Supporting information for

Ultra-high molecular weight tanglemer hydrogels

Md Saifur Rahaman, Brett Leslie Pollard, Luke A. Connal*

Research School of Chemistry, The Australian National University, Canberra, ACT 2601, Australia.

*Corresponding Author

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Table S1: Different polymerization parameters with gel fraction of hydrogels.

DP_{target} variation	Gel Fraction (%)	Constants (Crosslinker mol%)	Monomer: crosslinker mole ratio	Crosslinker:CTA ratio
500	**96.07** ± 0.86	**1**	**100**	**5**
1000	96.27 ± 2.20	**0.1**	**1000**	**1**
5000	98.63 ± 0.40	**0.1**	**1000**	**5**
10000	98.54 ± 0.36	**0.1**	**1000**	**10**
25000	98.66 ± 1.25	**0.1**	**1000**	**25**
50000	98.89 ± 0.24	**0.1**	**1000**	**50**
Crossslinker Mole % variation	Gel Fraction (%)	Constants (DPtarget)	Monomer to x-linker mole ratio	**Crosslinker:**CTA ratio
0.05	**98.39** ± 1.51	50000	2000	25
0.1	**98.58** ± 0.10	50000	1000	50
0.5	**98.11** ± 1.25	50000	200	250
1	**97.73** ± 1.52	50000	100	500
2	**98.80** ± 0.66	50000	50	1000
Monomer concentration variation	Gel Fraction (%)	Constants (DPtarget & mole % PEGDA	Monomer to x-linker mole ratio	**Crosslinker:**CTA ratio
0.5	98.11 ± 0.32	50000 & 0.1 %	50	1000
1	98.08 ± 0.30	50000 & 0.1 %	50	1000
3	98.37 ± 0.02	50000 & 0.1 %	50	1000
5	97.65 ± 2.59	50000 & 0.1 %	50	1000
Crosslinker Mole % variation with 5 M HEA	**Gel Fraction (%)**	**Constants (DP_{target} and monomer concentration)**	**Monomer to x-linker mole ratio**	**Crosslinker:**CTA ratio
1	99.22 ± 1.11	50000 & 5 M	100	500
0.1	98.51 ± 0.57	50000 & 5 M	50	1000
0.05	98.50 ± 1.11	50000 & 5 M	25	2000
0.005	98.45 ± 0.35	50000 & 5 M	2.5	20000
0.001	98.66 ± 0.27	50000 & 5 M	0.5	1000000

