Electronic Supplementary Information (ESI)

Structural Considerations for Physical Hydrogels Based on Polymer-Nanoparticle Interactions

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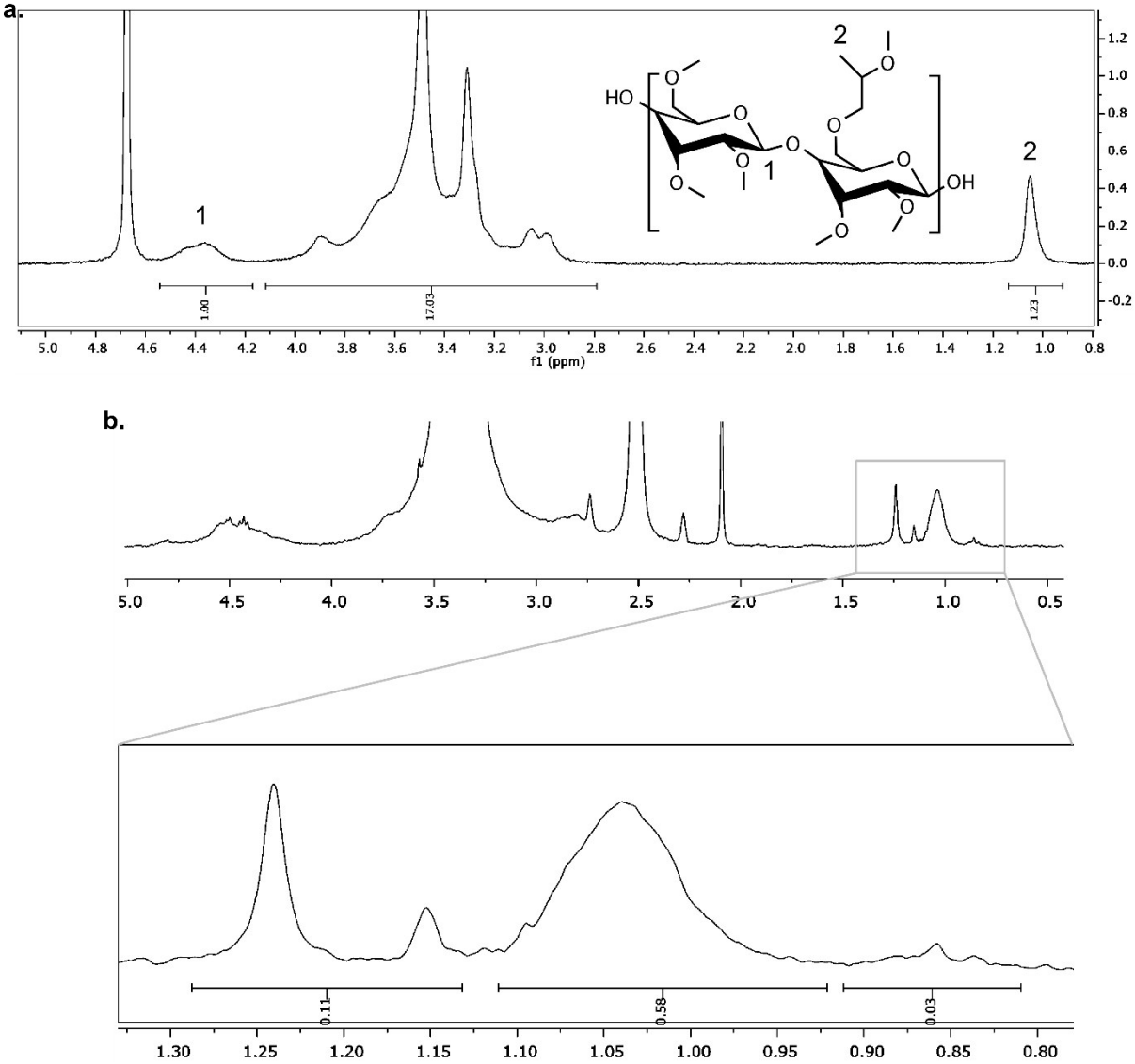

Fig. S1 (a) ^{1}H-NMR(D_2O) of HPMC: Broad singlet at δ 4.4 from proton on (1). Broad singlet at δ 1.05 show terminal CH_3 of 2-hydroxypropyl modification (2). These peaks were used to quantify 2-hydroxypropyl modification amount. **(b)** Quantification of the extent of modification on residual hydroxyls with isocyanates was done by comparison of (2) in DMSO-d6 spectra of hexyl and dodecyl modified HPMC. A ~2 mol% modification was achieved for both HPMC-C_6 and HPMC-C_{12}.

