Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Tuning Hydrogel Properties with Sequence-Defined, Non-Natural Peptoid Crosslinkers

Logan D. Morton,[1] Alexander Hillsley,[1] Mariah J. Austin,[1] Adrianne M. Rosales[1,*]

[1] McKetta Department of Chemical Engineering, University of Texas at Austin, Austin, TX USA

* Email address: arosales@che.utexas.edu; Tel: +1 512-471-6300

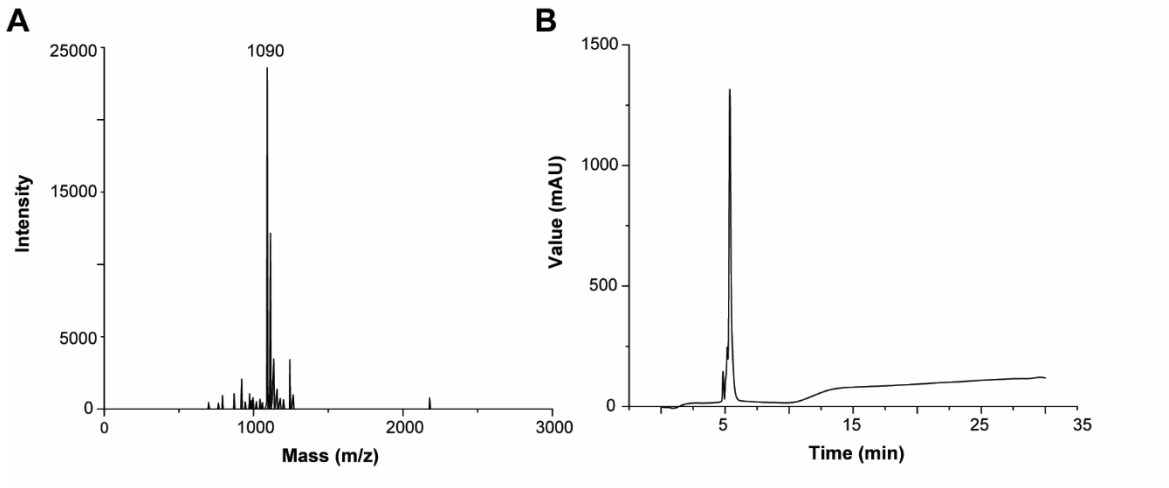

Figure S1: A) MALDI and B) analytical HPLC of sequence **1** confirming >95% purity.

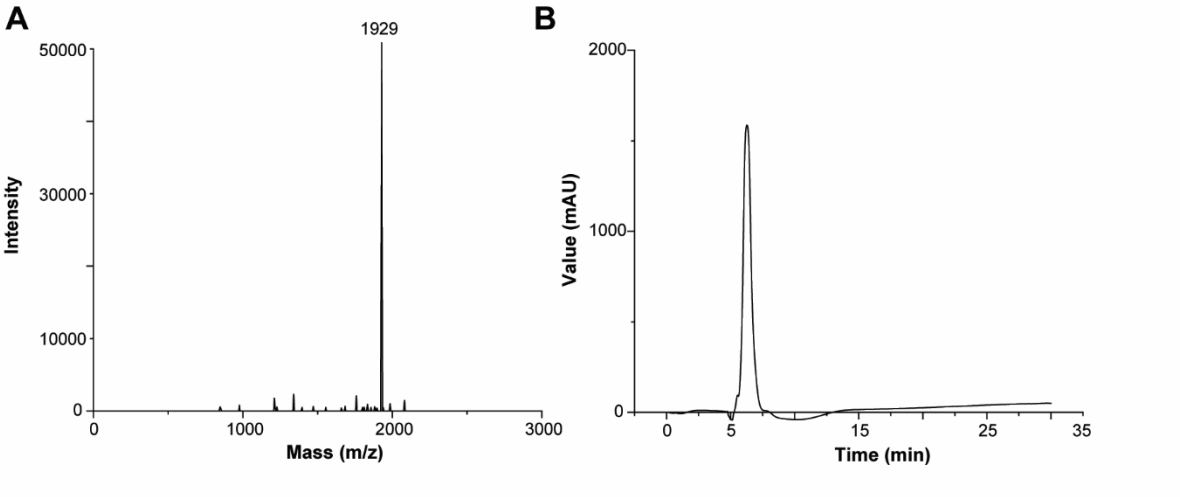

Figure S2: A) MALDI and B) analytical HPLC of sequence **2** confirming >95% purity.