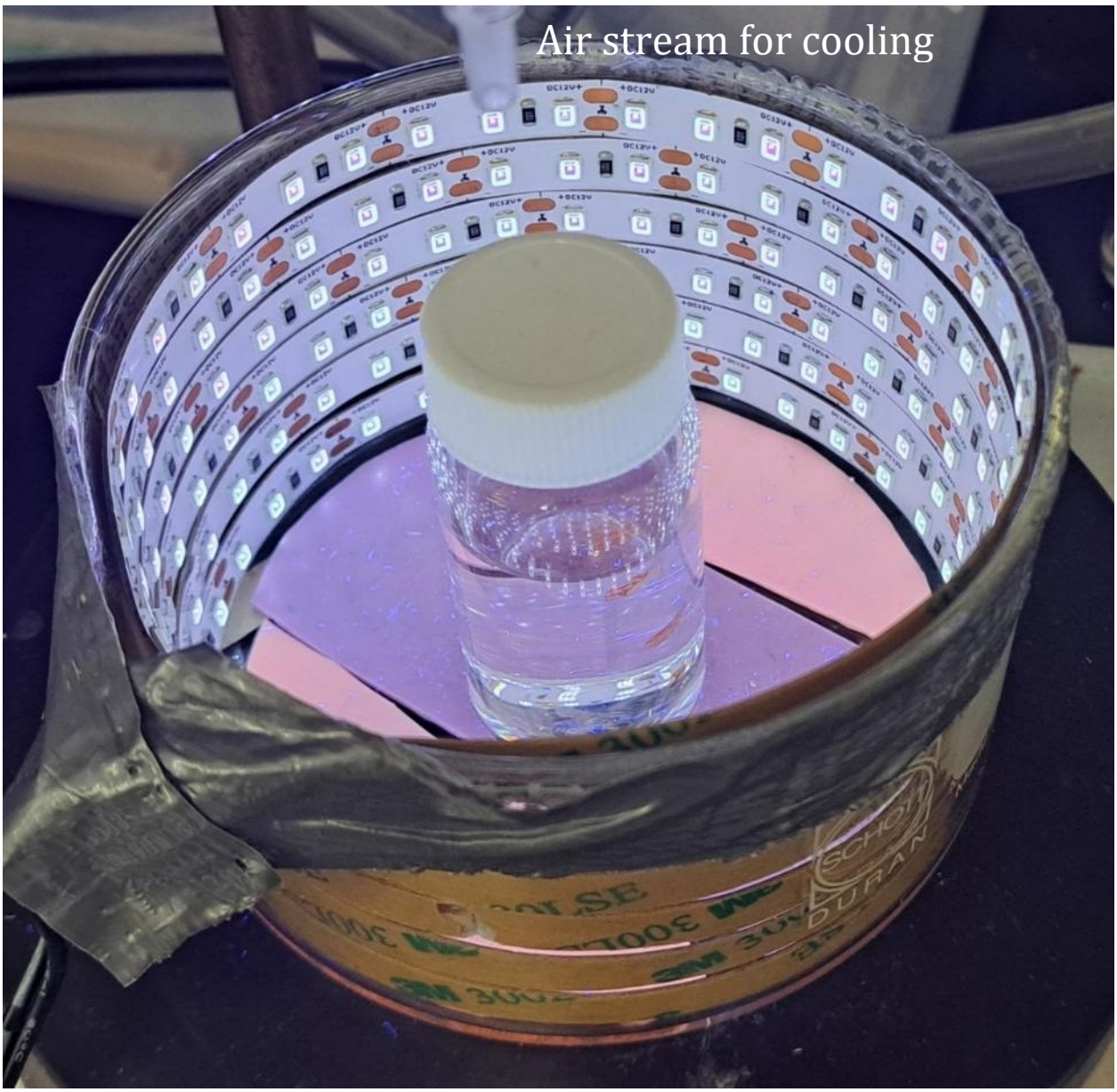

Air stream for cooling

Figure S1: Digital photograph of polymerization setup (14 W/m 12V Purple LED lights, λmax = 365 nm)