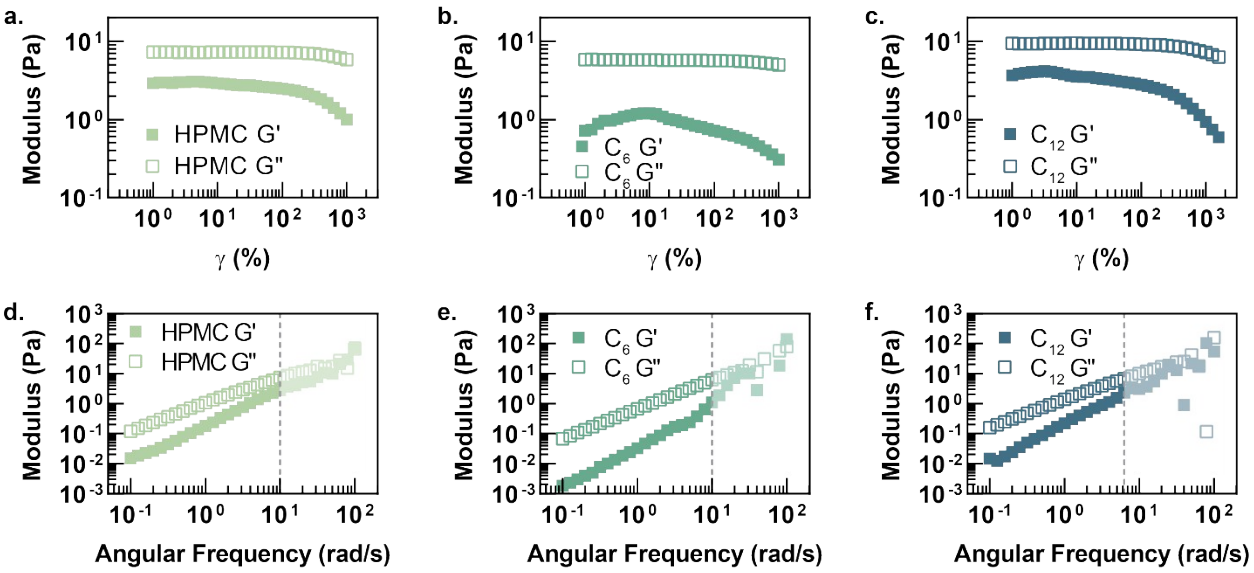

Fig. S2 Amplitude sweeps and frequency sweeps of hydrophobically-modified HPMC polymer components at 2 wt%. Loss moduli are greater than storage moduli for all samples, indicating a viscous response to stress and overall "liquid-like" materials properties.