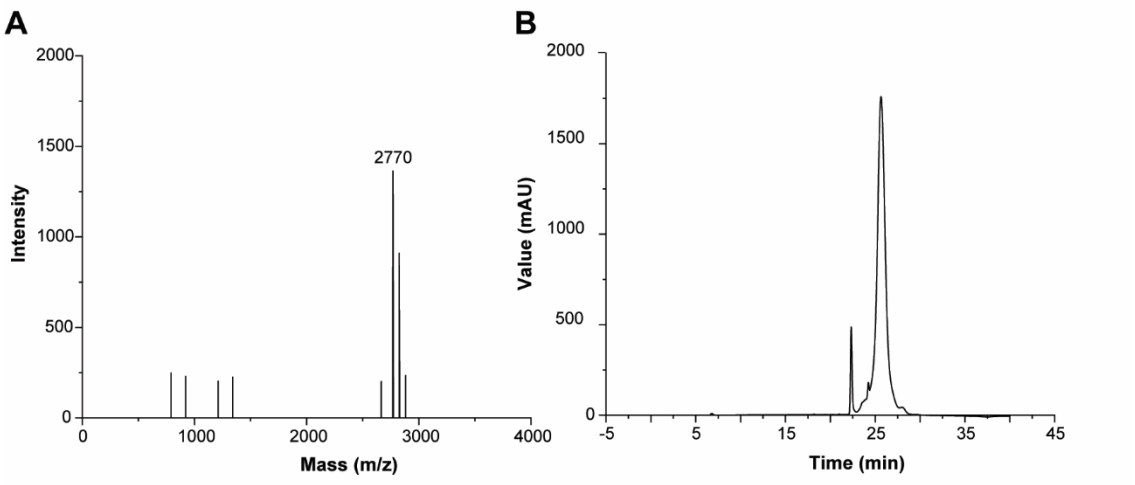

Figure S3: A) MALDI and B) analytical HPLC of sequence **3** confirming >95% purity.

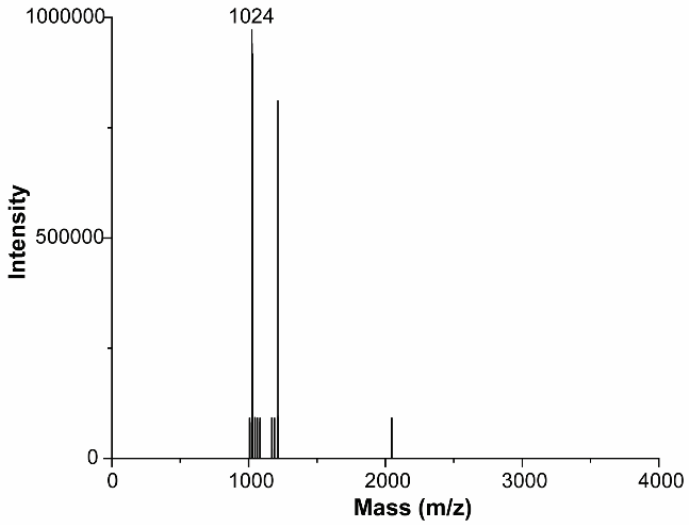

Figure S4: MALDI confirmation of the cell adhesive peptide (GCGYGRGDSPG).

