

Poly (ethylene oxide) (PEO) and Poly (vinylpyrrolidone)(PVP) Induce Different Changes in the Colloid Stability of Nanoparticles

(Supplementary File)

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Further Details of Experimental Methods

Adsorption isotherms

The polymer adsorption isotherm was determined from samples with a nanoparticle concentration of 0.36 wt% and varying polymer concentrations. The samples were centrifuged at 10,000 rpm for 3 hours in a centrifuge (Sorvall RC-6 ultracentrifuge) to settle and separate the nanoparticles as a dense sediment after which the polymer concentration in the supernatant was determined by either UV-vis spectroscopy or gel permeation chromatography (GPC). The adsorbed amount was then calculated by difference. Both methods yielded statistically indistinguishable results. The PVP concentration in the supernatant was measured by UV-vis absorption at 210 nm (Perkin-Elmer Lambda 2). The instrument was calibrated with the corresponding pure polymer used for adsorption studies. The presence of nanoparticles does not affect PVP absorbance as shown by the flat baseline at higher wavelengths where no PVP absorbance is expected (see below). Because PEO has no characteristic UV-vis peak and acetate also absorbs in the same wavelength range as PVP due to the carboxyl bond, GPC was used to measure the concentration of PEO in water and both PEO and PVP in the supernatants containing acetate buffer.

The surface saturation concentration of polymer adsorbed the nanoparticles (Γ_{satn}) and the equilibrium constant (K) were determined from a linearization of the Langmuir adsorption isotherm:^{1,2}

$$\frac{[P]}{\Gamma} = \frac{1}{K_{ads} \Gamma_{satn}} + \frac{[P]}{\Gamma_{satn}} \quad [S1]$$

where $[P]$ is the bulk polymer concentration (units mg/m^3), Γ (units mg/m^2) is the amount of polymer on the nanoparticle surface at any given $[P]$, Γ_{satn} is the amount of polymer adsorbed on the nanoparticle surface at saturation, and K_{ads} is the equilibrium constant (units m^3/mg), which describes the interaction between the polymer and the nanoparticle surface.

GPC & Densitometry

The weight-averaged (M_w), number-averaged (M_n) polymer molecular weights, and the polymer concentration in the supernatant of phase separated samples were measured by gel permeation chromatography (GPC) using a Waters 2695 separations module with a 2414 refractive index detector and a Precision Detectors Enterprise multi-angle laser light scattering (MALLS) detector. Two Waters Ultrahydrogel columns packed with hydroxylated polymethacrylate-based gel were used in series. Since the polymers are polydisperse the GPC peak is broad, so the peak area, instead of the peak height, was used to determine the concentration of the polymer in the supernatant. The density of the polymer and nanoparticle dispersions were measured with a vibrating tube densitometer (Anton Paar DMA 60 with an Anton Paar DMA 602 external measuring cell) over the range of polymer concentrations used in this study. Ideal mixing was assumed.

Light scattering

The hydrodynamic radii (R_h) of the nanoparticles and polymer coils were measured by dynamic light scattering (DLS) using a Brookhaven Instruments Corp. BI9000 digital correlator and an Argon ion laser operating at 488 nm. All measurements were made at 25 °C. The particle surface area was calculated from the hydrodynamic radius and the extent of the adsorbed polymer brush was also determined from the hydrodynamic radius of the complex.³ R_g and the weight average molecular weight (M_w) of the polymers were calculated from Zimm plots⁴ made using data gathered at scattering angles between 45 and 135° and from polymer concentrations below the polymer overlap concentration (c^*).

Intrinsic viscosity

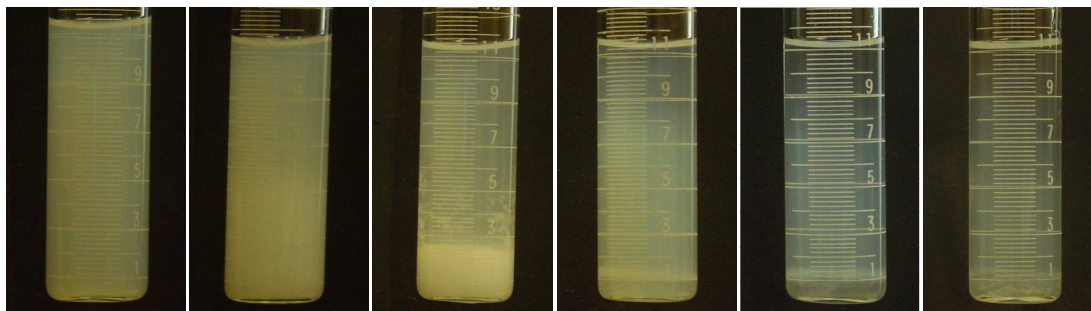
The intrinsic viscosity $[\eta]$ of the polymers were measured with a capillary viscometer (Cannon-Ubbelohde, 25 °C). The polymer viscosity-averaged molecular weight (M_v), R_g , and R_h were then calculated from the measured intrinsic viscosity using published empirical correlations.^{5,6} The overlap concentration c^* was calculated from measurements of the concentration dependence of the viscosity (see below). This was found not to vary significantly with change in solvent.

