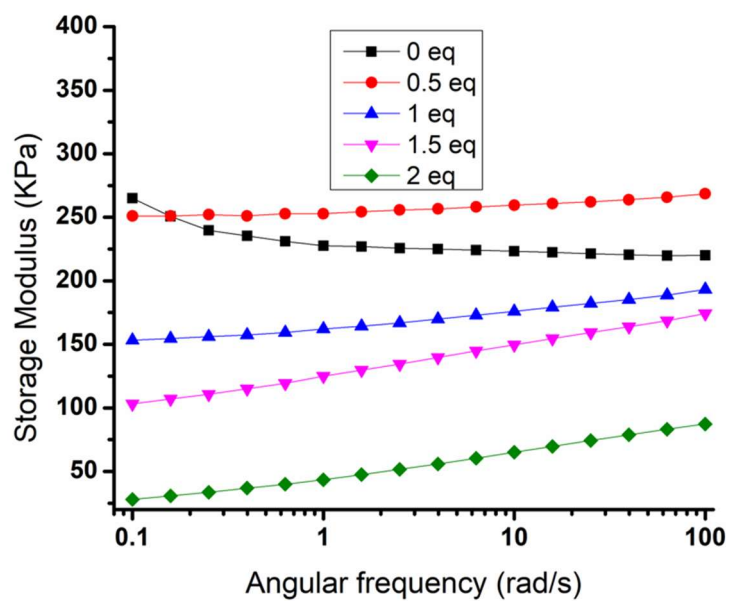
**Figure S15.** Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT immediately after EDT addition.



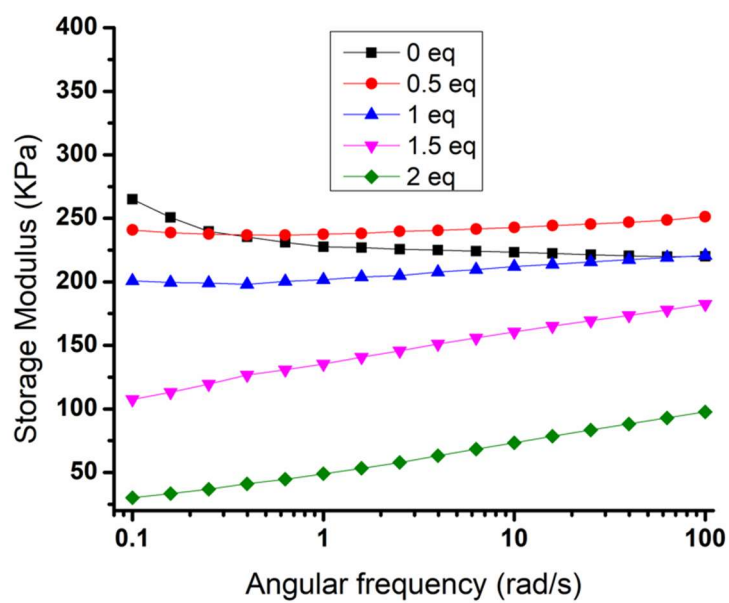
**Figure S16.** Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT 1 day after EDT addition.



**Figure S17.** Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT 3 days after EDT addition.



**Figure S18.** Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT 7 days after EDT addition.



**Figure S19.** Frequency sweep measurement of 30 wt% F127-BUM at 1% strain and 21 °C with varying equivalents of EDT 14 days after EDT addition.