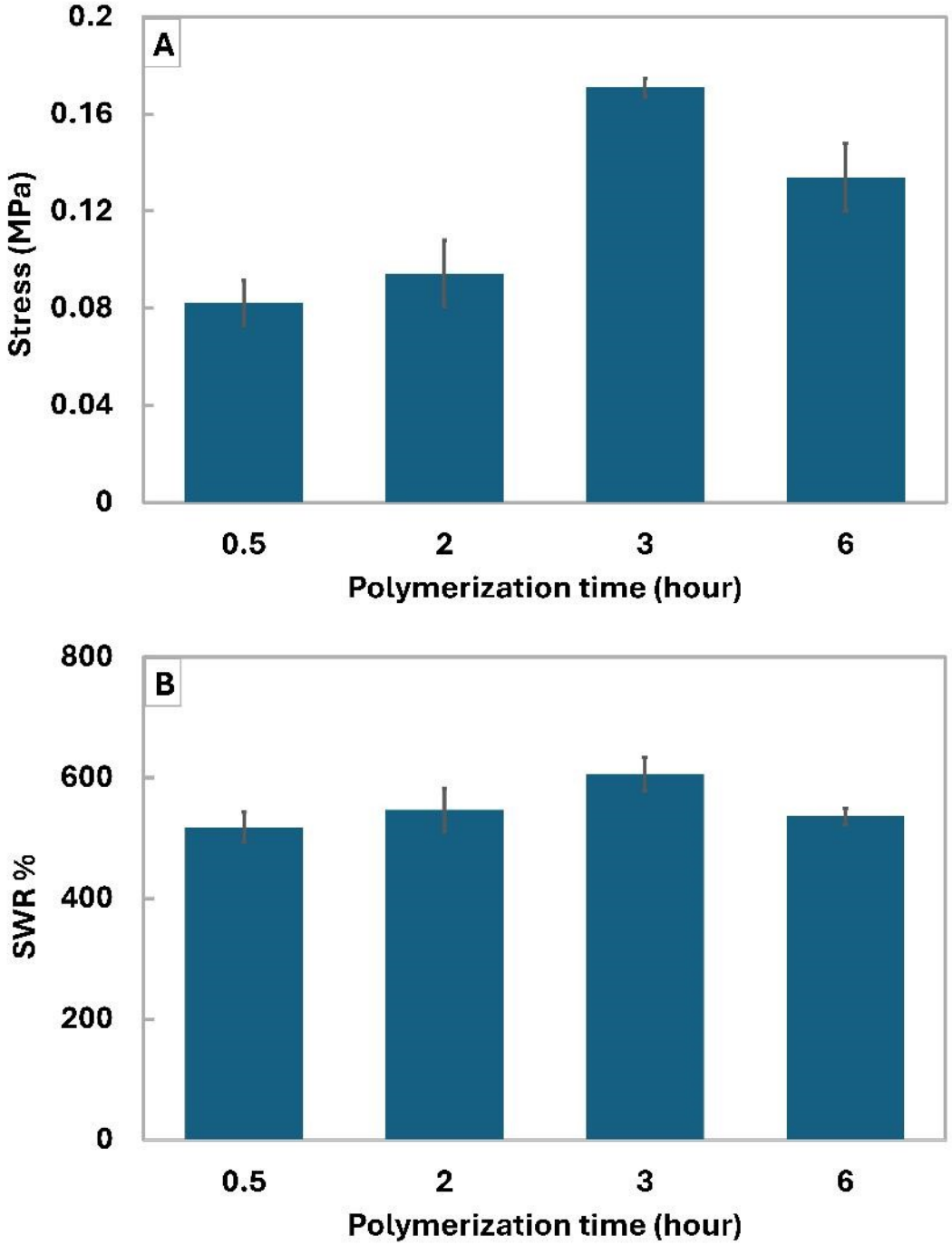


Figure S2: Effect of polymerization time variation with DPtarget 50000 and 0.1 mole % PEGDA on the A) mechanical strength and B) swelling ratio of the hydrogel.