Turbidity

Depletion flocculation is expected to yield a sharp boundary in a sample between two distinct regions or “phases”: an optically dense phase rich in nanoparticles and an optically clear polymer solution containing few if any nanoparticles. A critical polymer-colloid composition is needed to initiate this separation and a sharp transition is expected as the boundary is crossed. Polymer bridging, on the other hand, does not lead to a similar sharp “phase” transition. Therefore, with the addition of bridging polymer to a solution at a given colloid concentration,

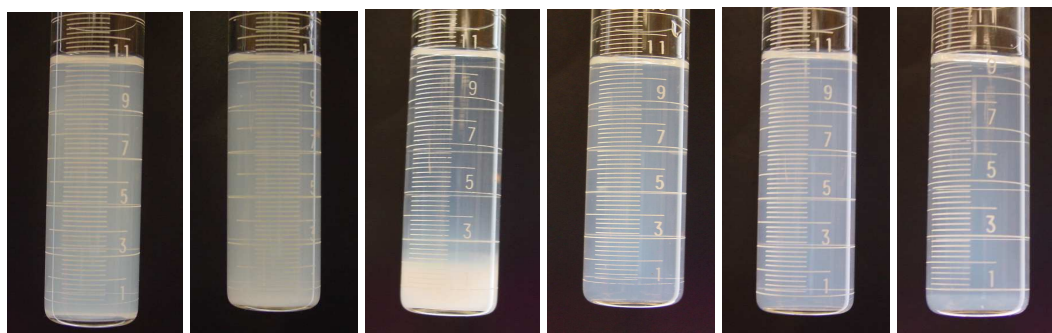
bridged samples are expected to form increasingly turbid flocs with increasing polymer concentration. Sedimentation of the larger flocs leaves smaller flocs in the supernatant. Consequently, the turbidity of single phase samples were measured as a function of increasing polymer concentration on a Bausch & Lomb Spectronic 20 turbidimeter at 488 nm to give information on the nature of the polymer-particle interactions leading to phase separation.

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2. Simon, S.; Cerf, D.L.; Picton, L.; Muller, G. *Colloids and Surf. A.* **2002**, 203, 77
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5. Armstrong, J.K.; Wenby, R.B.; Meiselman, H.J.; Fisher, T.C. *Biophysical J.* **2004**, 87, 4259
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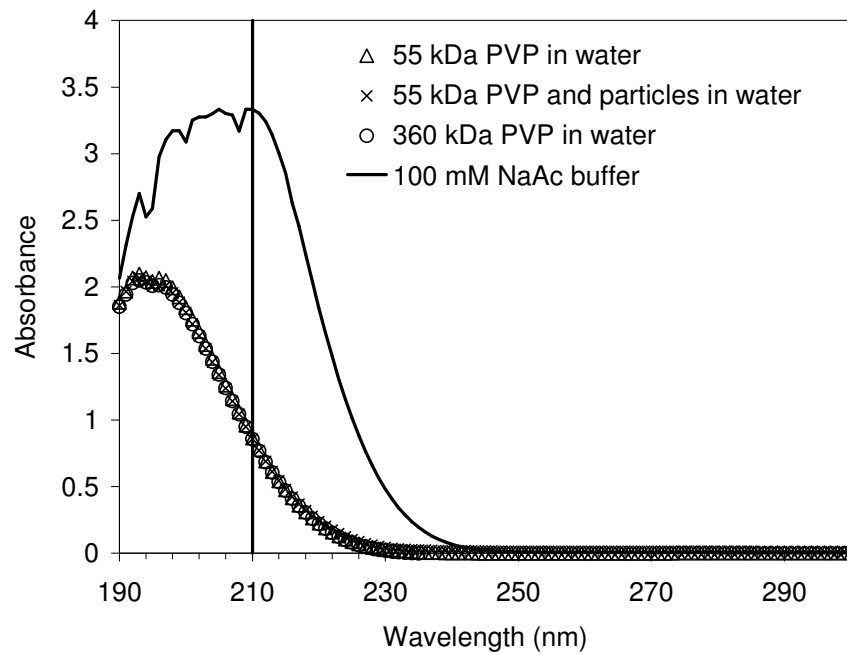
A **B** **C** **D** **E** **F**
PVP: 0.01 wt% **0.04 wt%** **0.2 wt%** **1 wt%** **4 wt %** **9 wt%**

S1a: Phase samples for 6 wt% nanoparticle in aqueous solution with 360 kDa PVP of given concentrations after phase equilibration. Plateau adsorption occurs between samples C and D.

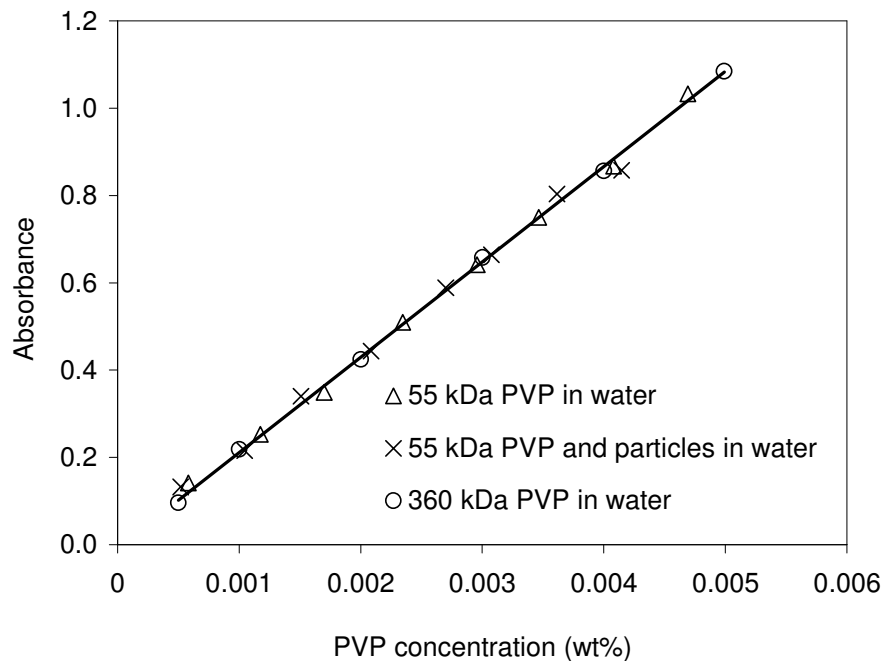


A **B** **C** **D** **E** **F**
PVP: 0.01 wt% **0.04 wt%** **0.2 wt%** **1 wt%** **4 wt %** **9 wt%**

