Rheological response of a modified polyacrylamide – silica nanoparticles hybrid at high salinity and temperature

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Electronic supplementary information (ESI)

The supporting information contains the calculation of the volume fraction of the ligand, pictures of samples to observe the stability of nanoparticles and hybrids over time, details of TEM performed on nanoparticles, tables which include the fitting parameters for Carreau – Yasuda model (eqn (4)), molecular weight estimation of HMPAM and PAM, estimation of overlap concentration, the radius of gyration and persistence length for HMPAM and ^{1}H NMR spectrum for t-butyl acrylamide.

Calculation of the volume fraction of the ligand

The volume fraction of a ligand (ϕ_l) in the shell is determined by the following equation[1]:

$$\phi_l = \frac{3\Gamma_{max}R^2}{\rho_l[(L+R)^3 - R^3]} \tag{S1}$$

where ρ_l is the bulk density of a pure ligand, Γ_{max} is the grafting density of the ligand in units of ligand mass per nanoparticle surface area, *R* is the radius of the nanoparticle and *L* is the thickness of particle coating by the ligand. Γ_{max} is derived from the following equation:

$$\Gamma_{max} = \frac{\sigma MW_l}{N_A} \tag{S2}$$

where σ, as calculated by eqn (3), is the grafting density of the ligand in units of molecules per nanoparticle surface area, MW_l is the molecular weight of the ligand and N_A is the Avogadro number.

Stability of NPs and hybrids

Fig. S1 shows the samples of GPTMS modified NPs dispersed in Brine2015 in different concentrations from 0.05 to 4.0 wt% over the course of three months. As can be seen, all the samples were colloidally stable and no sedimentation was observed.

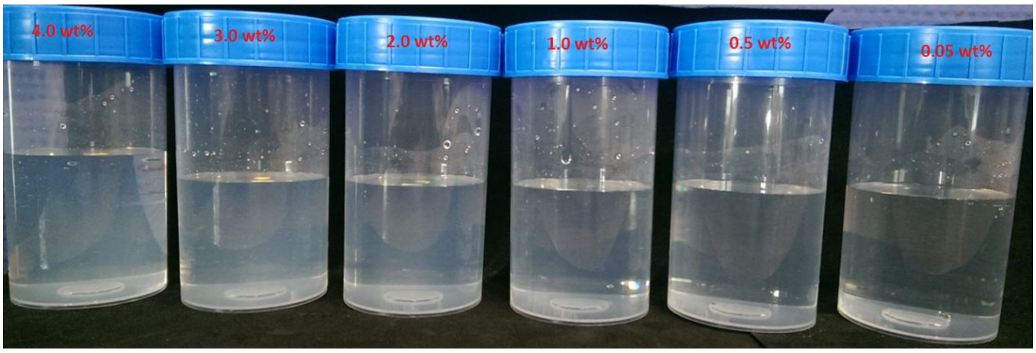

Fig. S1 Samples of GPTMS modified silica NPs at different concentrations dispersed in Brine2015; from right to left: 0.05, 0.5, 1.0, 2.0, 3.0 and 4 wt%

Fig. S2 shows the samples of bare and GPTMS modified NPs dispersed in DI water and in Brine 2015 at a concentration of 0.05 wt% after three months. Both bare and GPTMS modified NPs were stable in DI water but bare NPs showed some turbidity while the dispersion of GPTMS modified NPs was transparent. On the other hand, the dispersion of bare NPs in Brine2015 resulted in sedimentation whereas the dispersion of GPTMS modified NPs in Brine2015 was stable.

