Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information

A comparison of the network structure and inner dynamics of homogeneously and heterogeneously crosslinked PNIPAM microgels with high crosslinker content

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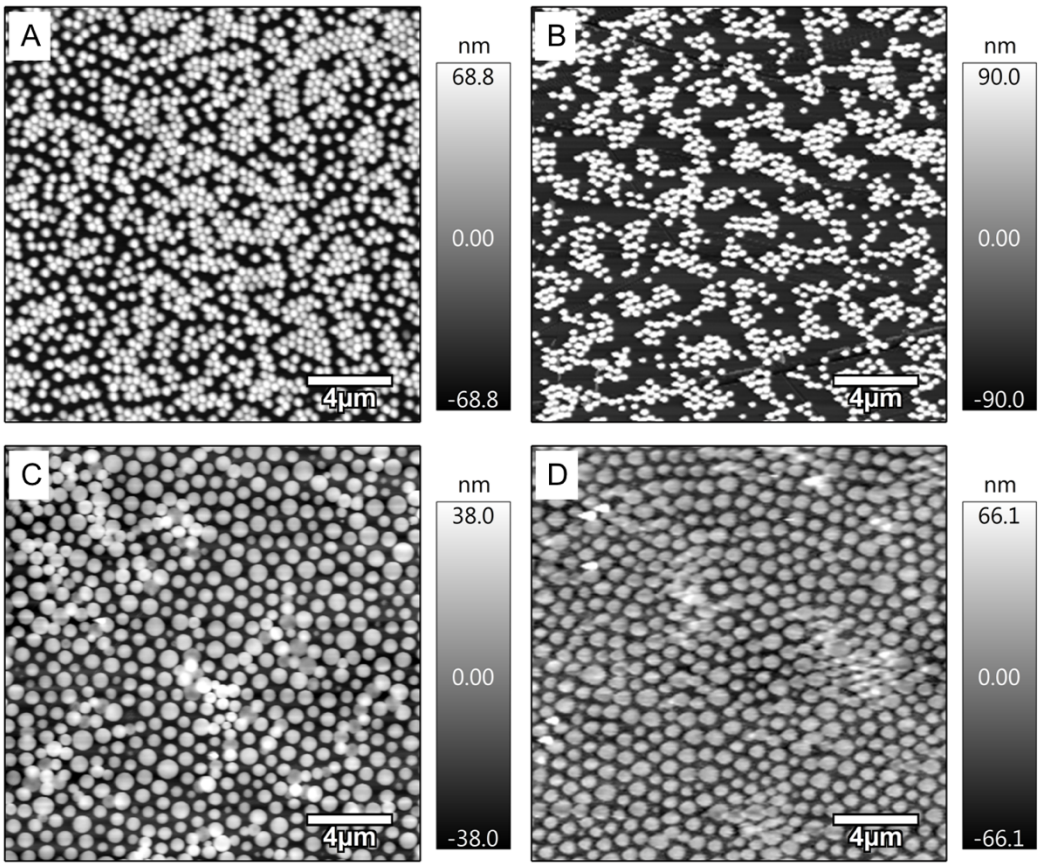

Figure S. 1: AFM images of A) HetMG10 under ambient conditions, B) HetMG10 swollen in H_2O, C) HomMG10 under ambient conditions and D) HomMG10 swollen in H_2O.

Table S. 1: Dry and swollen widths and heights of HetMG10 and HomMG10. Cross sections of 5 individual particles were analyzed and the standard deviation was calculated.

Microgel	$Width_{dry}$ (nm)	$Height_{dry}$ (nm)	$Width_{H2O}$ (nm)	$Height_{H2O}$ (nm)
HetMG10	626 ± 57	134 ± 8	650 ± 45	237 ± 15
HomMG10	885 ± 134	48 ± 1	1020 ± 138	106 ± 12

Images under ambient conditions were scanned in tapping mode with AC160TS cantilevers (Olympus). Images in H_2O were scanned with TR800PSA cantilevers (Olympus).