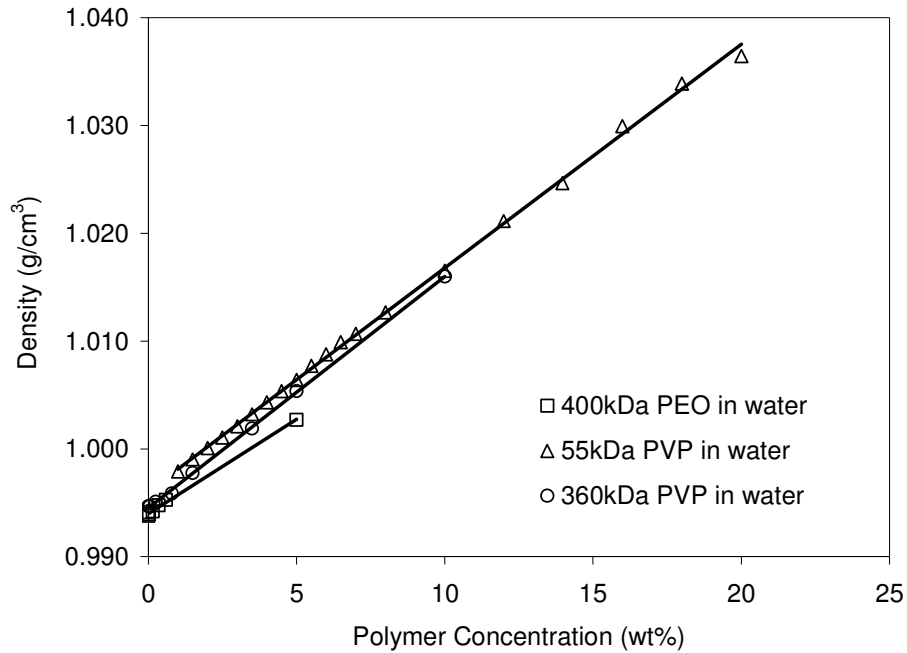
S1b: Phase samples for 6 wt% nanoparticle in aqueous solution with 360 kDa PVP of given concentrations after shearing for 2 minutes at 3,000 and 5,000 rpm in a Silverson mixer. Plateau adsorption occurs between samples C and D.



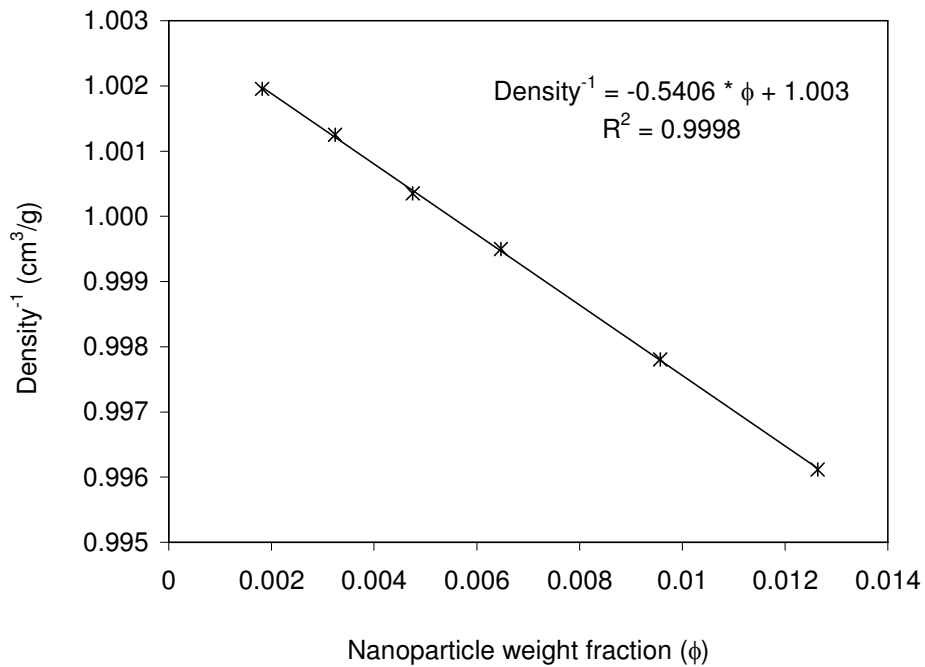
S2: UV-Vis spectra for 4×10^{-3} wt% aqueous 55 kDa PVP, 55 kDa PVP-nanoparticle mixtures, and 360 kDa PVP. Absorbance at 210 nm was used to calibrate the system. The maximum PVP concentration to reach absorbance of 1 at 210 nm is 4.2×10^{-3} wt%.