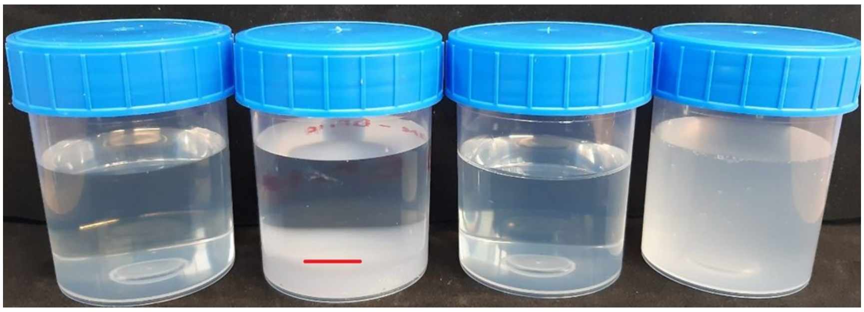

Fig. S2 Different samples of silica NPs. From right to left: bare silica NPs in DI water, GPTMS modified NPs in DI water, bare NPs in Brine2015 and GPTMS modified NPs in Brine2015. The dispersion of bare NPs in Brine2015 resulted in sedimentation

Fig. S3 shows hybrid samples of HMPAM and GPTMS modified NPs in Brine2015 at constant NPs concentration of 4 wt%. The concentration of HMPAM varied from 0.05 to 0.6 wt%. As can be seen, all the hybrids were stable after three months and no sedimentation was observed.

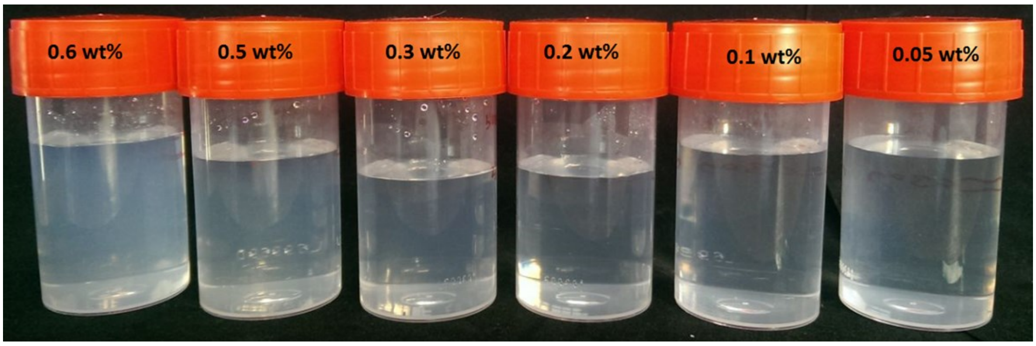

Fig. S3 Hybrid samples of HMPAM and GPTMS modified silica NPs in Brine2015. The concentration of NPs was 4 wt% for all the samples and the concentration of HMPAM varied. From right to left, concentration of HMPAM was 0.05, 0.1, 0.2, 0.3, 0.5 and 0.6 wt%.

TEM of nanoparticles

In order to disperse the bare silica NPs in DI water and Brine2015, the solutions were sonicated in a water bath for 30 min. After the sonication, a visually homogenous dispersion of NPs was observed in DI water. In the Brine2015, some nanoparticle aggregates were still visible. Particle size distribution (PSD) analyses on the bare silica NPs dispersed in DI water and brine confirm larger agglomerations of the particles in brine compared to water (Fig. S4).

