Electronic Supplementary Material (ESI) for Soft Matter.

Tuning the mechanical properties of alginate-peptide Hydrogels

Supporting Information

Calculation of peptide: polymer molecular ratio

It should be noted that the calculation below is based on the average molecular weight provided by the polysaccharide's suppliers.

$1\ mg\ \text{peptide}:100\ mg\ \text{polymer Ratio} \rightarrow$

$$n_{G_6KRGDY} = \frac{1*10^{-3}\,g}{979.98\,\frac{g}{mol}} = 1.02\cdot10^{-6}\,mol$$

$$n_{V_6KRGDY} = \frac{1*10^{-3}\,g}{1232.47\,\frac{g}{mol}} = 8.12\cdot10^{-7}\,mol$$

$$n_{A_6KRGDY} = \frac{1*10^{-3}\,g}{1064.15\,\frac{g}{mol}} = 9.39\cdot10^{-7}\,mol$$

$$n_{Alginate} = \frac{0.1g}{475{,}000\,\frac{g}{mol}} = 2.10\cdot10^{-7}\,mol$$

A_6KRGDY to Alginate molar ratio 1:0.20

V_6KRGDY to Alginate molar ratio 1:0.26

G_6KRGDY to Alginate molar ratio 1:0.22

Elements Analysis

Sample	N%	C%	H%
Alginate	0.13	28.74	4.83
Alginate-A_6KRGDY	2.29	32.79	5.24
Alginate-V_6KRGDY	2.57	32.94	5.33
Alginate-G_6KRGDY	2.18	32.70	5.32

Nitrogen (N) content, measured by Elemental analyzer, was found to be 2.29% in Alginate-A_6KRGDY, 2.57 % in Alginate-V_6KRGDY and 2.18% in Alginate-G_6KRGDY. This result support our previous NMR and FTIR measurements that the peptide is conjugate to the polymer.

SAXS of alginate/peptide hydrogels

The fit of the scattering patterns of alginate+ A_6KRGDY and alginate-V_6KRGDY gels to the broken rod model described by Eq. 1 is presented in Fig.S1. As can be seen the model fails to describe the data mainly in the mid-q regime.