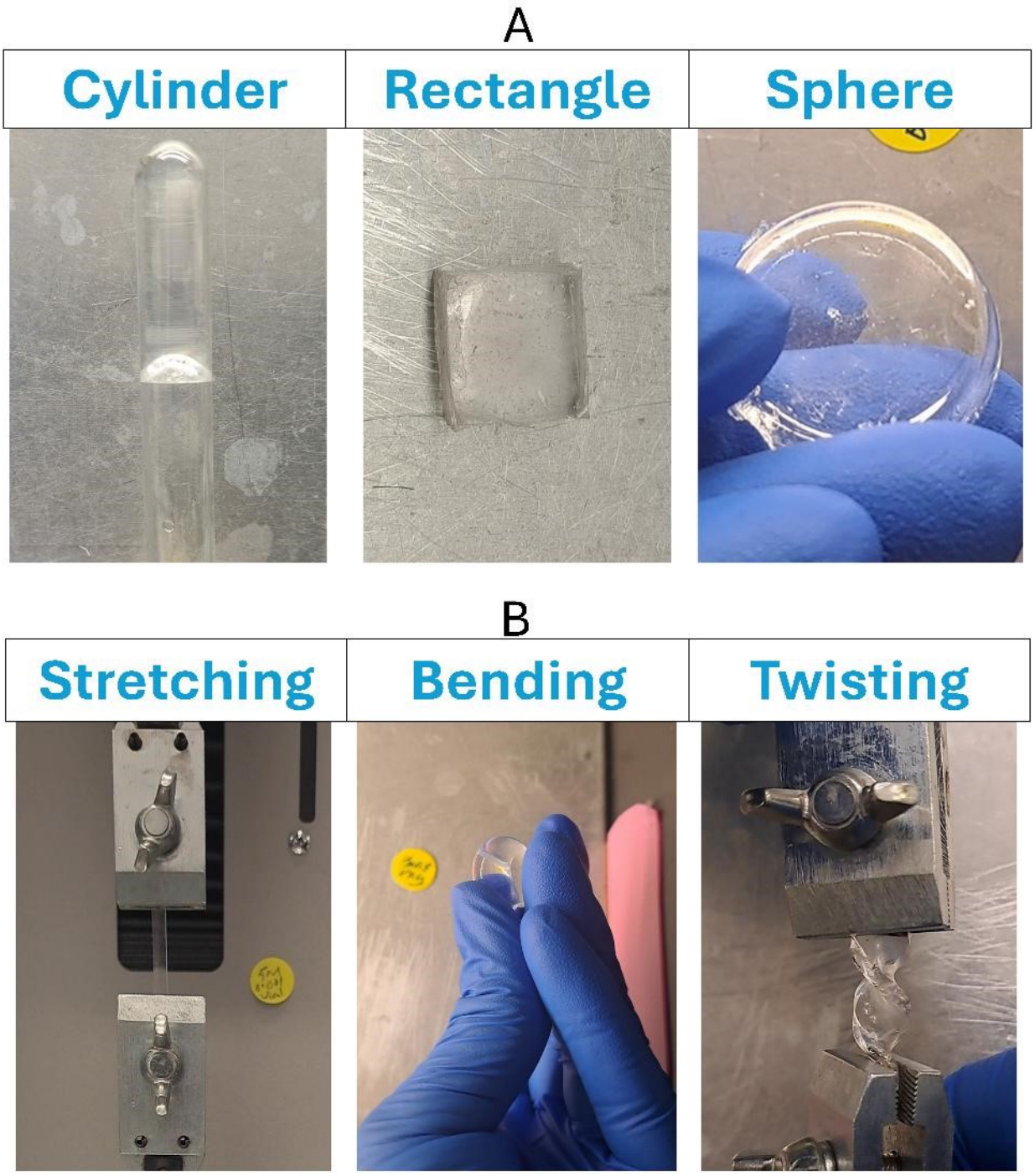


Figure S3: Digital photograph of the A) liquid hydrogel with DPtarget = 500 with 1 M HEA and 0.1 mole% PEGDA, B) Polymer with 0.5M HEA (left) and Hydrogel with same concentration (right), C) Polymer with 1M HEA concentration after 7 days of swelling in RO water.

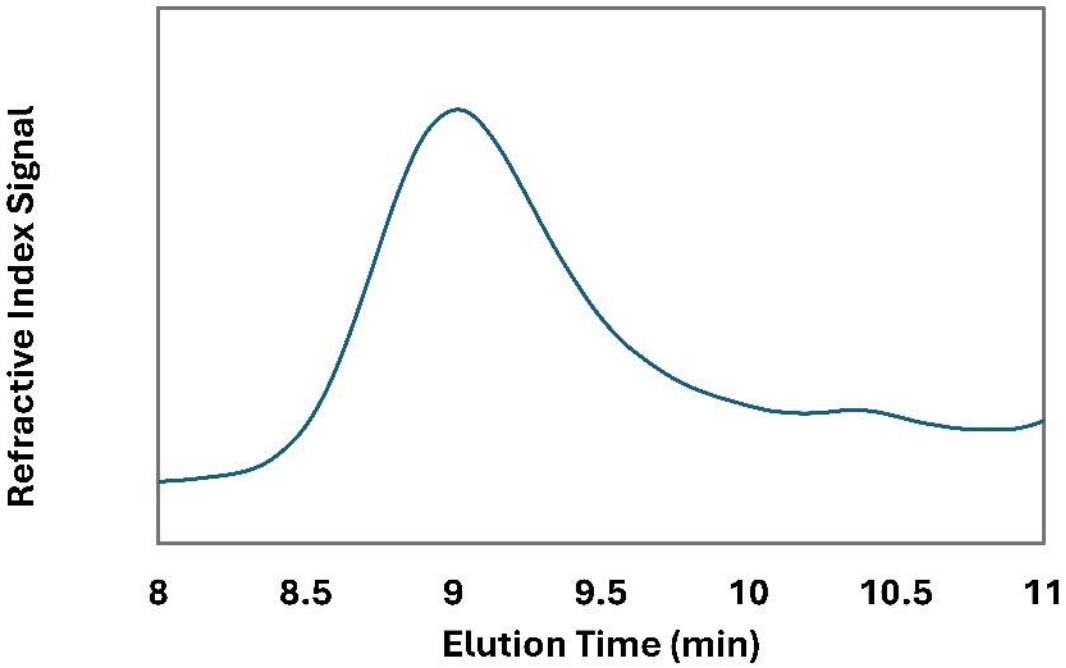


Figure S4. GPC trace of linear PHEA synthesized at DPtarget = 50,000 (MnGPC = 4.4 MDa, Đ = 1.358)