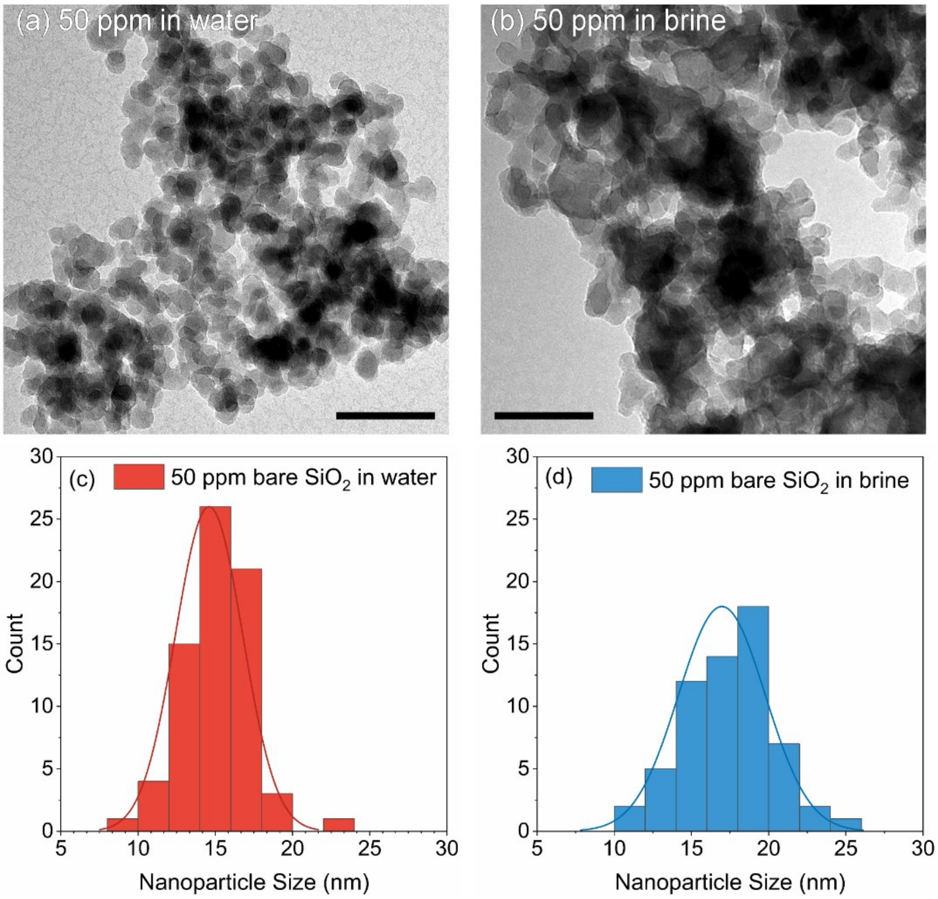

Fig. S4 50 ppm dispersion of silica NPs in (a, c) DI water TEM and PSD analysis, (b, d) Brine2015 TEM and PSD analysis (scale bar: 80 nm). The solid line is the normal distribution of data

The TEM analysis of the GPTMS modified NPs in DI water shows the presence of individual and small clusters of NPs with a narrow cluster size distribution which has an average size of 22 nm (Fig. S5a and S5c). For the NPs dispersed in Brine2015, larger agglomerates are formed resulting in clusters with a wider distribution averaging at about 42 nm (Fig. S5b and S5d).