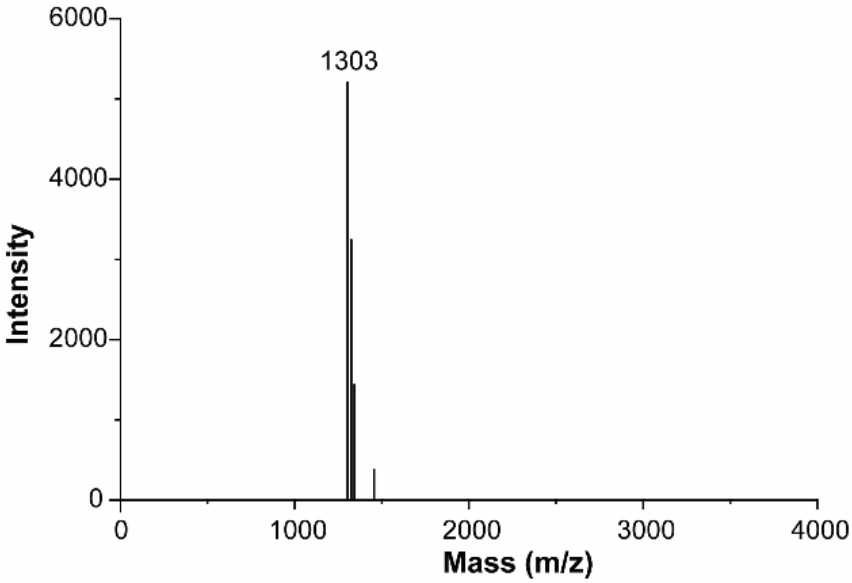

Figure S5: MALDI confirmation of the peptide crosslinker control (KCGGIQQWGPCK).

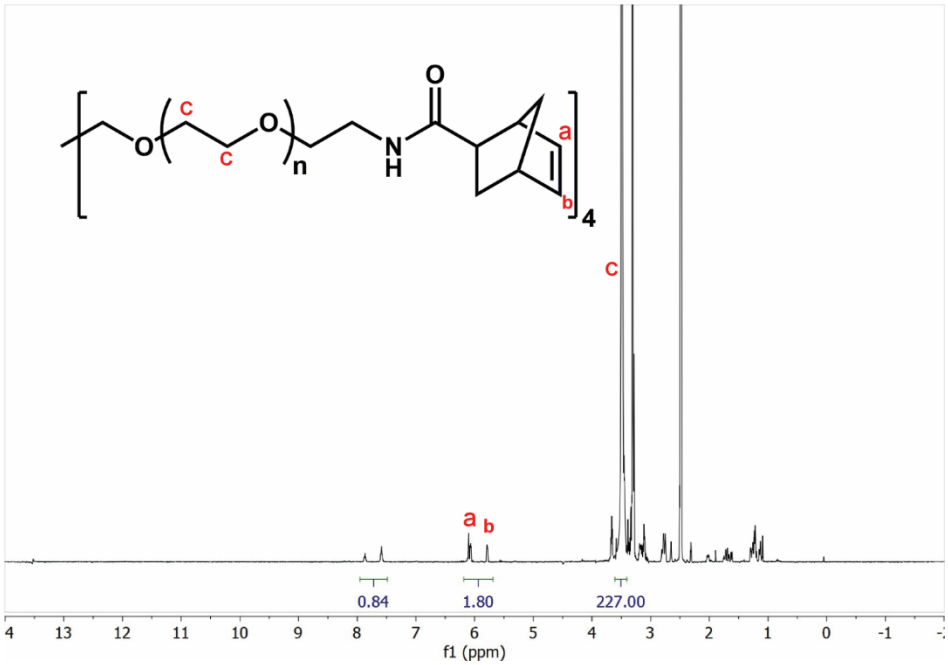

Figure S6: NMR of PEG-norbornene confirming a functionalization of 90%.