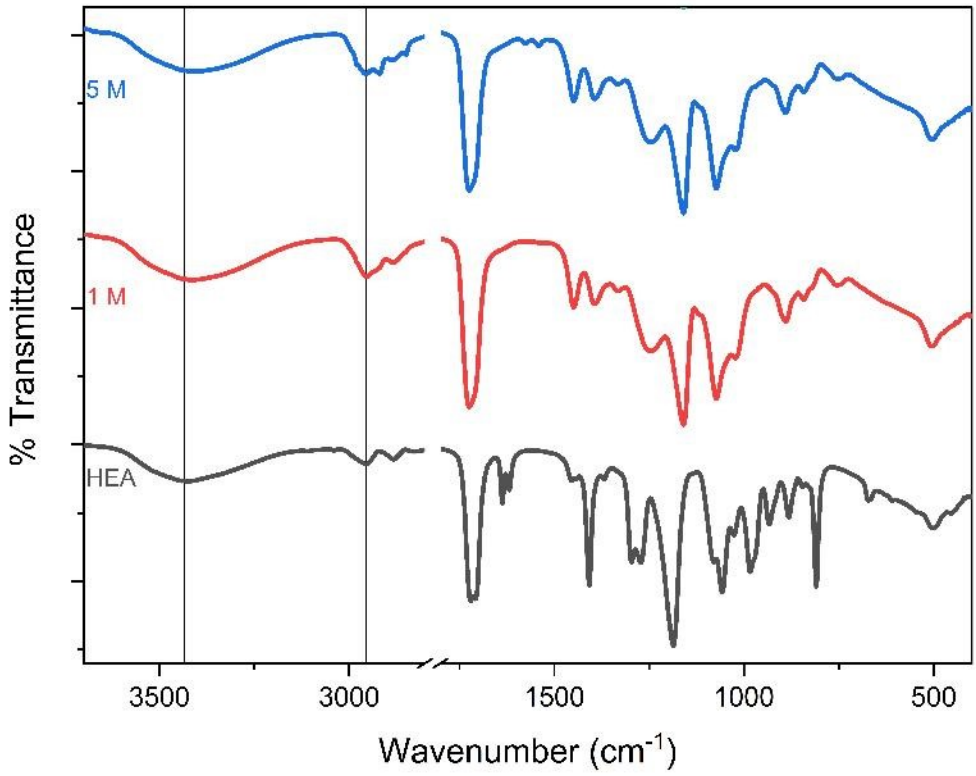
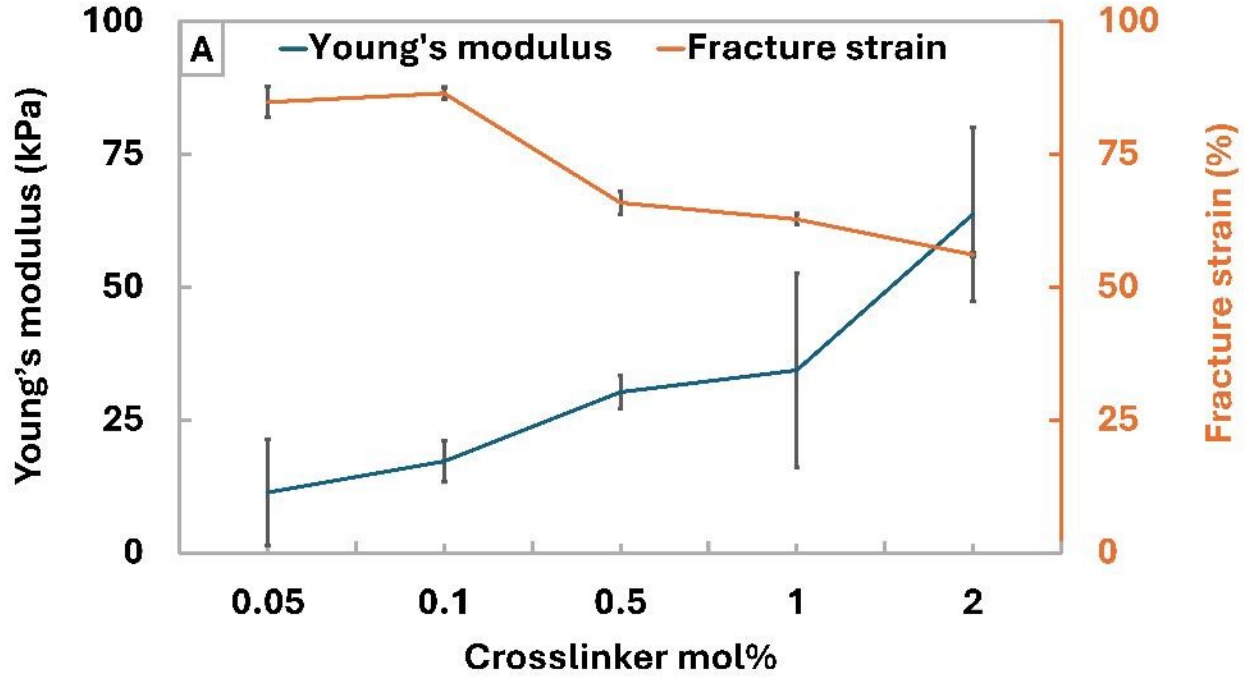