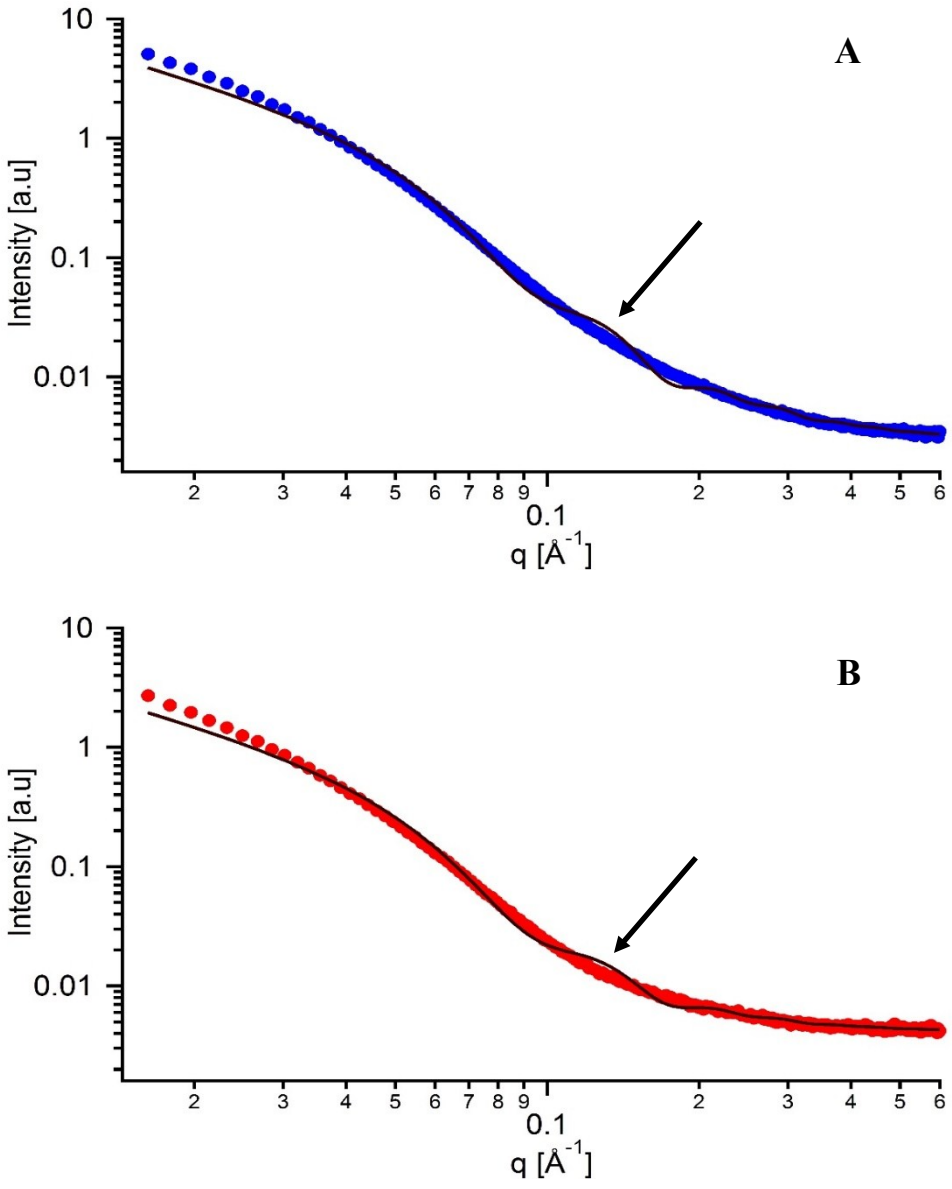

Figure S1 Small angle scattering curves of 1% wt. alginate gels. Broken model fit curves for (A) alginate+ A_6KRGDY and (B) alginate-V_6KRGDY the solid black lines represent fits to the model described by eq. (1)

The scattering from hydrogels may be evaluated as a combination of scattering from two components: 1) a dynamic component, representing the unoccupied crosslinking sites, and 2) a static component, for the occupied crosslinking sites. The scattering from the dynamic fluctuations can be represented by the Ornstein-Zernike [1] equation (the 1st term in Eqn. 2) and the scattering from static inhomogeneities can be represented by the Debye-Buche[2] equation (the 2nd term in Eqn. 2). Taken together, these two equations describe the form factor for gels

$$P(q) = \frac{k_1}{1+(q\xi_L)^2} + \frac{k_2}{\left(1+(q\xi_1)^2\right)^2} \qquad (2)$$

Where, k_1, k_2 are the constants that include the polymer concentration and scattering density. ξ_1 is the static correlation length, which is larger than ξ_L and that corresponds to the correlations within long-lived entanglements or their average size. ξ_L is the dynamic correlation length corresponding to the distance to which the movement of the flexible polymer chains is correlated. It was assumed that there was no interference between the two components in this model.

The best fits and best fit parameters for this models are presented in Fig.S2 and tables S1 and S2. As can be seen while the model describes the data well, the obtained parameters were sensitive to our initial guesses and do not portray an accurate presentation of the gels' structure.

