Electronic Supplementary Material (ESI) for Soft Matter

Analysis of the Mesh size in a Supramolecular Hydrogel by PFG-NMR Spectroscopy

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Supporting Information

Probing Specific Interactions between Probe and Guest

The CH_2 resonances of the dextran are of the same intensity and broadness in gels and micellar solutions as in D_2O (Figure S1). Similarly, the glucose resonances are sharp and display a complex coupling pattern in the gels. Therefore, these probes do not interact strongly with the network. In contrast ,when poly(ethylene glycol)s (PEGs) of molecular masses 6 KDa and 400 KDa were incorporated into gels, the resonances became noticeably broader (Figure S2).

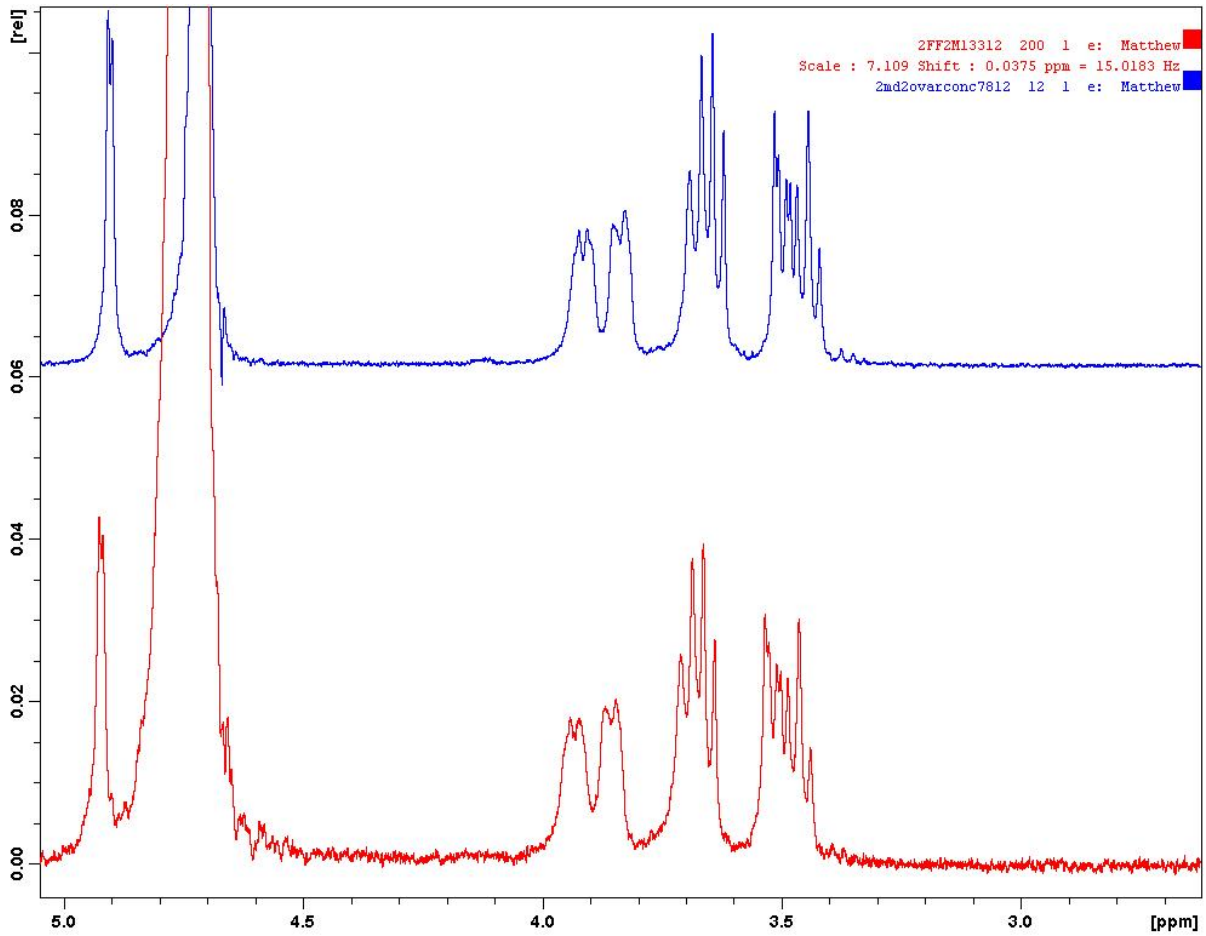

Figure S1. Dextran CH_2 resonances in D_2O (top) and gel (bottom). Resonances are of same broadness and intensity. HOD and dextran OH resonances are on the far left.

