Experimental report

10/12/2020

Proposal: **9-12-575**

Council: 4/2019

Title: Probing polymer conformation in nanoparticle confinement and the origin of their electrostatic stability

Research area: Engineering

This proposal is a new proposal

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Samples: h/d-poly(styrene) nanoparticles

Instrument	Requested days	Allocated days	From	To
D22	2	2	24/02/2020	26/02/2020

Abstract:

Nanoscale colloids are a crucial component of biomedical, optoelectronic and catalytic technologies. FlashNanoPrecipitation emerges as a novel approach for high throughput nanoparticle production and involves the confined jetting of opposite streams of dilute polymer solution and non-solvent. Several outstanding questions remain regarding the formation and stability of nanoparticles by this approach; How are the polymer chains arranged within the NP, following their collapse during NP formation and what are their dimensions under nanoscale confinement? Secondly, nanoparticles generated by FlashNanoPrecipitation are often highly stable despite the lack of charged end groups and additional block copolymer or surfactant stabilisation. What is the origin of this stabilisation?

In our proposal, we seek to address these questions through the use of a microfluidic contrast variation, to investigate chain conformation, and dilution experiments, to resolve the inter-particle interactions, from h/d polystyrene nanoparticle suspensions. In doing so, we aim to resolve the conformation of polystyrene chains confined within nanoparticles and the anomalous origin of their stability.

Experimental Report 9-12-575: Probing Polymer Conformation in Nanoparticle Confinement and the Origin of their Electrostatic Stability

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Ambition: Our initial proposal sought to exploit the potential of our microfluidic-SANS contrast matching technique to resolve the electrostatic stability of hydrophobic polystyrene nanoparticles, generated by Flash-NanoPrecipitation. Given the proposed experimental schedule we instead performed measurements of poly(vinyl alcohol)/water/non-solvent systems from proposal 9-11-1937 and instead addressed this proposal in experiment 9-11-1937.

System Studied: We investigated two 25k M_w random poly(vinyl alcohol) (PVA) samples with two degrees of hydrolysis (88% and 99%). Degree of hydrolysis is the ratio of vinyl alcohol to vinyl acetate monomers within the polymer. At room temperature we measured a range of compositions for binary mixtures of PVA/D_2O and ternary mixtures of PVA/D_2O/non-solvent. Two non-solvents were selected; partially miscible ethyl acetate and fully miscible acetone.

Results: We first measured the solution structure of varying concentrations of PVA in D_2O with both 88% and 99% hydrolysis. Example SANS profiles for the 88% hydrolysed PVA are shown in Figure 1 (a). Offset curves with fits to the ubiquitous Ornstein-Zernike equation:

$$I(q) \simeq \frac{I(0)}{1 + (q\xi)^{1/\nu}} \tag{1}$$

are shown in Figure 1 (b). The equation yields the intensity at $q = 0$ I(0), the correlation length of the polymer network in solution ξ and the effective solvent quality $1/\nu$. The same equation was fitted to the SANS profiles from 99% hydrolysed PVA solutions.

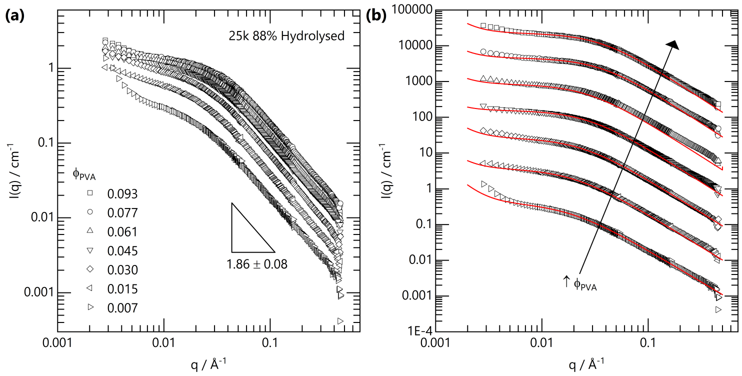

Figure 1: (a) Coherent SANS profiles of 25k PVA with 88 % degree of hydrolysis in D_2O. The scattering decays at intermediate to high-q with a power law of ~ 1.86. (b) Offset curves ($5\times$) from (a). Symbols correspond to the legend in (a) and are offset with increasing volume fraction of polymer (ϕ_{PVA}). Red lines are fits to Equation 1 and are also offset with the corresponding raw data.