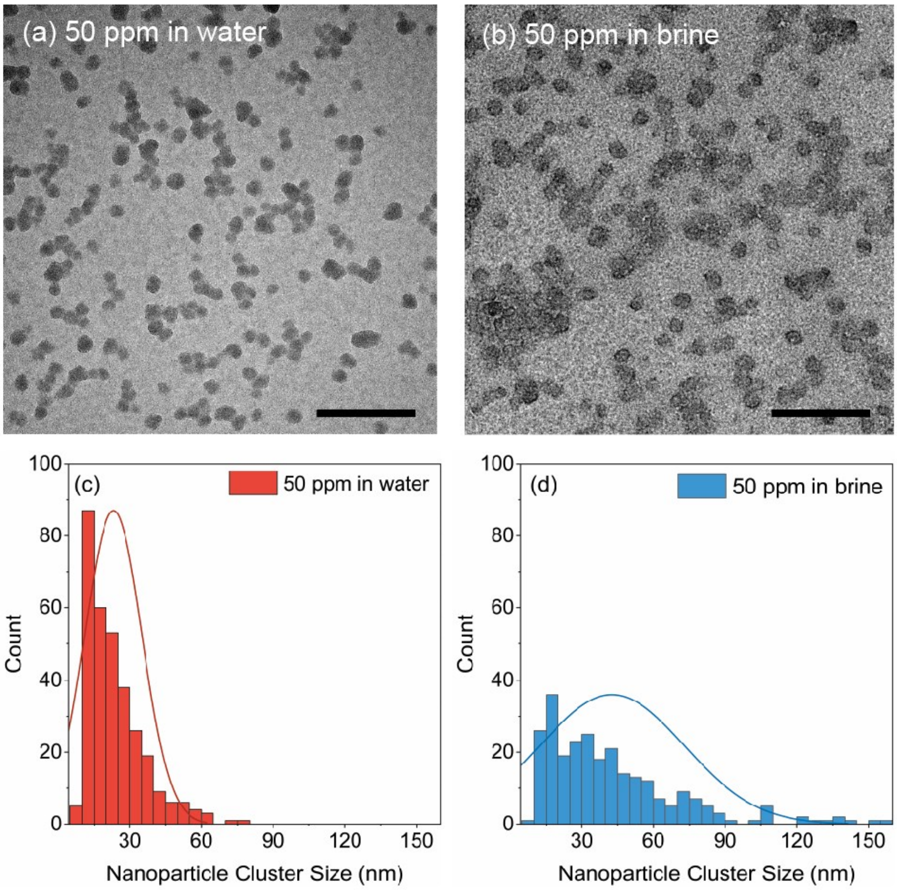

Fig. S5 50 ppm dispersion of GPTMS modified silica NPs in (a, c) DI water TEM and PSD analysis, (b, d) Brine2015 TEM, and PSD analysis (scale bar: 100 nm). The solid line is the normal distribution of data

Carreau – Yasuda model for the shear-thinning response of polymer solutions

The viscosity of polymer solutions as a function of shear rate was fitted in Carreau–Yasuda model. The results were shown in Fig. 3. In Table S1 the fitting parameters are shown for HMPAM solutions in DI water at 25 °C. The DI water viscosity was considered 0.9 mPa s (i.e. η_∞=0.9 cp). Table S2 shows the fitting parameter for HMPAM solutions in Brine2015 at 25 °C with solvent viscosity of 1.4 mPa s (i.e. η_∞=1.4 cp). In Table S3 fitting parameters of HMPAM solutions in Brine2015 at 70 °C is shown (η_∞=0.65cp)

Table S1 Fitting parameters for HMPAM solution in DI water at 25 °C (η_∞=0.9 cp)

Polymer conc. (wt%)	η_o (mPa s)	λ (s)	n	a
0.70	46.9	0.042	0.71	1.49
0.50	19.8	0.038	0.82	1.90
0.40	12.7	0.035	0.86	2.47
0.30	8.2	0.033	0.90	1.11

0.20	4.8	0.025	0.94	1.00
0.15	3.7	0.013	0.96	0.73
0.10	2.0	0.004	0.98	2.65

Table S2 Fitting parameters for HMPAM solution in Brine2015 at 25 °C (η_∞=1.4 cp)

Polymer conc. (wt%)	η_o (mPa s)	λ (s)	n	a
0.50	36.7	0.045	0.77	1.98
0.40	22.8	0.043	0.83	2.62
0.30	16.1	0.032	0.87	3.00
0.20	7.4	0.025	0.93	0.83
0.10	3.5	0.0025	0.95	2.51
0.05	2.4	0.002	0.97	2.45

Table S3 Fitting parameters for HMPAM solution in Brine2015 at 70 °C (η_∞=0.65 cp)

Polymer conc. (wt%)	η_o (mPa s)	λ (s)	n	a
0.50	11.2	0.019	0.84	1.45
0.40	7.4	0.017	0.90	2.00
0.30	4.2	0.009	0.98	1.31
0.20	2.7	0.003	0.99	1.50
0.10	1.4	0.0025	0.99	2.51
0.05	1.0	0.002	0.99	2.45

Molecular weight estimation of HMPAM and PAM

The free-radical based polymerization techniques employed to synthesize the polyacrylamide derivatives is anticipated to yield high molecular weight polymers (> 10^6 g·mol^{-1}). Measuring molecular weights of these polymers via standard size exclusion chromatography proved to be challenging. Therefore, the molecular weights were estimated based on viscosity measurements. Wu et al.[2]

reported the Mark-Houwink parameters for PAM homopolymers relating the intrinsic viscosity ($[\eta]$), which is directly related to the coil dimension of polymers in solution, to their molecular weight.