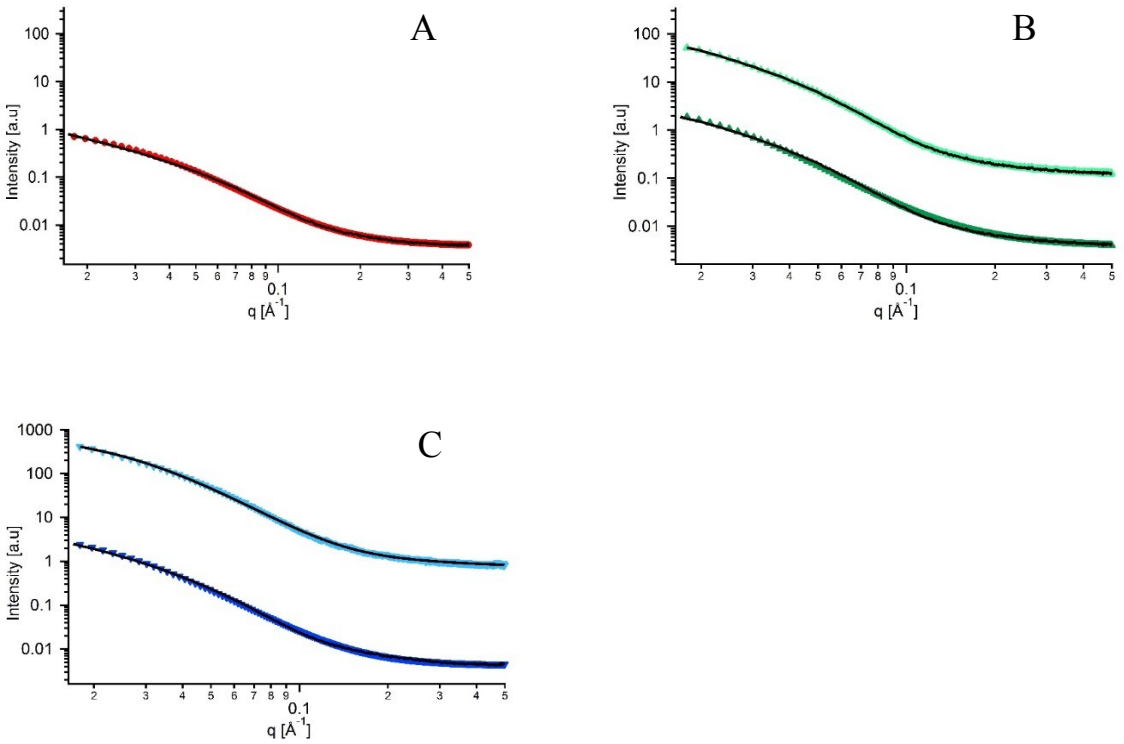

Figure S2: Model fit curves for alginate (A), alginate/ A_6KRGDY (B), alginate/ V_6KRGDY (C). The solid black lines represent fits to the model described by eq. (2).

Table S1: Best fit parameters for the model described by equation 2 for alginate/peptides

Polymer	ξ_L **[Å]**	**[Å]**$^{\xi_1}$
Alginate	11±1	24±1
Alginate+A_6KRGDY	11±1	36±2
Alginate+V_6KRGDY	15±1	38±2
Alginate+G_6KRGDY	14±1	29±2
Alginate-A_6KRGDY	12±1	37±2
Alginate-V_6KRGDY	13±1	38±2
Alginate-G_6KRGDY	13±1	28±2

Table S2: Best fit parameters for the model described by equation 2 for alginate/peptides with constant ξ_L

Polymer	**ξ_L [Å]**	**[Å]$^{\xi_1}$**
Alginate	11±1	25±1
Alginate+A_6KRGDY	11±1	38±2
Alginate+V_6KRGDY	11±1	37±2
Alginate+G_6KRGDY	11±1	25±1
Alginate-A_6KRGDY	11±1	36±2
Alginate-V_6KRGDY	11±1	40±2
Alginate-G_6KRGDY	11±1	23±3

Unlike the solution characteristics, the obtained fitted model parameters are roughly the same for the covalent and the self-assembly systems.