The corresponding fit parameters for both 88% and 99% are shown in Figure 2. For 88 % PVA, a non-linear dependence is observed which appears proportional to $\phi_{PVA}^{0.38\pm0.04}$. For 99 % hydrolysed PVA, the variation appears linearly proportional to polymer concentration. $I(0)$ should be linearly proportional to $\phi(1-\phi) \approx \phi$ given no change in contrast or incomplete dissolution. The fitted ξ decreases with increasing concentration for the 88 % hydrolysed sample. A plateau is observed as $\phi_{PVA} \to 0.1$. A power law dependence of ξ on ϕ_{PVA}, over the range $\phi_{PVA} = 0.01 - 0.07$, appears as $\xi = (12.0 \pm 1.7)\phi_{PVA}^{-0.35\pm0.04}$ Å. In contrast, a non-monotonic dependence of ξ with ϕ_{PVA} is observed for the 99 % hydrolysed PVA sample. Given no physical rationale for this observation, an average value of $\xi = 48.5 \pm 6.3$ Å could be assumed. The high-q slopes of the SANS data yielding average values of the solvent quality parameter $\nu = 0.54$ and $\nu = 0.61$ for 88 and 99 % hydrolysed samples and thus scaling theories would predict $\xi \sim \phi_{PVA}^{-0.87}$ and $\sim \phi_{PVA}^{-0.73}$, respectively, which are not observed. The observed scaling exponent for the 88 % sample appears more consistent with the power law dependencies extracted from DLS measurements of PVA solutions and gels [1], SANS measurements of PEO solutions [2] and is much lower than scaling theories would predict.

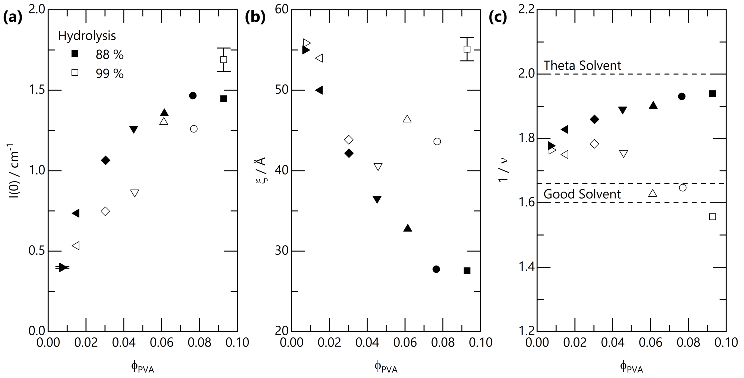

Figure 2: $I(0)$ (a), ξ (b) and $1/\nu$ extracted from fitting Equation 1 to PVA/D_2O solutions for 88% and 99% hydrolysed polymers. Typical error bars obtained from data fitting are shown on a single data point in (a) and (b) and not shown in (c), owing to the negligible size. Dashed lines in (c) indicate the $1/\nu$ values which correspond to Θ-solvent and bounds for 'good' solvent, as per a mean-field approach ($\nu = 0.6$) and with renormalisation group theory ($\nu \simeq 0.588$).

We then investigated the effect of added non-solvent a fixed polymer concentration for both 88% and 99% hydrolysed polymers. We again fit our measured SANS profiles (not shown here) with Equation 1 and extract values of I(0), ξ and $1/\nu$. For addition of d-acetone, these are shown in Figure 3.

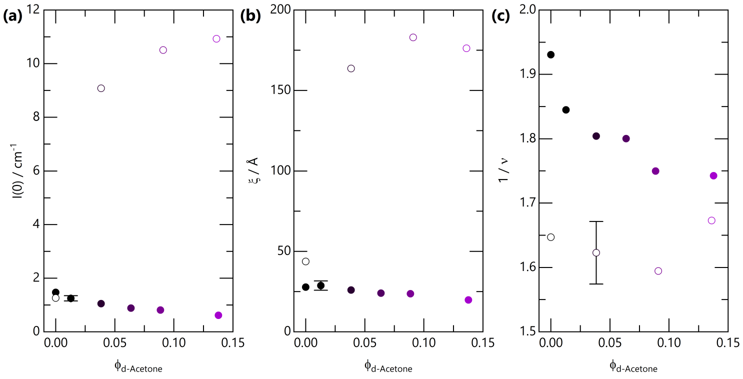

Figure 3: Extracted $I(0)$ (a), ξ (b) and $1/\nu$ (c) from fits to Equation 1 to data from 88% and 99% hydrolysed PVA/D_2O/d-acetone mixtures. Solid symbols correspond to 88 % hydrolysis and open symbols to 99 % hydrolysis, respectively.