The intrinsic viscosity can be determined by measuring the solution viscosity (η) with respect to the solvent viscosity (η_0) in the dilute regime (no overlap between polymer coils) and extrapolation to zero polymer concentration as described by eqn (S3). η_{sp} represents the specific viscosity here.

$$[\eta] = \lim_{c\to 0}\left(\frac{\eta - \eta_0}{\eta_0}\right)/c = \lim_{c\to 0}\frac{\eta_{sp}}{c} \tag{S3}$$

As the fraction of hydrophobic comonomers in HMPAM is only small, we assumed that this equation for polyacrylamide homopolymers holds for the hydrophobically modified polyacrylamide derivatives as well. Following the protocol from Wu et al.[2], η were measured in an aqueous 0.2 M $Na2_SO_4$ solution for HMPAM and PAM in a concentration window ranging from 0 – 0.4 g/dL. A rolling ball micro-viscometer was used for the viscosity measurements, as this instrument is able to measure viscosities at significantly higher accuracy as a conventional rheometer. These measurements yielded a fairly linear relationship between η and the polymer concentration for both PAM (Fig. S6a) and HMPAM (Fig. S6c). This indicates that the measurements were performed in the dilute regime, ensuring that the intrinsic viscosities and hence molecular weights of single polymer chains were measured. Plotting the data according to eqn (S3) and perform the extrapolation yields intrinsic viscosities of 6.8 and 5.6 dL/g for PAM (Fig. S6b) and HMPAM (Fig. S6d) respectively. Based on these values, molecular weights of 2.7 $\pm$ 0.1 $\cdot$ 10^6 and 2.1 $\pm$ 0.03 $\cdot$ 10^6 g$\cdot$mol^{-1} were obtained for PAM and HMPAM, respectively. The molecular weights of both polymers are approximately the same, indicating that incorporating hydrophobic co-monomers in the PAM polymers is not significantly altering the polymerization kinetics and achievable monomer conversions.

We must note that the molecular weights reported here are merely estimates. Wu et al.[2] reported that the Mark-Houwink parameters depend on the degree of hydrolysis of the incorporated acrylamide monomers. At higher hydrolysis degrees the polymers behave more like polyelectrolytes. The introduction of charged moieties increases the coil volume of the polymers and hence the value for $[\eta]$. As the measured intrinsic viscosities were converted to molecular weights using parameters for polyacrylamide polymers with no hydrolysis, the reported molecular weights might be overestimated. As we did not attempt to measure the degree of hydrolysis for PAM or HMPAM, the reported values can be treated as an upper bound to the true molecular weight. Besides the unknown degree of hydrolysis, the relation reported by Wu et al.[2] was only verified for polymers of molecular weights up to 1.5 $\cdot$ 10^6 g$\cdot$mol^{-1}. Small deviations of this relation when increasing the molecular weight a factor of 2 – 3 could be present.