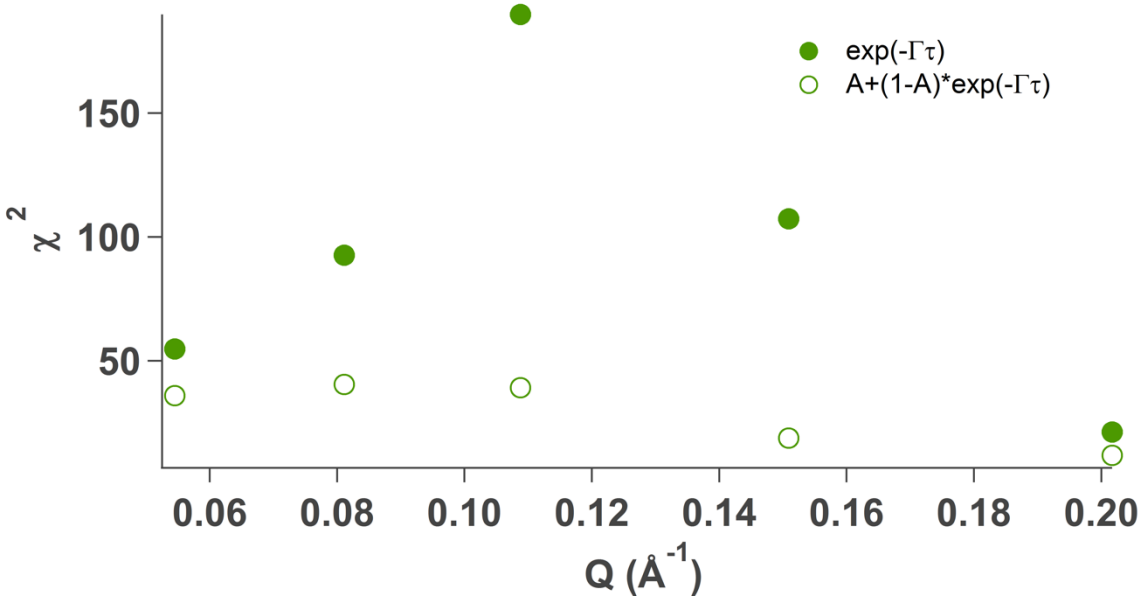

Figure S. 2: χ^2 for fits of the normalized intermediate scattering functions of HetMG10 with and without the elastic contribution.