Upon addition of d-acetone to both partially and 99 % hydrolysed PVA solutions, different trends are observed with $\phi_{d-acetone}$ dependent on PVA hydrolysis. For the 99 % hydrolysed PVA, aggregation is observed and manifests itself in a monotonically increasing $I(0)$ and ξ with $\phi_{d-acetone}$, whilst no change in the local solvation of the changes can be seen. The partially hydrolysed PVA with added d-acetone yields a remarkably different scattering curve and therefore structure. Again, no change in the high-q slope suggests that the added non-solvent does not affect the solvation locally. However, with added $\phi_{d-acetone}$, a monotonic decrease in $I(0)$ and ξ is observed at the same time as an increasing clustering factor (A/q^n) with a fixed exponent $(n = 3)$. The values of $I(0)$ and ξ are consistent with those found in PVA/D_2O solutions. This suggests a different mechanism of aggregation and could be related to the formation of fringed micelles rather than from physical crosslinks.

Upon addition of d-EA to a solution of 99 % hydrolysed PVA solution, significant changes to the observed scattering and therefore solution structure are observed. Whilst the local conformation of PVA chains does not change significantly, indicated by the high-q slope, the apparent $I(0)$ and ξ both increase substantially to the equivalent PVA/D_2O solutions. This observation is remarkably similar to the time-dependent aggregation effect in PVA/D_2O solutions and suggests that d-EA promotes aggregation. A small, ϕ_{d-EA} independent upturn can be observed in all scattering curves and can be attributed to the presence of d-EA microdroplets arising from liquid-liquid demixing of the mixtures.

Overall these results, summarised graphically in Figure 4, demonstrate the effect of degree of hydrolysis, concentration and addition of non-solvent on the solution structure of PVA in binary and ternary mixtures. A framework to describe the local 'solvent quality' and inter-chain distances is provided by a descriptive model based on the well-known Orstein-Zernike expression. The results give insight into the molecular scale and supra-molecular transformations, particularly aggregation, which may occur during solvent extraction pathways, common in polymer membrane and microparticle formation.

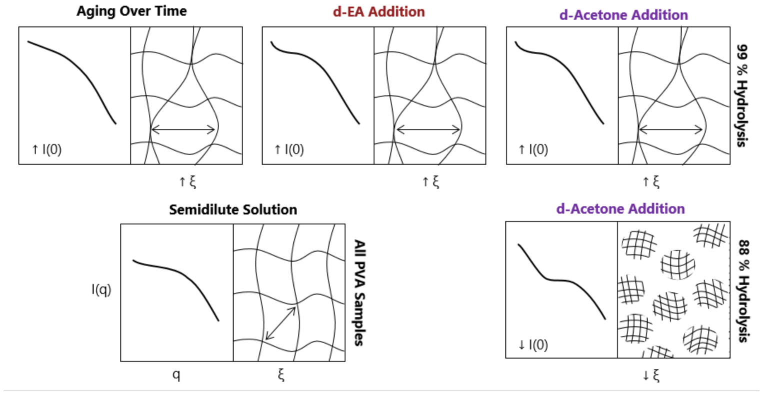

Figure 4: Schematic summary of the effect of degree of hydrolysis and addition of non-solvent on the structure of PVA solutions by SANS. Both a physical picture of the semidilute solution and an inset detailing the expected profile of SANS signal are included for the conditions studied here. PVA solutions, irrespective of degree of hydrolysis appear to be well-described by an Ornstein-Zernike type expression, typical of semidilute polymer solutions, with different local solvation characteristics dependent on degree of hydrolysis. However, the variation of ξ with concentration, much like PEO/D_2O solutions, does not follow expected scaling theories. Over time, the scattering from 99 % hydrolysed samples increases and can be described by an increase $I(0)$ and ξ in the solution. This is attributed to formation of intramolecular crosslinks in the solution, *i.e.* physical gelation. Addition of d-EA and d-acetone for both degrees of hydrolysis do not affect the high-q slope and therefore do not significantly change the local solvation of PVA. For 99 % hydrolysed PVA solutions addition of both non-solvents imparts the same effect as 'aging' on the SANS signal at intermediate to low-q and therefore promotes physical gelation. Addition of d-acetone to 88 % hydrolysed PVA solutions has a significantly different effect; $I(0)$ and ξ both decrease and a large upturn at low-q appears. This suggests that small clusters are formed and can be thought of analogously to fringed micelles.

References

[1] F. Horkay, W. Burchard, E. Geissler, and A. M. Hecht, "Thermodynamic properties of poly(vinyl alcohol) and poly(vinyl alcohol-vinyl acetate) hydrogels," *Macromolecules*, vol. 26, no. 6, pp. 1296–1303, 1993.

[2] B. Hammouda, D. Ho, and S. Kline, "Sans from poly(ethylene oxide)/water systems," *Macromolecules*, vol. 35, no. 22, pp. 8578–8585, 2002.