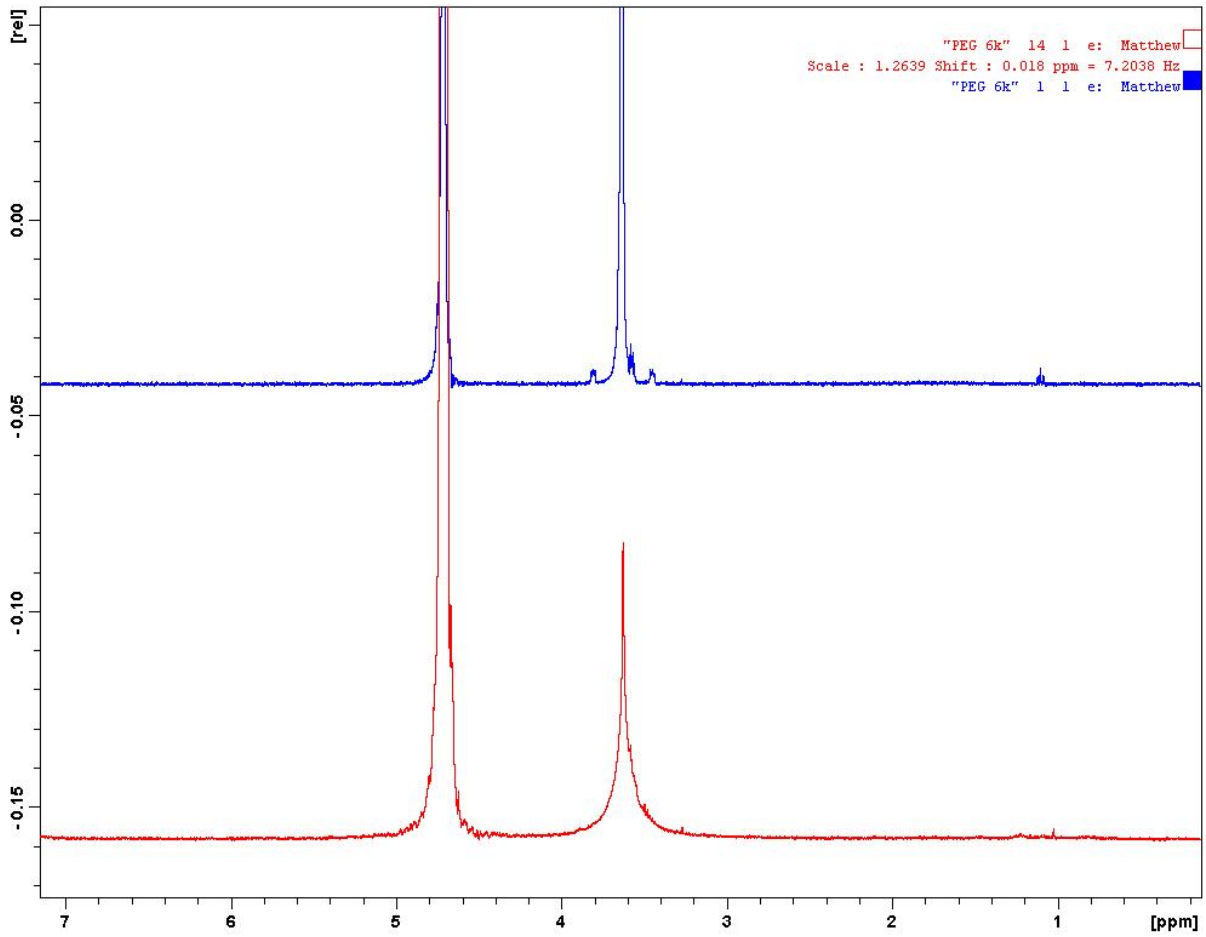

Figure S2. PEG 6 kDa (3.6 ppm) in D_2O (top) and gel (bottom). The resonance in the gel is clearly broader indicating specific interactions with either the gel.

Justification of the use of the Mean Inverse Diffusion Coefficient

The mean inverse diffusion coefficient is defined as:

$$\langle \frac{1}{D} \rangle = \sum \frac{f_i}{D_i}$$

where f_i is the fractional intensity of species possessing diffusion coefficient D_i. Similarly, the mean diffusion coefficient is defined as:

$$< D >= \sum f_i D_i$$

The mean inverse diffusion coefficient is weighted to slower (larger) species whereas the mean is weighted to faster species. Thus the restriction suffered by the larger molecules in a polydisperse sample is expected to be under-represented by the mean. This is shown by the diffusion quotients in the gel, but not so much by those in the micellar solution (Table S1):

Dextran M_r /KDa	$<1/D>_{D2O}/<1/D>_{gel}$	$<D>_{gel}/<D>_{D2O}$	$<1/D>_{D2O}/<1/D>_{micelles}$	$<D>_{micelles}/<D>_{D2O}$
6	0.98±0.03	1.1±0.1	0.96±0.05	0.98±0.12
40	0.89±0.03	0.89±0.03	0.93±0.03	0.91±0.06
70	0.86±0.03	0.87±0.03	0.87±0.03	0.87±0.04
100	0.83±0.09	0.93±0.1	0.86±0.09	0.89±0.09
500	0.77±0.05	0.92±0.1	0.74±0.03	0.77±0.06
670	0.67±0.07	0.69±0.03	0.77±0.08	0.75±0.06

Table S1. Diffusion quotients in gel and micellar solutions using the mean and inverse mean diffusion coefficients.