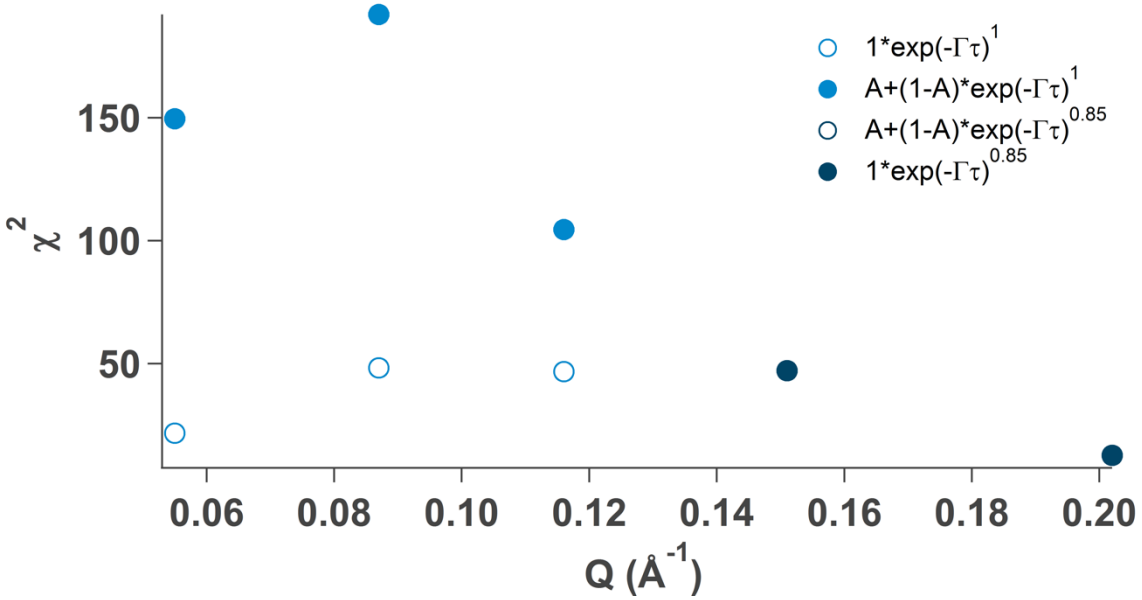

Figure S. 3: χ^2 for fits of the normalized intermediate scattering functions of HomMG10 with and without the elastic contribution. Q = 0.15 Å^{-1} and Q = 0.20 Å^{-1} were fitted with a stretched exponential with exponent β = 0.85.

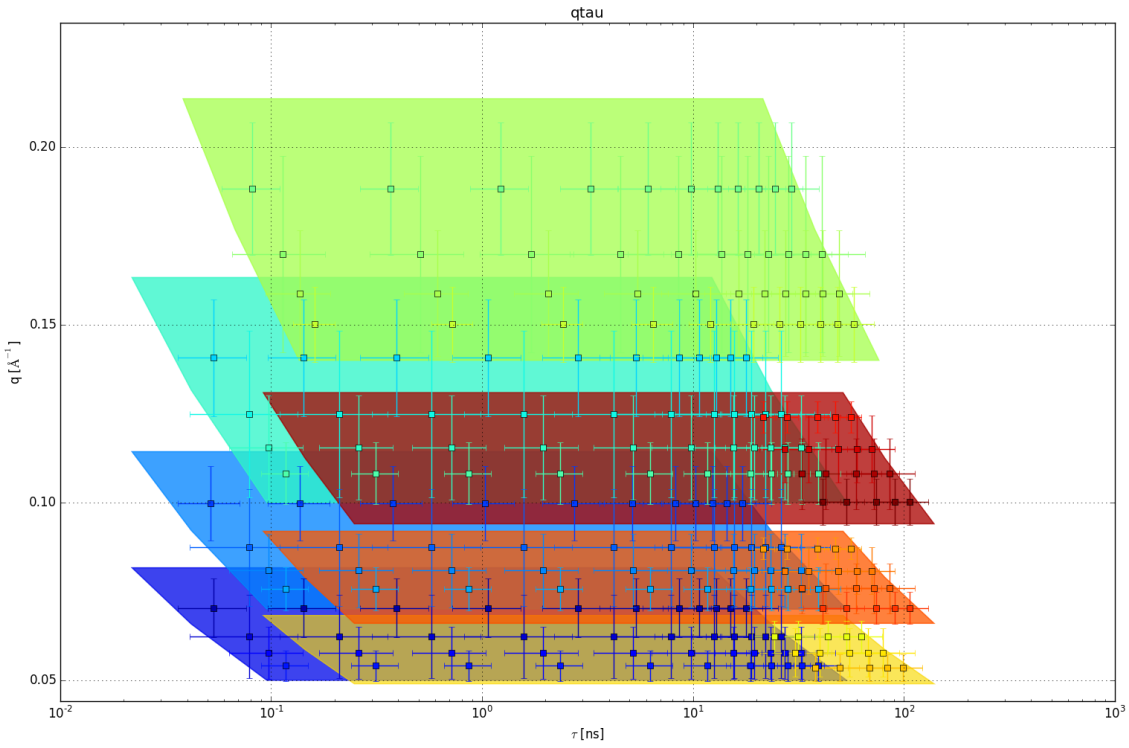

Figure S.4: Q-τ map for the measurements at the SNS-NSE at the spallation neutron source in Oak Ridge, TN.