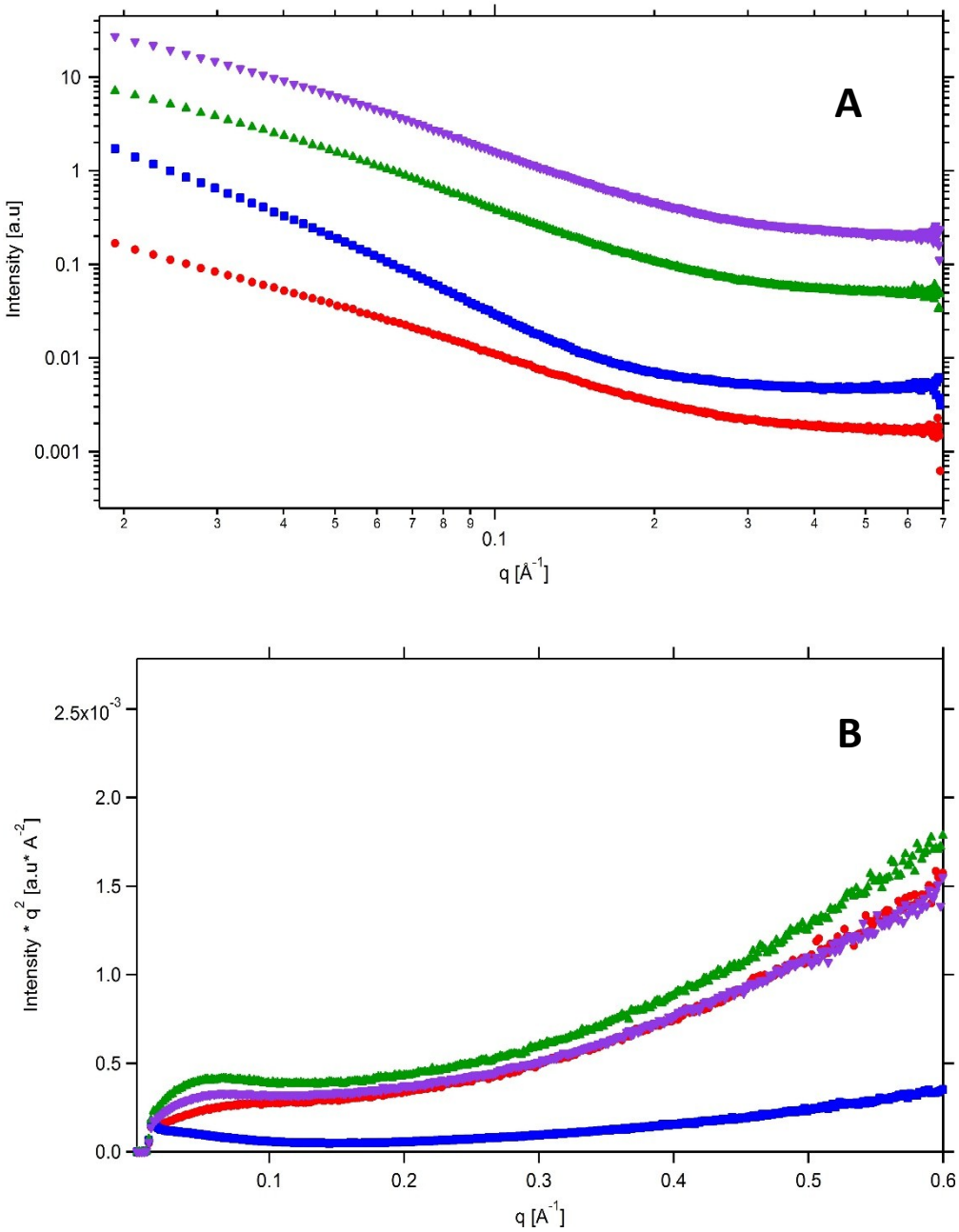

Figure S3. A. Small angle scattering curves of 1% wt. alginate gels in PBS. Alginate (●), alginate-A_6KRGDY (■), alginate-V_6KRGDY (▲) and alginate-G_6KRGDY (▼) formed by covalent binding. B. Kratky plots for alginate gels.

.1 Daoud, M., et al., *Solutions of flexible polymers. Neutron experiments and interpretation.* Macromolecules, 1975. **8**(6): p. 804-818.
.2 Debye, P. and A. Bueche, *Scattering by an inhomogeneous solid.* Journal of Applied Physics, 1949. **20**(6): p. 518-525.