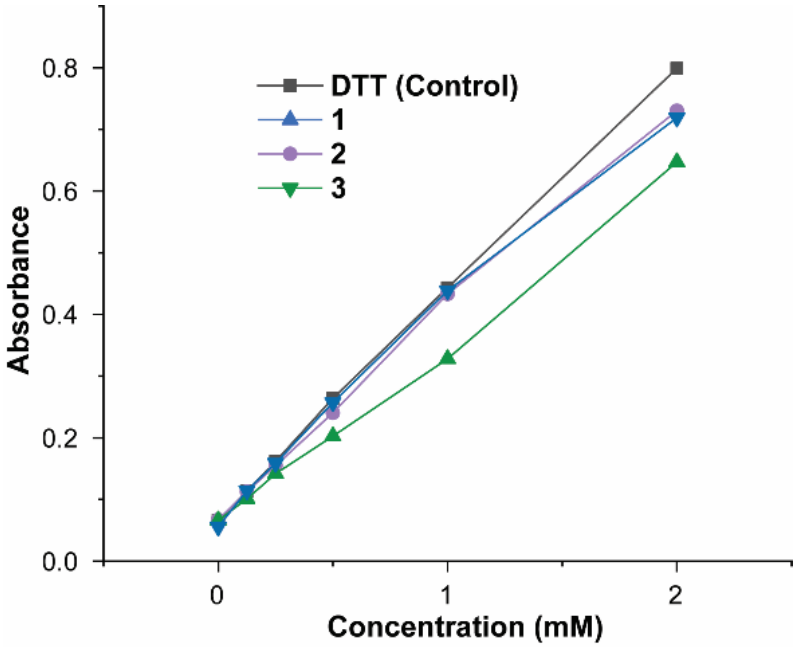

Figure S7: Tests with Ellman's reagent were performed to compare the relative amount of thiol between sequences and confirm viability as a crosslinking agent in hydrogel formation. Dithiothreitol (DTT) was used as a control with two thiols to compare to the peptoid crosslinkers.

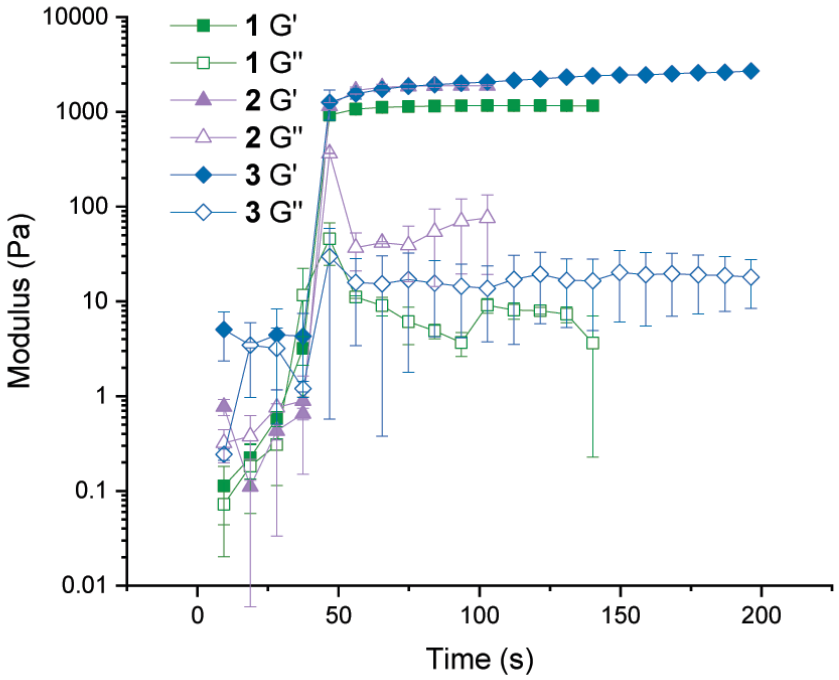

Figure S8: Representative in situ rheology for 5 wt% hydrogels crosslinked with each peptoid sequence showed the large difference between storage and loss moduli for all sequences.

Calculation of ρ_c

The degree of conversion at the gel point may be calculated via Flory-Stockmayer theory for a 0.75:1 thiol:ene hydrogel,[1–3] as shown below:

$$f_a = \frac{\sum f_{ai}^2 N_{ai}}{\sum f_{ai} N_{ai}} = 2$$

$$f_b = \frac{\sum f_{bj}^2 N_{bj}}{\sum f_{bj} N_{bj}} = 3.6\ (with\ 90\%\ functionalization)$$

$$r = \frac{N_a}{N_b} = 0.4167$$

$$\rho_c = \frac{1}{\sqrt{r * (f_a - 1) * (f_b - 1)}} = 0.9608$$

Where N_{ai} is the number of moles of a_i containing f_{ai} functional groups for each a-type molecule (in this case our a type is the thiol-containing molecules). Similarly, N_{bj} is the number of moles of b_j containing f_{bj} functional groups for each b-type molecule (in this case it is our norbornene containing groups). Therefore, f_a and f_b are the weighted average functionalities of reactive molecules a and b. r is the ratio of reactive sites in the system, representing the stoichiometric proportions of reactive sites.