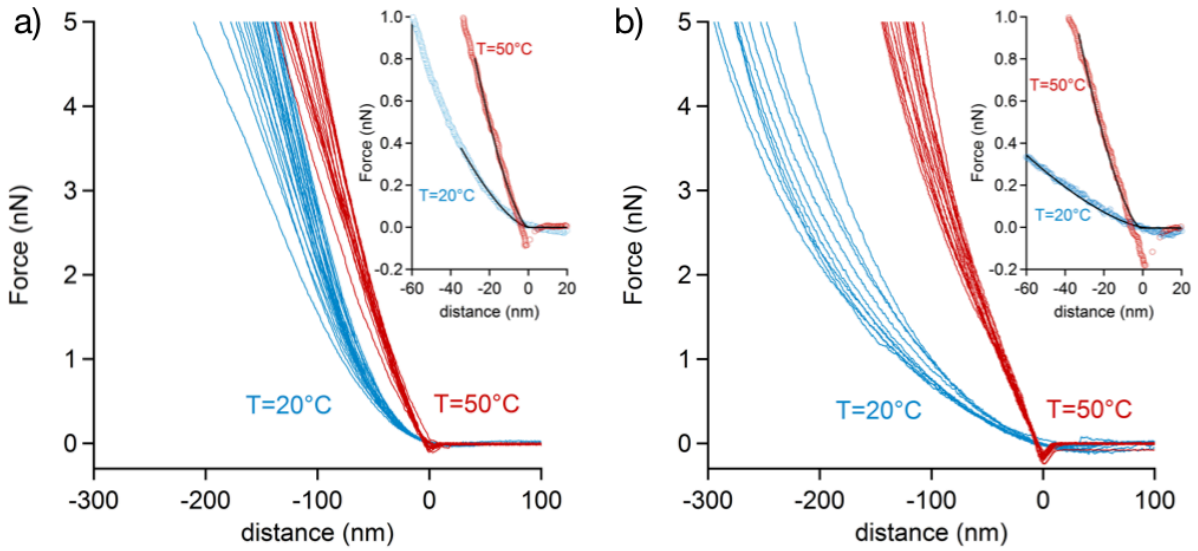

Figure S. 5: AFM force-distance curves for a) $MG_{10}P$ and b) $MG_{10}F$ at T = 20°C (blue) and T = 50°C (red). Insets show an exemplary fit according to the Hertz model (equation 1 in main text) at T = 20°C (blue) and T = 50°C (red). The positive indentation depth values were transferred into negative tip-sample-distances.