Clearly the uncertainties associated with the diffusion quotient will be high as they are derived from two experimental measurements; however the downward trend shown by those derived from the inverse mean diffusion coefficients is more significant. The 670 kDa has a polydispersity index of just 2.01 and is also the largest dextran so that all components may be restricted significantly. In addition, diffusion coefficients are related to the number of protons rather than the number of polymers. As such, the similarity of the two diffusion quotients in the gel for this dextran is not particularly disturbing and the use of <1/D> as the metric of diffusivity is justified based on the results from the other dextrans.

Rheological Data for Gels with and without dextran

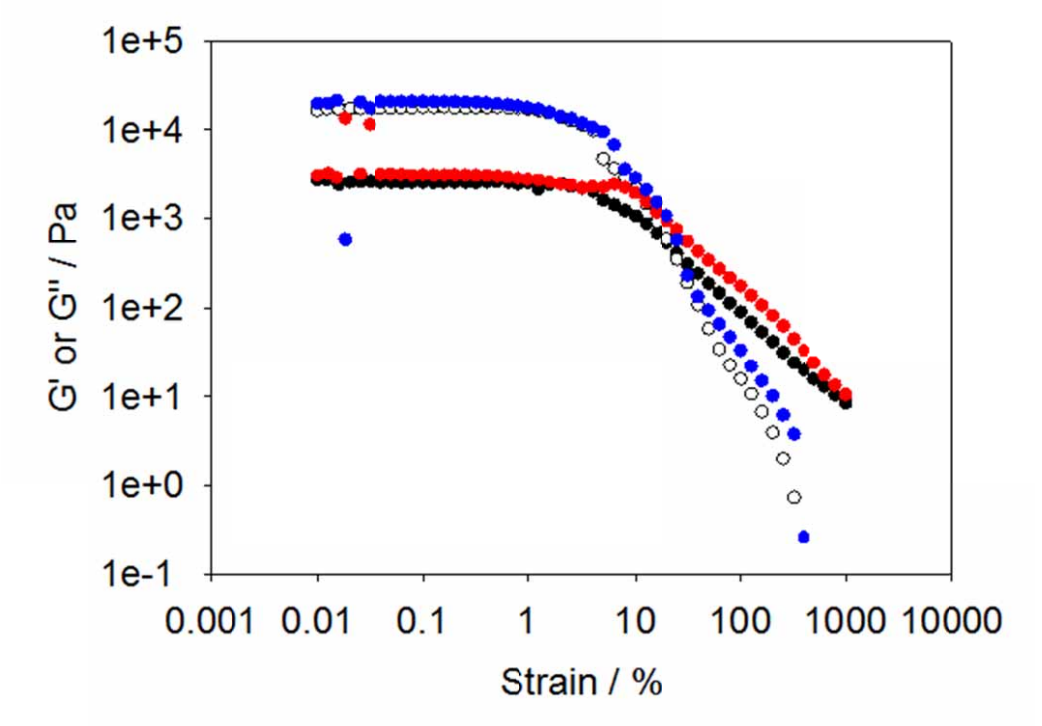

Figure S3. Strain sweeps for gels formed from 2FF. Data is shown in the absence of dextran (G′, open circles, G″, closed circles) and in the presence of 1 mg/mL dextran 2000 kDa (G′, blue circles and G″, red circles). The data for gels with and without dextran overlay well inplying that the presence of the dextran does not have an impact on the gel structure.

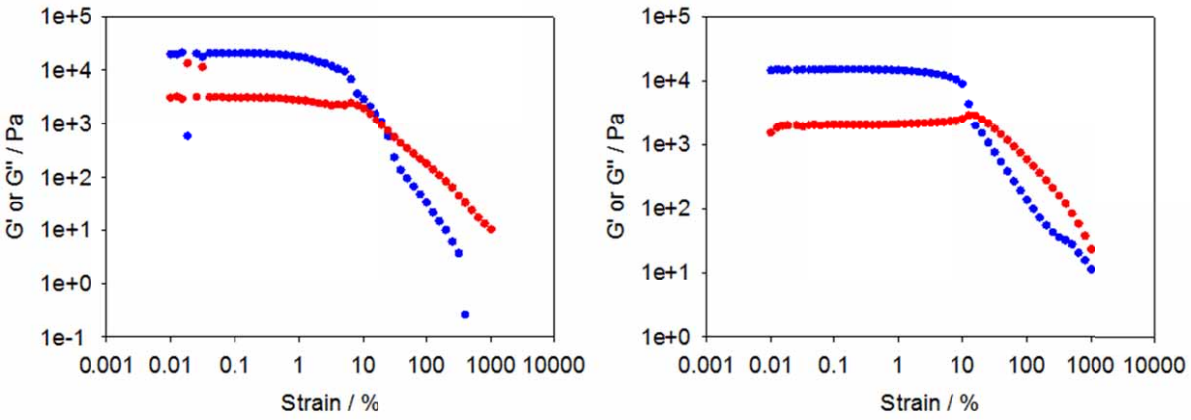

Figure S4. Strain sweeps for gels formed from 2FF at 0.55 wt% (left) and 1.1 wt% (right). For both data sets, G′, blue circles and G″, red circles.