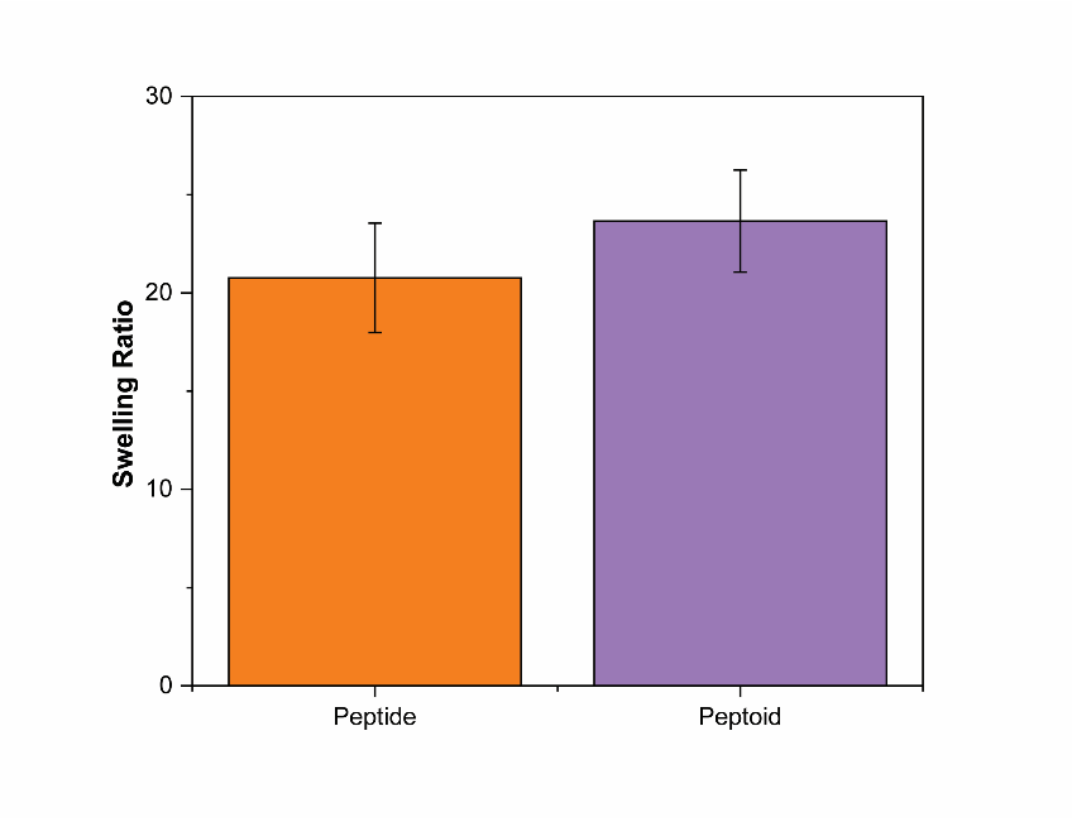

Figure S9: Swelling ratios of peptide and peptoid-crosslinked hydrogels (10 wt% concentration) showed no significant difference.