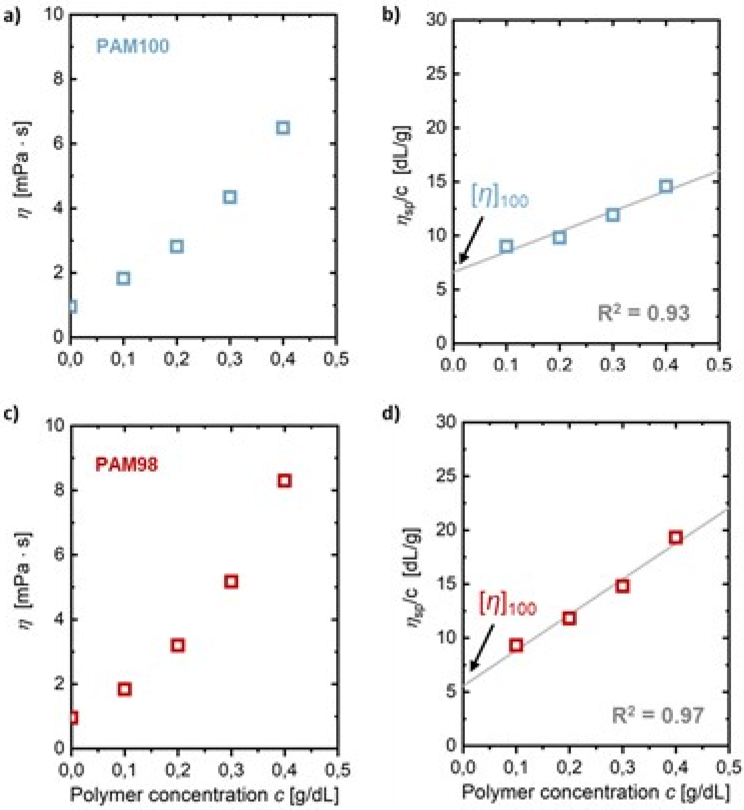

Fig. S6 *Solution viscosity (η) versus polymer concentration c for a) PAM and c) HMPAM. The plot of the specific viscosity (η_{sp} = (η – η_0)/η_0, with η_0 = viscosity of the pure solvent) divided by the polymer concentration versus the polymer concentration for b) PAM and d) HMPAM. Extrapolation to c = 0 yields the intrinsic viscosities ([η]) of the polymers. Measurements were performed in 0.2 M Na_2SO_4 at 25* °C.

Estimation of overlap concentration and radius of gyration

As can be seen in Fig. S7 the overlap concentration of HMPAM in DI water and Brine2015 was found to be 0.49 ± 0.01 wt% and 0.30 ± 0.01 wt% respectively. The radius of gyration R_G of HMPAM was estimated from the following equation[3]:

$$R_G = \left(\frac{[\eta]MW}{\Phi}\right)^{1/3} \qquad (S4)$$

where $[\eta]$ is the intrinsic viscosity, *MW* is the molecular weight of polymer and Φ is a universal constant (4.2×10^{24} mol^{-1}). R_G in DI water and in Brine2015 was found to be 70 ± 5 and 80 ± 5 nm respectively.

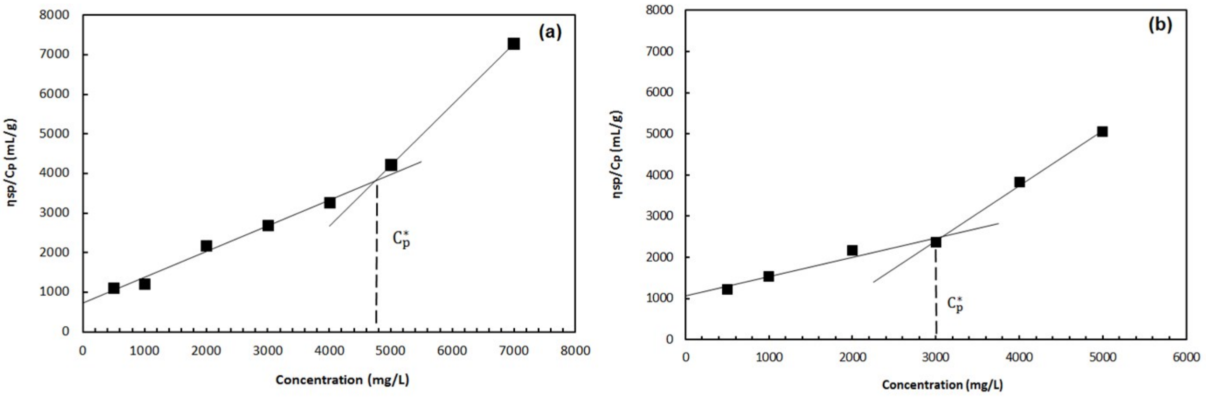

Fig. S7 Determination of C_p^* for HMPAM (a) in DI water and (b) in Brine2015

Estimation of HMPAM persistence length

To calculate the persistence length of HMPAM chains, we estimated the intrinsic viscosity (see Fig. S7) from which the radius of gyration (R_G) was estimated (see eqn (S4)). For a non-branched wormlike chain, the persistence length can be estimated from R_G based on the following equation:[4]

$$< R_G^2 > \ = \frac{LL_t}{3} - L_t^2 + \frac{2L_t^3}{L} - \frac{2L_t^4}{L^2}\left(1 - e^{-\frac{L}{L_t}}\right) \tag{S5}$$