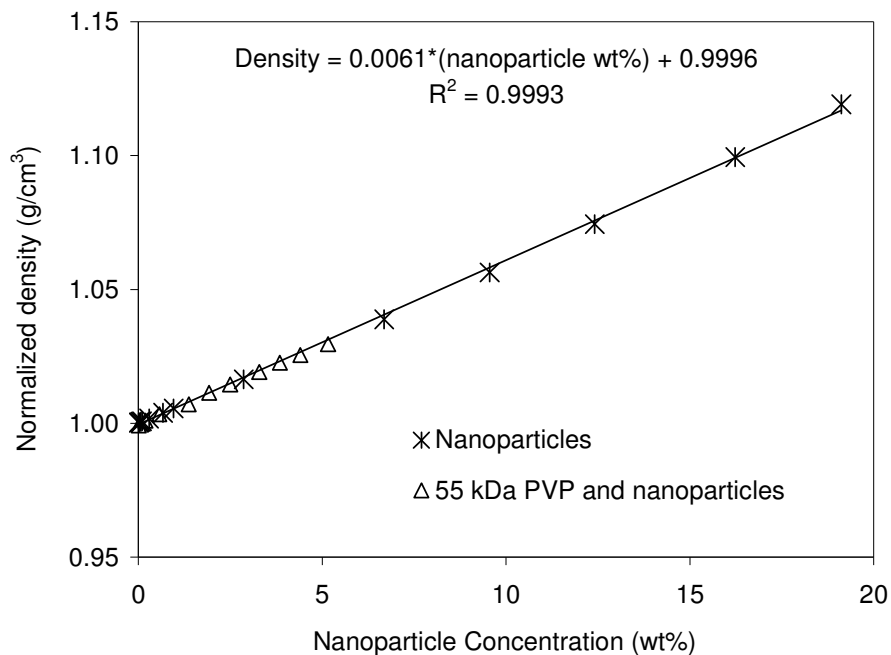
S3: UV-Vis calibration curve at 210 nm for aqueous 55 kDa PVP, 55 kDa PVP-nanoparticle dispersions, and 360 kDa PVP.



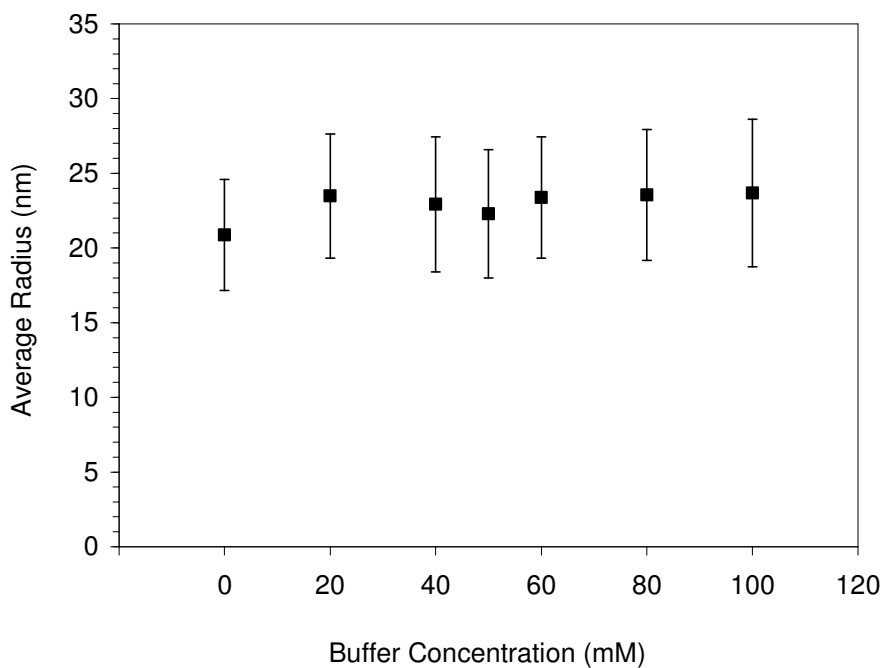
S4: Density of polymer in water.



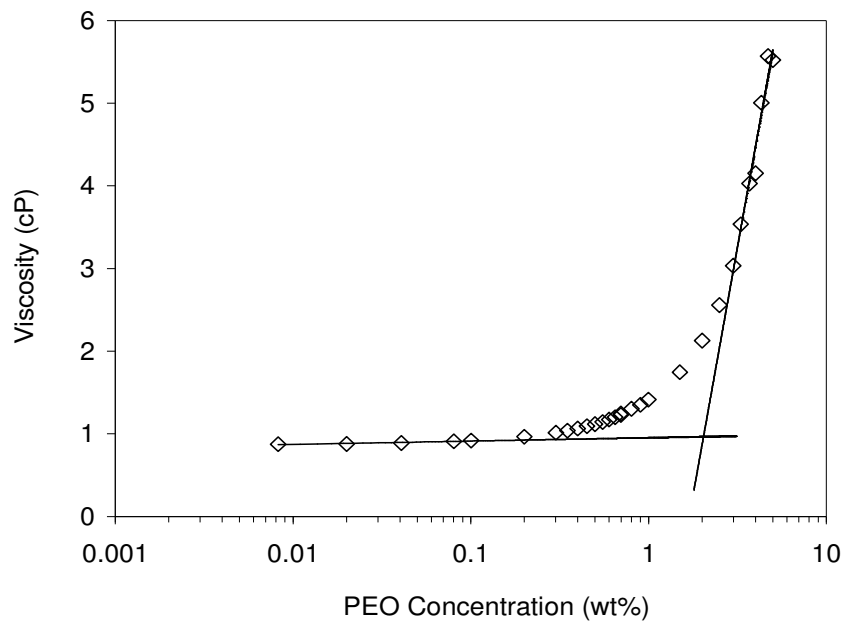
S5: Density of pure nanoparticle dispersions in water. The density of nanoparticles was found to be 2.2 g/cm³.