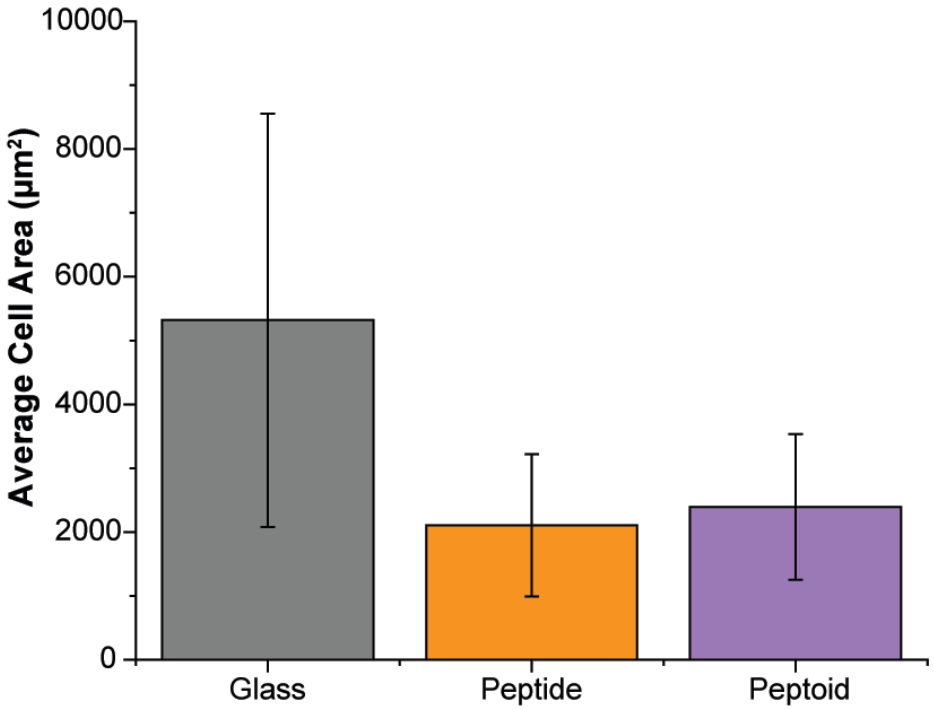

Figure S10: The average cell area on glass was larger than that of the cells on the hydrogels. Glass is much stiffer than either the peptide or peptoid-crosslinked hydrogels investigated.

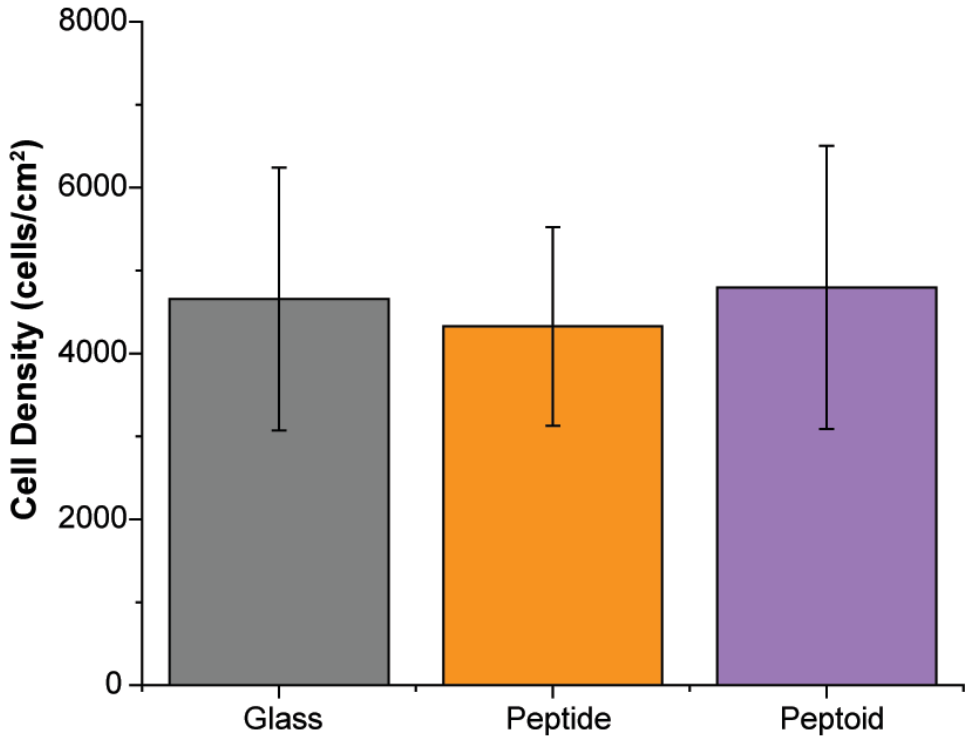

Figure S11: Calculated seeding densities on peptide or peptoid-crosslinked hydrogels compared to the seeding density calculated on glass.

References

1 W. H. Stockmayer, *J. Chem. Phys.*, 1943, **11**, 45–55.

2 P. J. Flory, *J. Am. Chem. Soc.*, 1941, **63**, 3083–3090.

3 A. P. Pizzi, , DOI:10.1201/9780203912225.ch8.