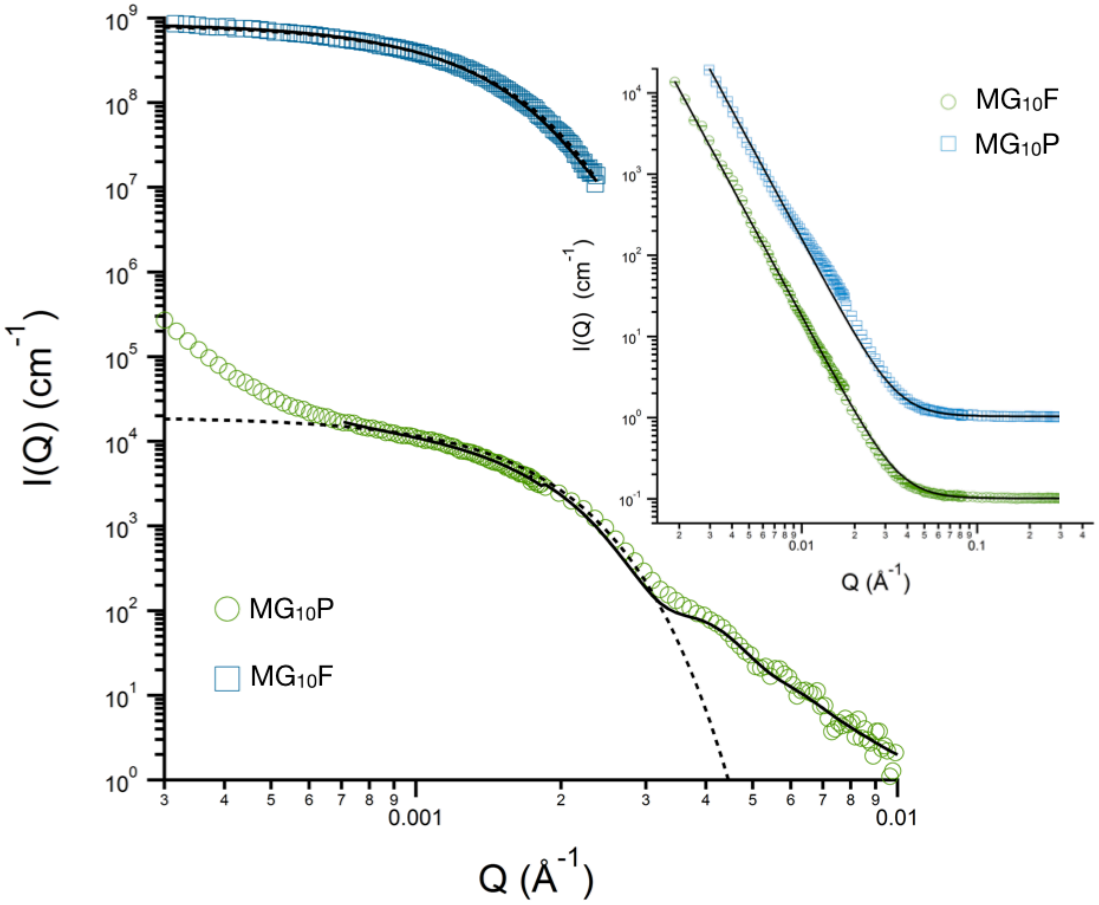

Figure S. 6: SANS curves of MG10P and MG10F measured at 50°C in a wide Q range. A Guinier analysis of the data yields the radius of gyration Rg at 50°C.The dashed line in the figure are the Guinier fits to the data. Solid lines are fits to the fuzzy sphere model. Results are given in Table 2 and 3 in section 4.4 of the paper. The inset shows the medium and high Q-range. For both samples, the intensity decreases in this range according to the Porod law, I ∝Q-4 until the incoherent background level is reached.