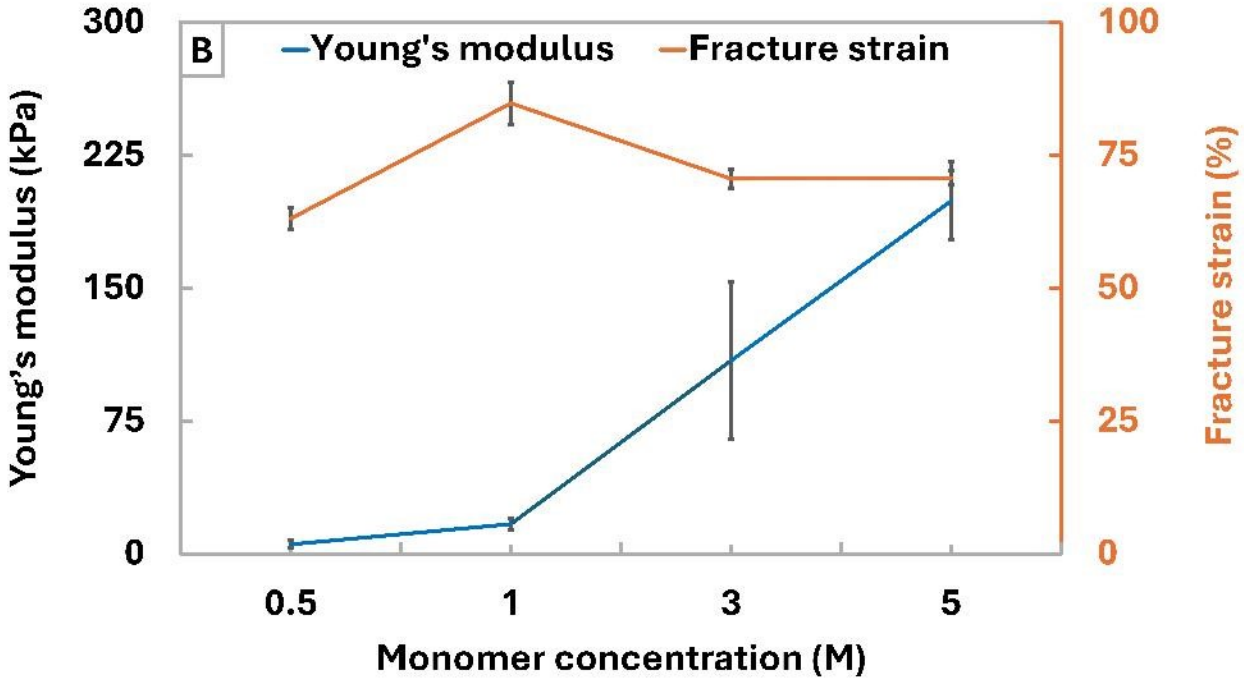
Figure S5: FTIR-ATR spectra of HEA monomer (black line) along with hydrogels with different concentrations (red line = 1.0 M, blue line = 5.0 M) and 0.1 mole% PEGDA crosslinker.

FTIR-ATR of the hydrogel

The FTIR-ATR spectrum of 2-hydroxyethyl acrylate (HEA) and its polymer (PHEA) show several characteristic absorption bands that provide crucial information about the molecular structure and chemical environment. For the HEA monomer, the broad absorption band appearing around 3300-3500 cm^{-1} corresponds to the hydrogen bonded hydroxyl (-OH) stretching vibration (Lee et al., 2004; Vargun & Usanmaz, 2005). For the hydrogels there is an enhanced intensity and signal complexity in the 2800 - 3000 cm^{-1} region for the peaks associated with the aliphatic side chain of HEA, including C-H stretching vibrations (Smith, 2022). The carbonyl group (C=O) peak of HEA appears at 1721 cm^{-1}. This peak is slightly blue shifted in the hydrogels (1725 and 1724 cm^{-1} for 1.0 M and 5.0 M, respectively) due the contribution from the PEGDA crosslinker (Lukatsky et al., 2024; Fockaert et al., 2020; Smith, 2022). The acrylate double bond (-C=C-) for HEA at 1638 cm^{-1}

disappeared in the hydrogel indicating that the polymerization reaction was complete and any residual monomer had been removed. (Vargun & Usanmaz, 2005; Lee et al., 2004). The peak at 1455 cm^{-1}, corresponding to CH_2 bending vibrations for HEA, showed an increased intensity due to the ordered polymer chain packing in the hydrogel (Thompson et al., 2015).