where L_t is the persistence length and L is the contour length ($L = \frac{Mb}{m}$, with M and m being the polymer and monomer molecular weight and b is the contour length per monomer. Since both acrylamide and t-butyl acrylamide have the same "acrylamido" backbone, thus the same carbon-carbon bond length, the whole chain can be assumed as a connection of acrylamide. Therefore, for the sake of calculation, we assumed HMPAM as a pure polyacrylamide. The HMPAM contour length per monomer was considered to be within the range of 0.27 – 0.40 nm.[5] As a result the HMPAM contour length and persistence length was estimated to be 9.9 ± 1.9 µm and 2.2 ± 0.6 nm respectively. Since the contour length is much larger than the persistence length, therefore, our long-chain polymer behaves like a random coil. Considering that the distribution of hydrophobic groups on HMPAM is random, three types of interactions are possible in an HMPAM – NPs hybrid: (a) intra-chain hydrophobic association within an HMPAM chain (b) inter-chain hydrophobic association between HMPAM chains, and (c) hydrophobic – hydrophobic interaction between t-butyl acrylamide units on HMPAM and hydrophobically modified silica NPs. Here, beyond $C_{np,c}$, NPs facilitate the bridging between different HMPAM chains.

^{1}H NMR for t-butyl acrylamide

Fig. S8 shows ^{1}H NMR spectrum for t-butyl acrylamide in D_2O. Peak c' corresponds to the methyl groups in t-butyl acrylamide.

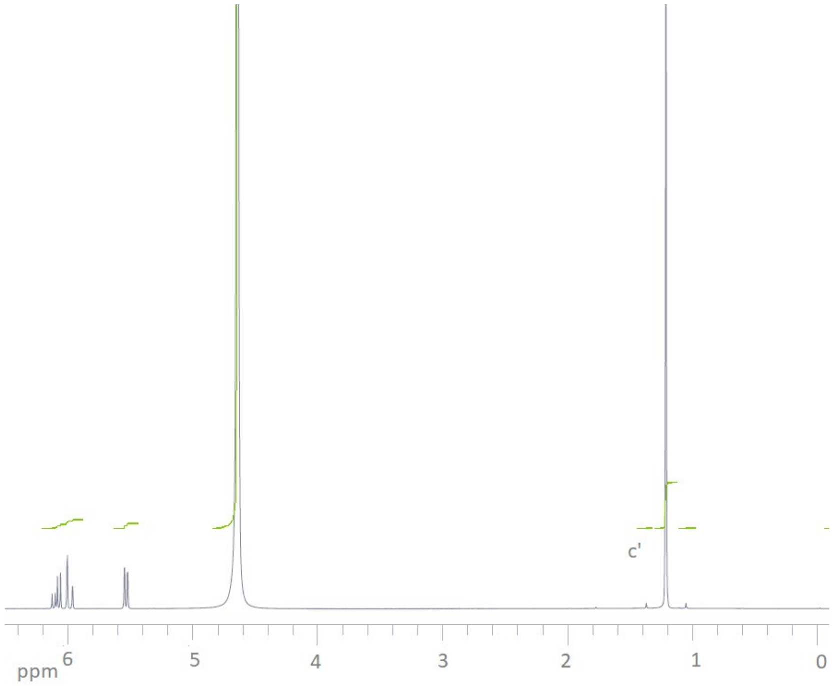

Fig. S8 ^{1}H NMR spectrum for t-butyl acrylamide

References

1. M. R. Ivanov and A. J. Haes, *Analytical Chemistry*, 2012, **84**, 1320-1326.
2. X. Y. Wu, D. Hunkeler, A. E. Hamielec, R. H. Pelton and D. R. Woods, 1991, **42**, 2081-2093.
3. A. Ait-Kadi, *Journal of Rheology - J RHEOL*, 1987, **31**.
4. C. Walldal and B. Åkerman, *Langmuir*, 1999, **15**, 5237-5243.
5. D. Bruns, T. E. de Oliveira, J. Rottler and D. Mukherji, *Macromolecules*, 2019, **52**, 5510-5517.