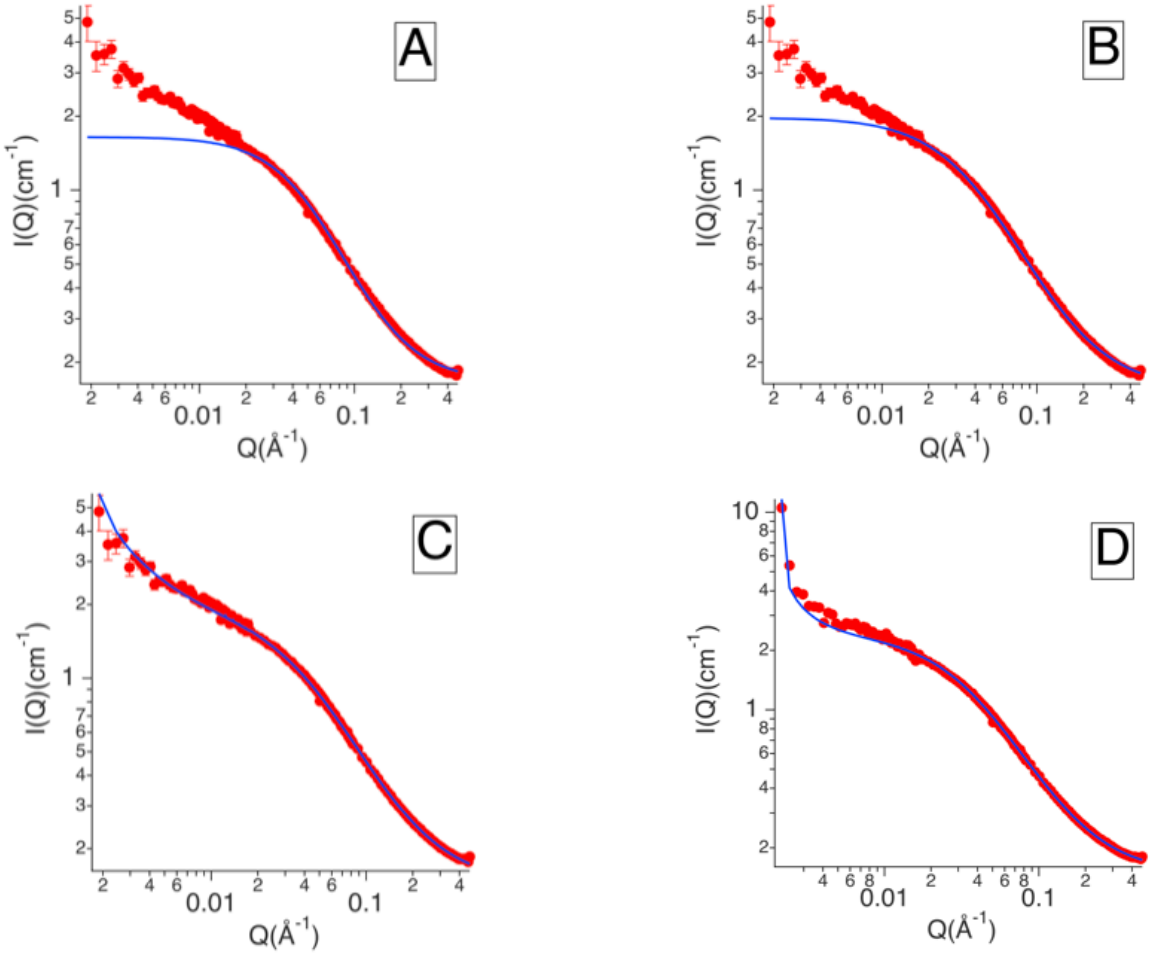

Figure S. 7: A: Ornstein Zernike fit with m=2, no clustering term
B: modified fit equation with m=1.7, according to Rubinstein and Colby for semi dilute polymers in good solvent
C: correlation length fit with m=1.7 and a low Q exponent of n=1.2±0.002 indicating clustering within the PNIPAM solution as described by Hammouda et al. ***(J. Chem. Phys. 133, 084901 (2010))***
—> low exponent, no scattering from an interface as in Porod scattering (1/q^4), but structural inhomogeneities in the semi dilute solution on larger length scales at low Q's
D: data at 20°C: correlation length fit with m=1.7 and a low Q exponent of n=2.0 +- 0.01 indicating clustering within the PNIPAM solution as described by Hammouda et al. The scattering intensity seems to be increased compared to 15°C (10 vs. 5) and the clustering exponent is higher.

	A	B	C	D
m	2	1.7±0.001	1.7±0.001	1.7±0.001
n			1.2±0.002	2.1±0.01
ξ (nm)	2.1±0.03	2.7±0.03	2.4±0.02	2.9±0.01

Figure 7.A-C displays data at 15°C and Figure 7.D at 20°C. As described by Hore and Hammouda we also observe that the low-Q feature becomes steeper with increasing temperature.
However, for our purposes we are concerned with the intermediate and high-Q region, which give us information about the correlation length ξ. As can be seen in the table the values for ξ are similar independent of the chosen fit (between 2.1 and 2.9) with an average value of 2.5 nm and a standard deviation of 0.35 nm.

The exponent m=1.7 was used as suggested by Rubinstein and Colby for polymers in good solvent. (M. Rubinstein, R. H. Colby, *Polymer Physics*, Oxford University Press, New York, 2003, pp. 189-190.)
Since water is a good solvent for PNIPAM below the LCST of 32°C and we measured at 15°C and 20°C, this assumption is valid for our data.