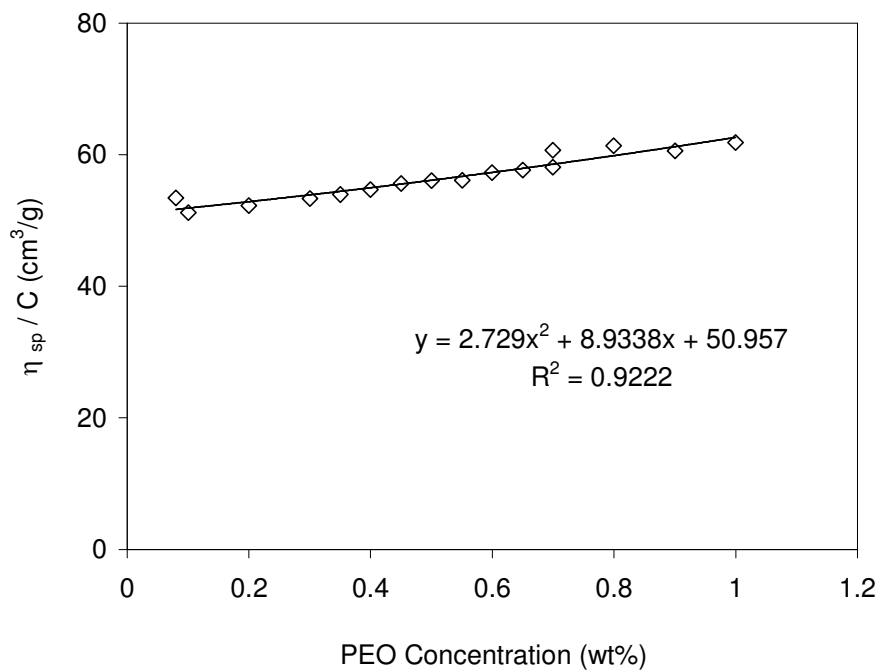
S6: Nanoparticle density calibration. The presence of 20 wt% 55 kDa PVP did not affect the solution density. This implies the concentration of nanoparticles in polymer-nanoparticle mixtures can be determined by density measurements without interference from the polymer present in solution.



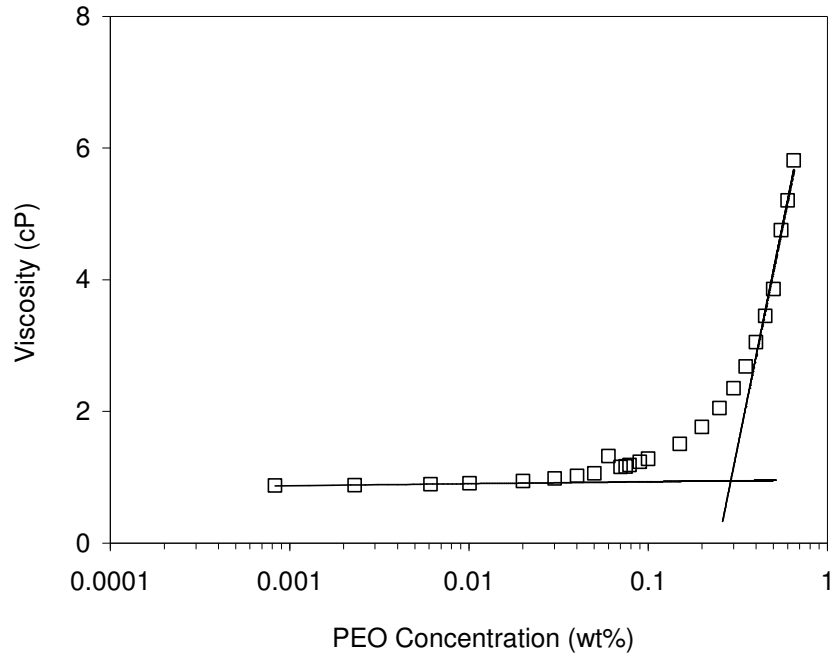
S7: Hydrodynamic radius of the nanoparticles in various strengths of NaAc buffer concentrations. There is no measurable aggregation of the particles in buffer.



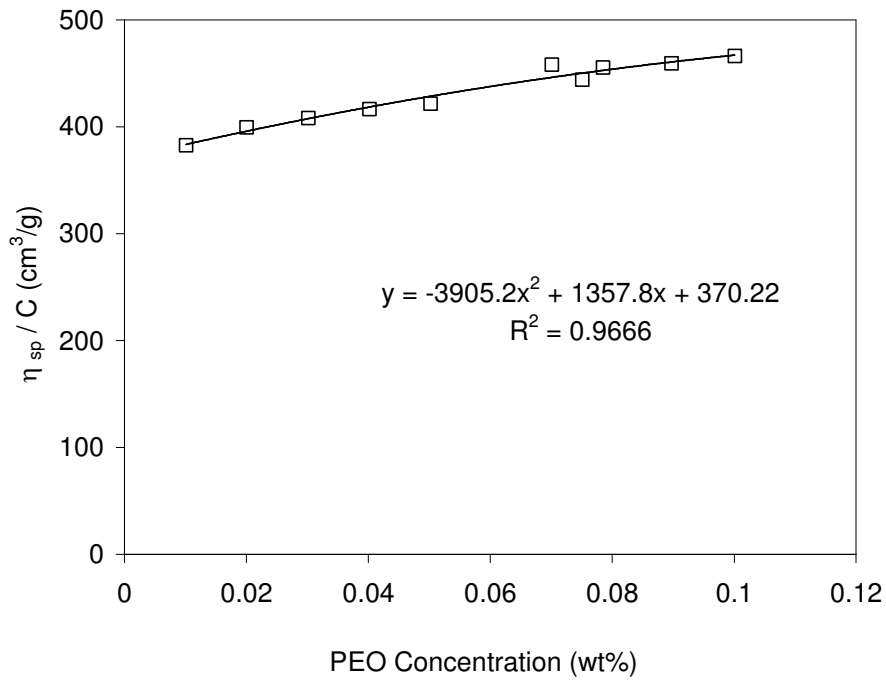
S8: Viscosity of 35 kDa PEO with increasing polymer concentration. c^* is 2.04 ± 0.011 wt%.



