

Heterogeneous structure and its role in the properties of poly(ethylene glycol) hydrogels.

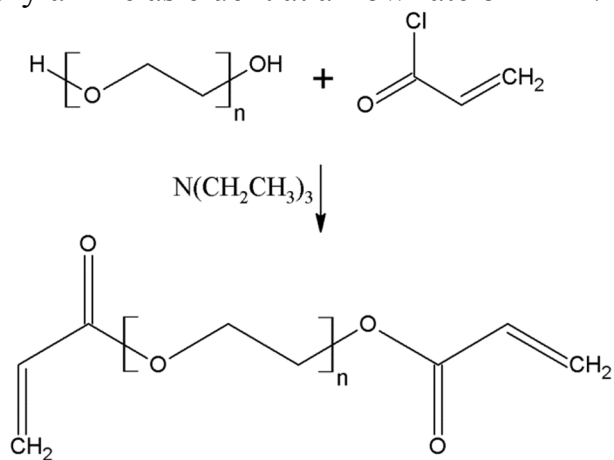
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Supplementary Information

S1. Polymer synthesis and characterization

Polymer Characterization. ^1H NMR spectra were measured on a Varian 600 MHz spectrometer using the solvent signal as internal standard. Gel permeation chromatography (GPC) was performed on a Waters 2690 separation module equipped with Waters 2414 refractive index and 2996 photodiode array detectors using CHCl_3 containing 0.25% triethylamine as eluent at a flow rate of 1 mL/min



Scheme S1. Synthetic route to PEGDA.

Table S1. Molecular parameters of the PEGDA polymers.

Sample	M _w (PEG)	Yield, %	M _n (GPC)	M _w (GPC)	PDI
PEG2kDA	2050	91.51	1587	1644	1.04
PEG6kDA	6000	76.16	4257	4528	1.06
PEG10kDA	10,000	80.00	8070	8891	1.10
PEG20kDA	20,000	81.65	15424	17402	1.13
PEG35kDA	35000	88.89	26648	46755	1.75
PEG100kDA	10,0000	49.09	28051	79482	2.8

S3. Hydrogel formation and linear rheology

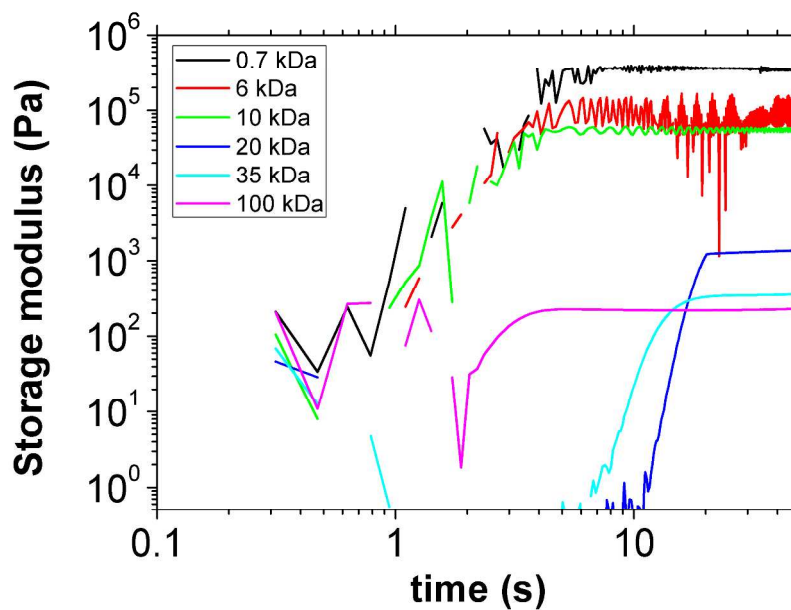


Figure S1. Storage modulus G' as a function of the UV exposure time.

The frequency dependence of the storage modulus (G') and loss modulus (G'') for fully cross-linked PEGDA hydrogels of varying molecular weight at the same polymer volume fraction is depicted in Figure 4. The hydrogels exhibit a typical gel like viscoelastic behavior with a frequency independent elastic modulus higher than the viscous modulus. At a constant polymer volume fraction, the elastic modulus decreases with the macromonomer molecular weight whereas there is not so much change on the viscous modulus.