A
Young's modulus
Fracture strain
Young's modulus (kPa)
Fracture strain (%)
100
75
50
25
0
0.05
0.1
0.5
1
2
Crosslinker mol%


B
Young's modulus
Fracture strain
Young's modulus (kPa)
Fracture strain (%)
300
225
150
75
0
100
75
50
25
0
0.5
1
3
5
Monomer concentration (M)

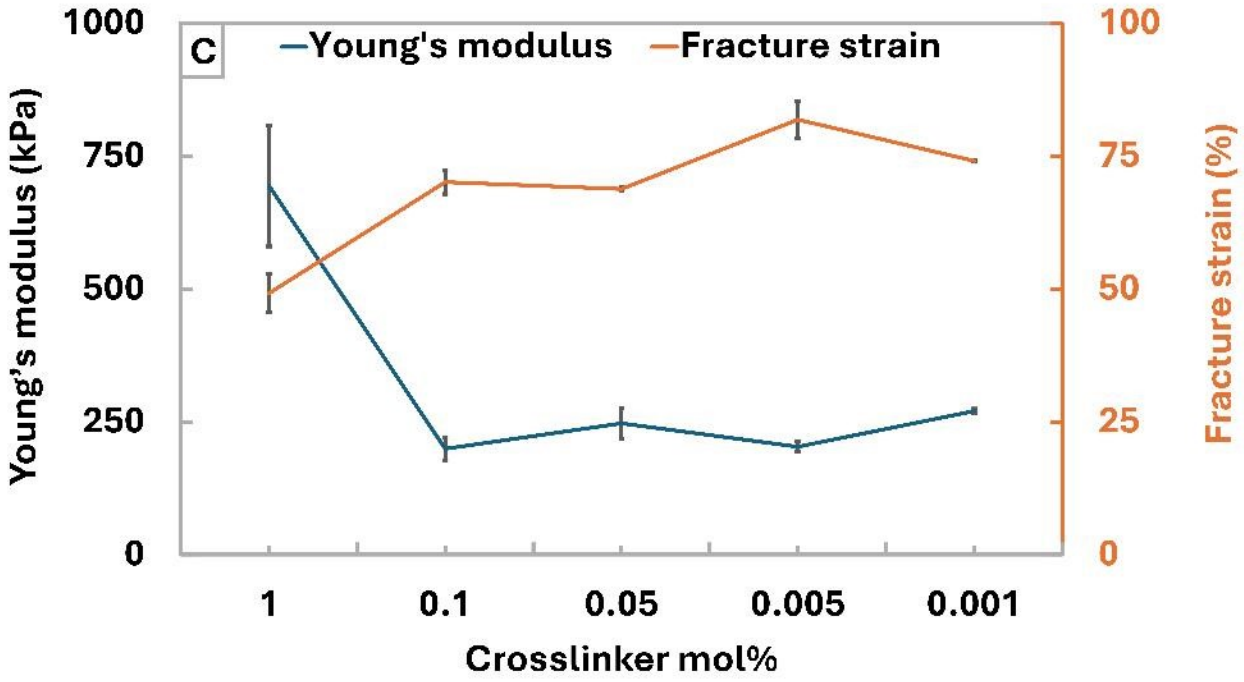


Figure S6: Effect of A) crosslinker mol% of 1M PHEA hydrogel, B) monomer concentrations and B) crosslinker mol% with 5M PHEA hydrogel on the Young's modulus (kPa) (blue line) and Fracture strain (%) (orange line).