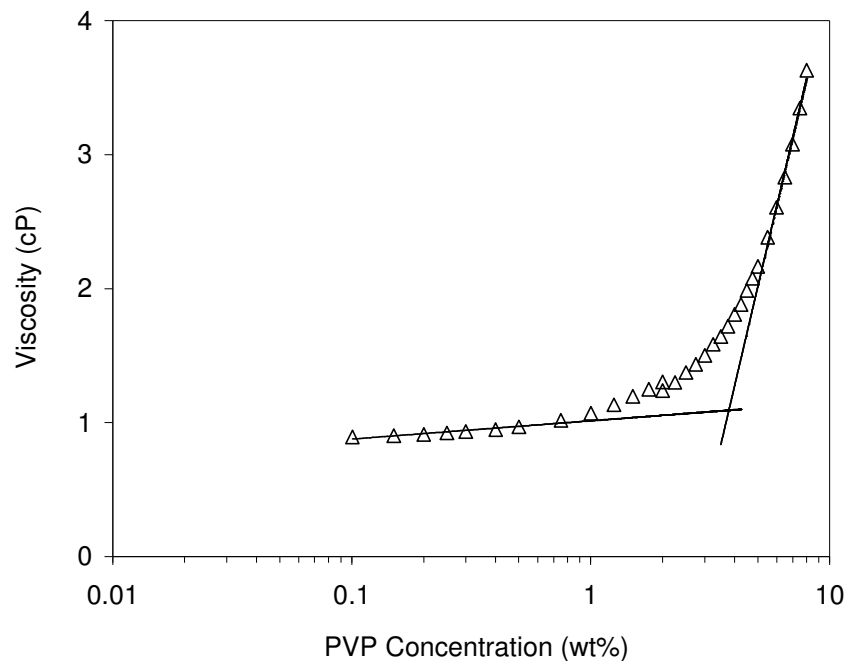
S9: Intrinsic viscosity determination for 35 kDa PEO. $[\eta]$ is 50.9 cm³/g.



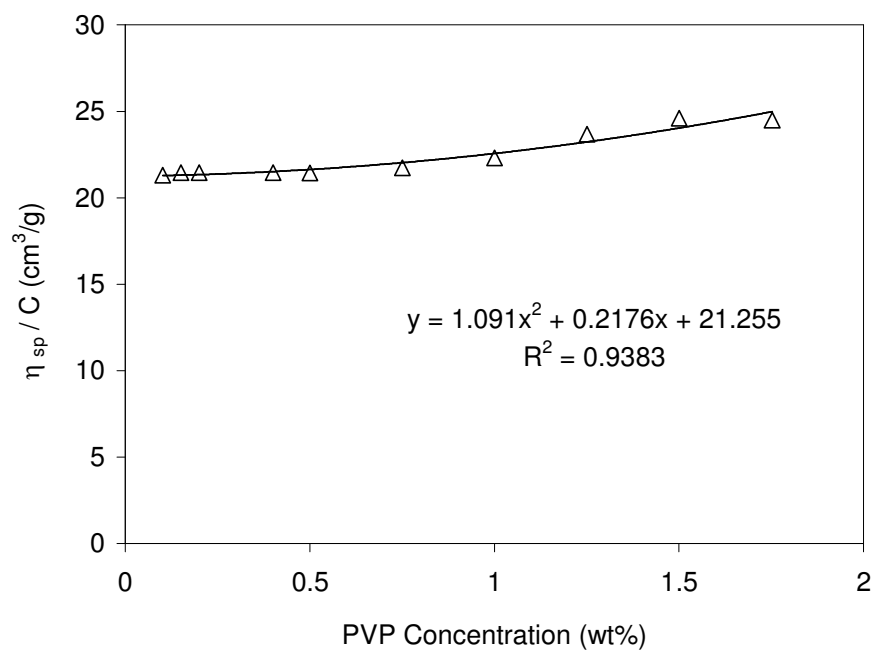
S10: Viscosity of 400 kDa PEO with increasing polymer concentration. c^* is 0.300 ± 0.0061 wt%.



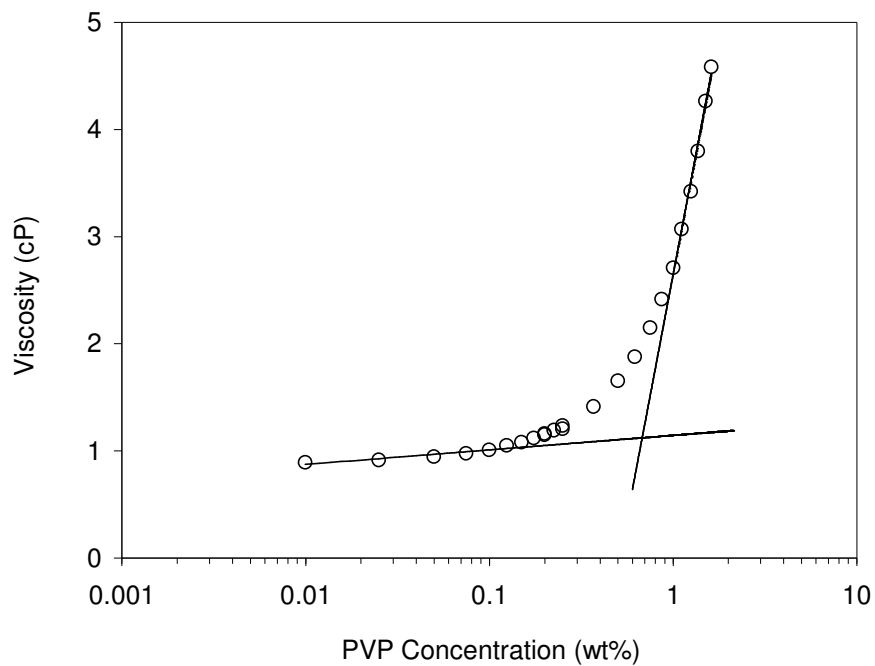
S11: Intrinsic viscosity determination for 400 kDa PEO. $[\eta]$ is $370 \text{ cm}^3/\text{g}$.