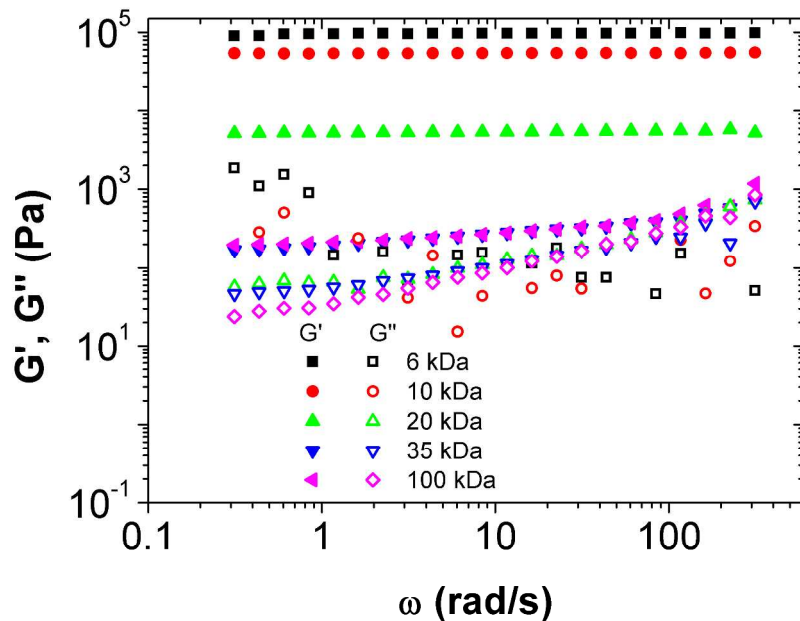


Figure S2. Storage G' and loss G'' moduli of hydrogels formed with PEGDAs with volume fraction $\phi=0.2$ as a function of the PEGDA molecular weight as function of the angular frequency ω .

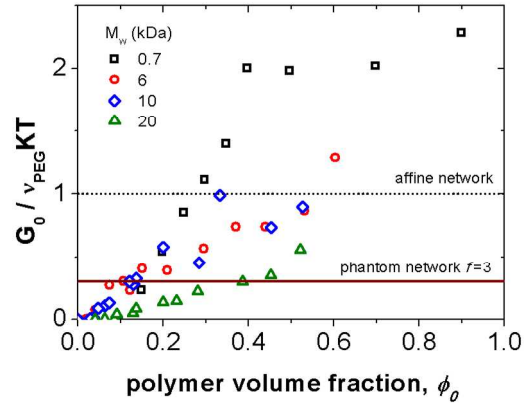


Figure S3. Plateau Modulus G_0 reduced to the number density of PEG chains as a function of the polymer volume fraction. The dotted line is the reduced modulus of an affine network and the solid line for a phantom network with cross-linking functionality $f=3$.

S4. SANS

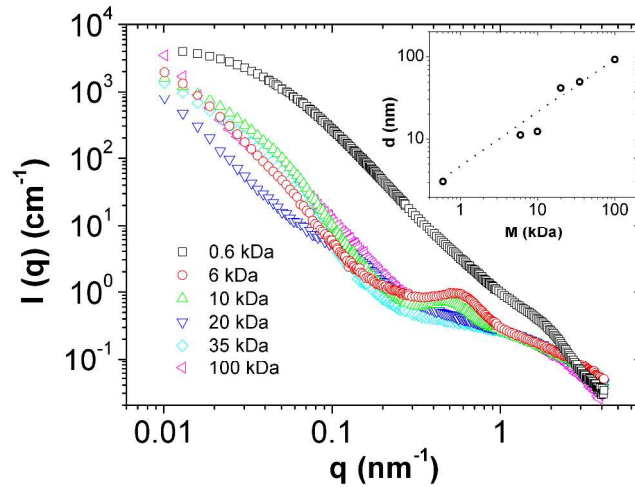


Figure S4. SANS spectra of hydrogels formed with PEGDAs 0.7, 6, 10, 20, 35 and 100 KDa with volume fraction $\phi=0.2$ Inset: distance between cross-links calculated from the peak position as $d = 2\pi/q_{max}$.

Hard Sphere Structure Factor

The structure factor for the hard sphere model according to the Percus-Yevick closure depends on the magnitude q of the wave vector, the hard sphere radius R_{HS} , and the hard sphere volume fraction ϕ_{HS} , according to:

$$S_{HS}(q, R_{HS}, \phi_{HS}) = \frac{1}{1 + 24\phi_{HS} \frac{G(\phi_{HS}, qR_{HS})}{qR_{HS}}} \quad S1.1$$

$$G(\phi_{HS}, qR_{HS}) = \alpha \frac{\sin \sigma - A \cos \sigma}{\sigma^2} + \beta \frac{2\sigma \sin \sigma + (2 - \sigma^2) \cos \sigma - 2}{A\sigma^3} + \gamma \frac{-\sigma^4 \cos \sigma + 4[(3\sigma^2 - 6) \cos \sigma + (\sigma^3 - 6\sigma) \sin \sigma + 6]}{\sigma^5} \quad S1.2$$

$$\sigma = 2qR_{HS} \quad S1.3$$

$$\alpha = \frac{(1 + 2\phi_{HS})^2}{(1 - \phi_{HS})^4} \quad S1.4$$

$$\beta = -6\phi_{HS} \frac{(1 + \phi_{HS}/2)^2}{(1 - \phi_{HS})^4} \quad S1.5$$

$$\gamma = \phi_{HS} \alpha / 2 \quad S1.6$$