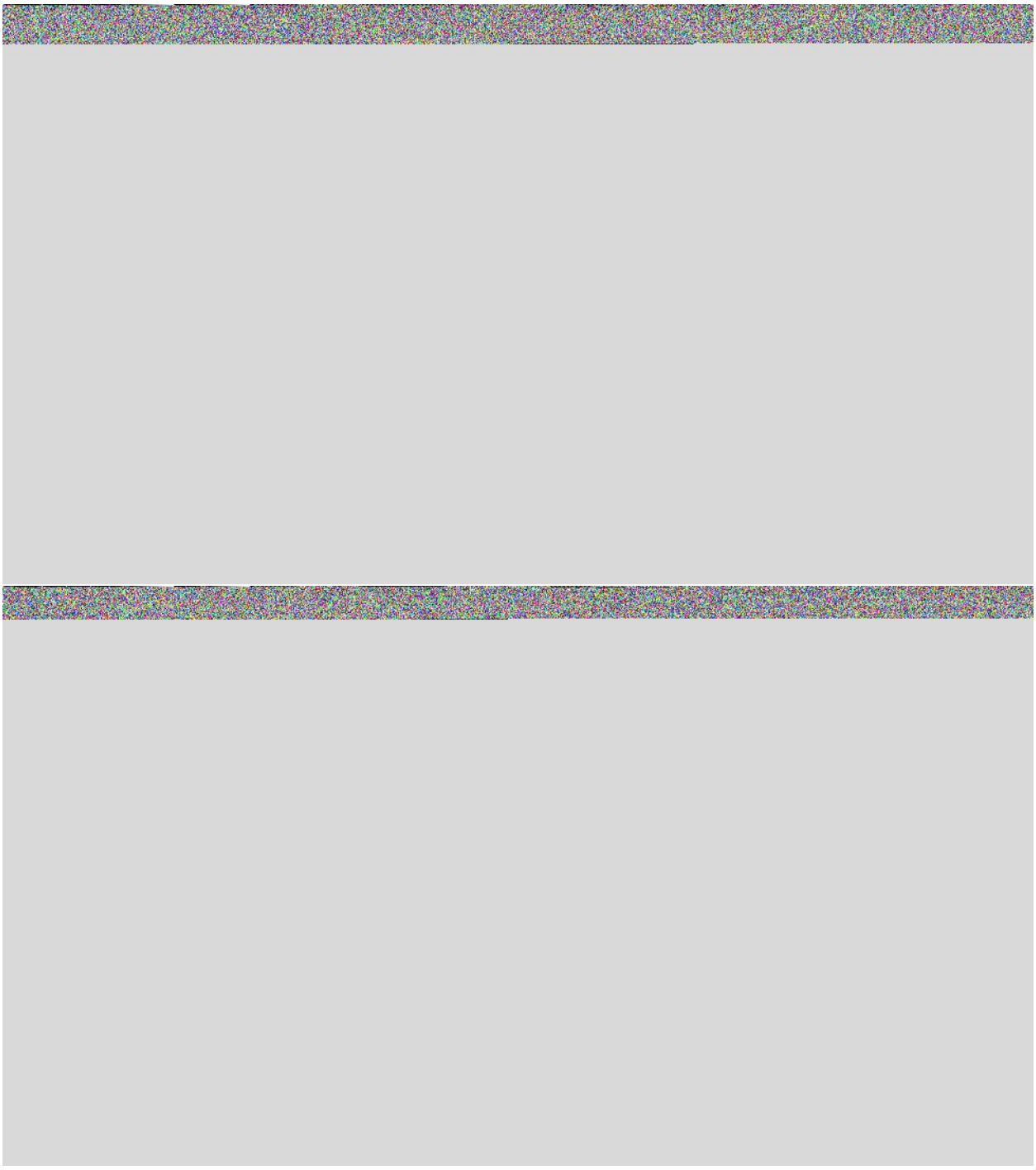


Figure S7: Photographs of the optimized PHEA tanglemer hydrogel (5.0 M HEA, DPtarget =50,000, 0.005 mol% PEGDA) in A) different shapes and B) under various deformation modes.

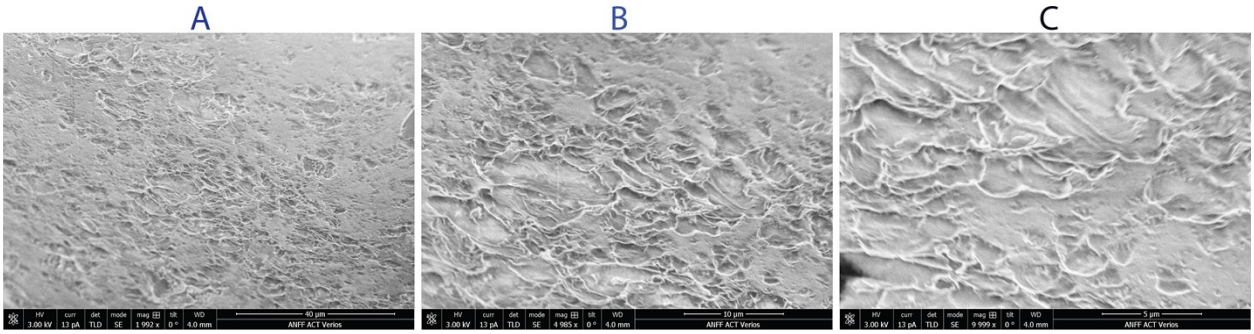


Figure S8. Scanning electron microscopy (SEM) images of the freeze-dried optimized PHEA tanglemer hydrogel (5.0 M HEA, 0.005 mol% PEGDA, DPtarget 50,000) at (A) 2000x and (B) 5000x and (C) 10000x magnification.

Optimized hydrogel (5.0 M HEA, 0.005 mol% PEGDA, DP_{target} 50,000) was freeze-dried for morphological study of the tanglemer network by scanning electron microscopy (SEM) (Figure S8). Molecular-level topological entanglements cannot be directly resolved by standard SEM, but that is not expected as the length scales of entanglement can not be easily imaged.

References

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