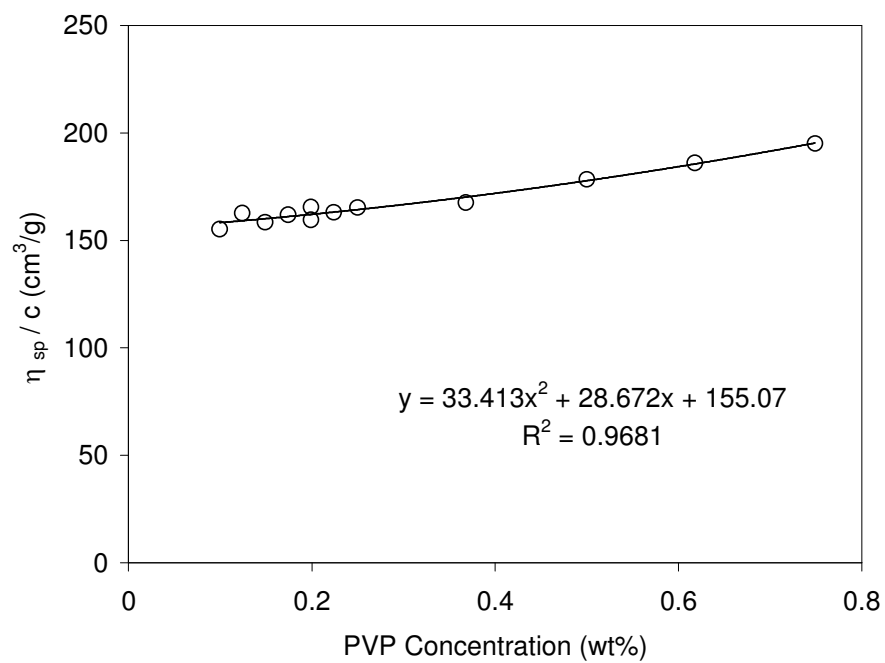
S12: Viscosity of 55 kDa PVP with increasing polymer concentration. c^* is 3.78 ± 0.0021 wt%.



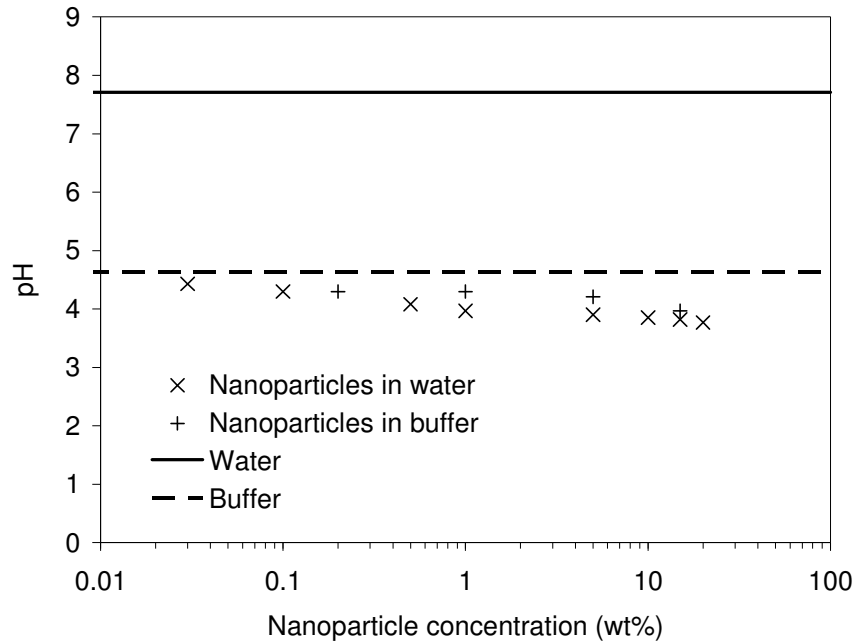
S13: Intrinsic viscosity determination for 55 kDa PVP. $[\eta]$ is $21.2 \text{ cm}^3/\text{g}$.



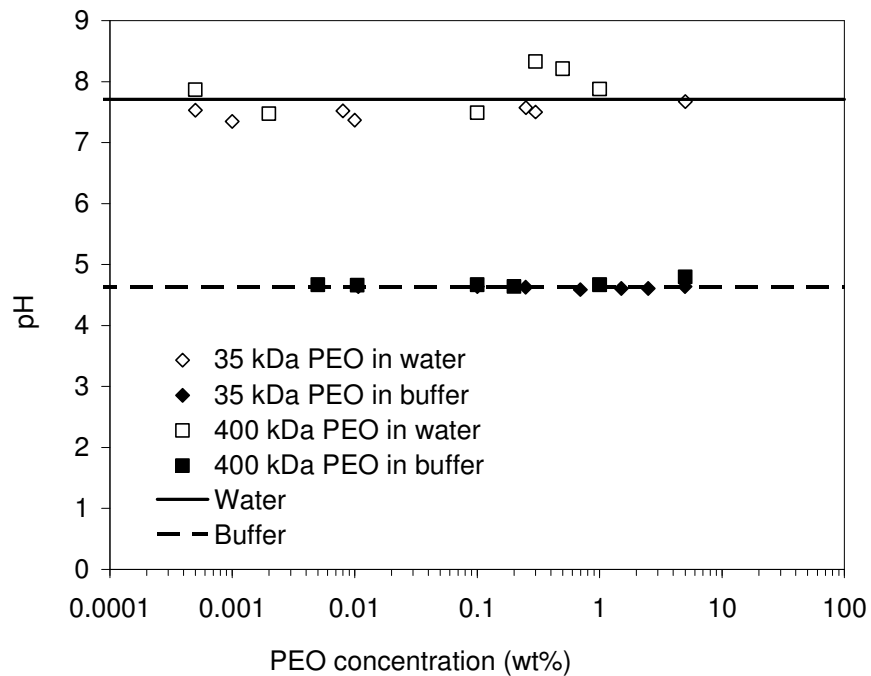
S14: Viscosity of 360 kDa PVP with increasing polymer concentration. c^* is 0.680 ± 0.0048 wt%.