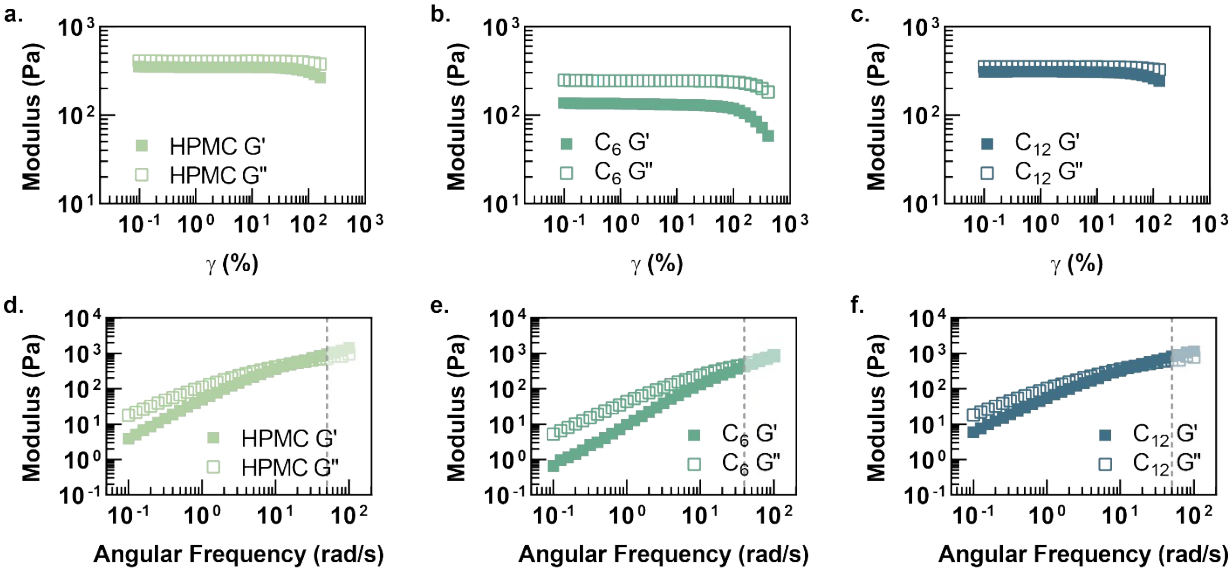

Fig. S3 Amplitude sweeps and frequency sweeps of hydrophobically-modified HPMC polymer components at 6 wt%. Loss moduli are greater than storage moduli for all samples, indicating a viscous response to stress and overall "liquid-like" materials properties. Even at 6 wt% polymer these materials' G' and G" exhibit high frequency dependence and a tan(δ) >1 for the majority of the range tested, indicating that particles are necessary for robust (tan(δ) <1, low frequency dependent moduli) network formation.

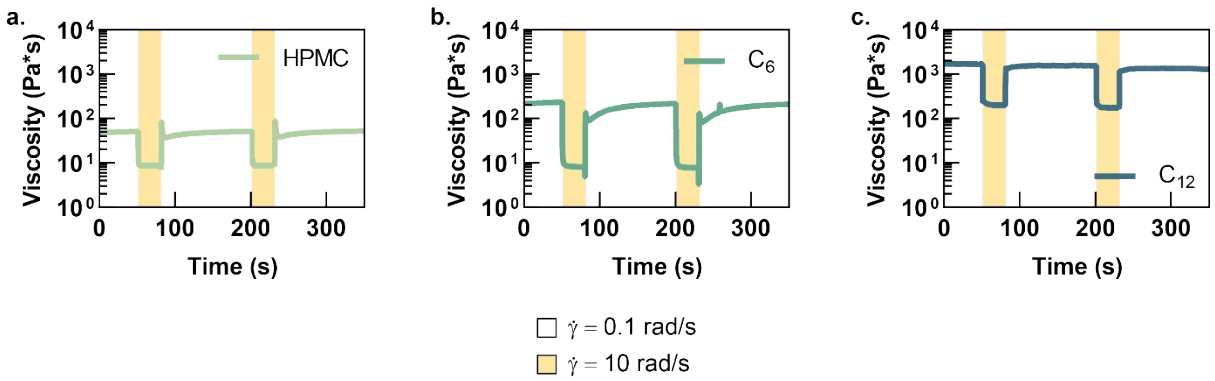

Fig. S4 Step shear experiments of PNP hydrogels made with (a) HPMC, (b) HPMC-C_6, and (c) HPMC-C_{12}. HPMC and C_6 gels exhibit some stress overshoot artifacts. All gels recover their viscosities at low shear rates, with C_{12} gels recovering the structure almost immediately. These properties indicate that the structural and mechanical differences in C_{12} gels result in faster recovery times after shear, which may be critical in certain drug delivery applications.

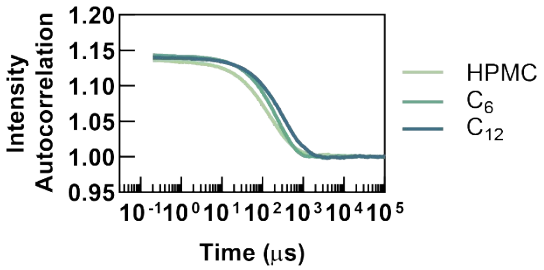

Fig. S5 Intensity autocorrelation plotted versus time. Data shown are representative curves taken for each group and exhibit single phase decays for all groups. Each curve shown represents the average data from 10 scans of the same well.

Table S1. Dynamic light scattering data on the hydrodynamic diameter and the corresponding calculated corona heights.

	PSNP	HPMC (no modification)	C_6	C_{12}
Hydrodynamic Diameter (nm) [mean (SD)]	57.2 (1.5)	87.5 (1.2)	91.8 (3.7)	135.5 (8.3)
Corona Height (nm) [mean (SD)] $0.5*(Mean_{HPMCx} - Mean_{HPMC})$	0.0 (1.0)	15.2 (0.9)	17.3 (2.0)	39.2 (4.2)