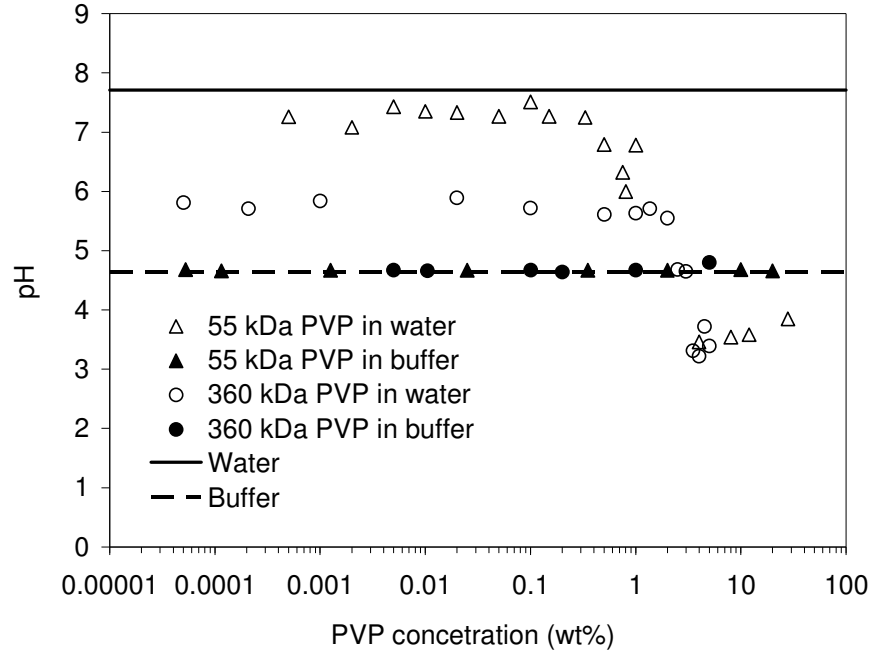
S15: Intrinsic viscosity determination for 360 kDa PVP. $[\eta]$ is $155 \text{ cm}^3/\text{g}$.



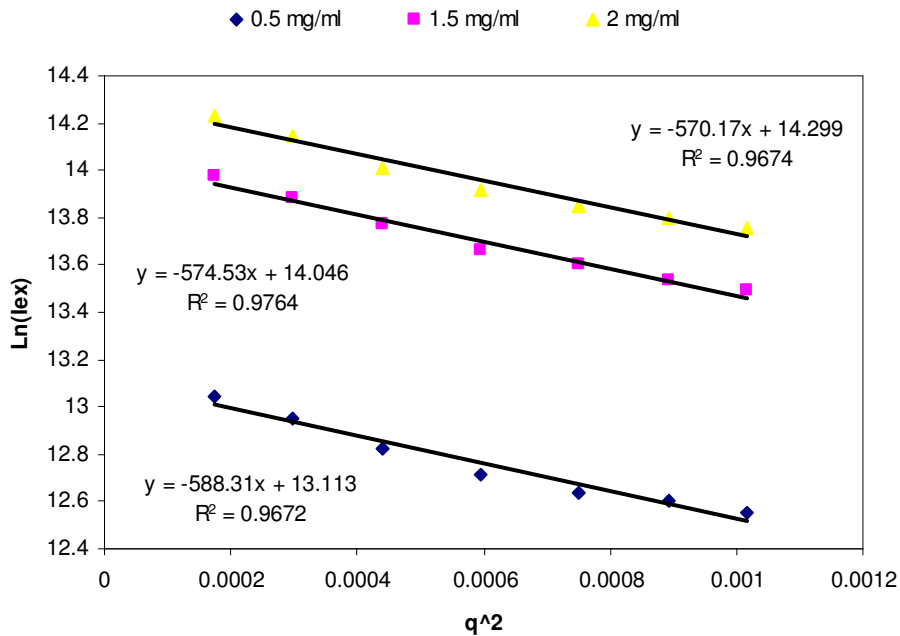
S16: pH of the nanoparticles in water and in 100 mM buffer. The pH of the nanoparticles is independent of buffer pH. Also shown for reference are the pH of water and pure buffer.



S17: pH of 35 kDa and 400 kDa PEO in water and in 100 mM buffer showing the ability of the buffer to control the pH of the system. Also shown for reference are the pH of water and pure buffer.



S18: pH of 55 kDa and 360 kDa PVP in water and in 100 mM buffer showing the ability of the buffer to control the pH of the system. Also shown for reference are the pH of water and pure buffer.



S19: Guinier plots of 100 kDa PEO in water showing that the radius of gyration is independent of polymer concentration below the entanglement concentration.