Experimental report

24/05/2016

Proposal:	**9-12-422**	**Council:**	4/2015

Title: Probing the thermoresponsive nature of poly(N-isopropylacrylamide) functionalsied silica nanoparticles using contrast variation

Research area: Soft condensed matter

This proposal is a new proposal

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Samples:
poly(N-isopropylacrylamide)
thiolated silica nanoparticles
poly(N-isopropylacrylamide) functionalised silica nanoparticles

Instrument	Requested days	Allocated days	From	To
D22	1	0		
D11	0	1	05/11/2015	06/11/2015

Abstract:

Smart nanoparticles are becoming increasingly more popular, as they allow the surface characteristics of nanoparticles to be manipulated to a specific job. Poly(N-isopropylacrylamide) (pNIPAM) is a well known thermoresponsive polymer which undergoes a coil to globule phase transition at 32 degrees C, becoming hydrophobic and aggregating. When this polymer is bound to the surface of nanoparticles, 2 effects are observed; a gradual decrease in particle size below 32 degrees C, followed by a sudden increase. Interestingly, the size remains very uniform both during and after the phase transition, suggesting a controlled aggregation, an effect not seen in the free polymer in solution. We hypothesize that the initial decrease is due to changes in the solvation shell (confirmed by looking at particle size in methanol and preliminary SANS data), but further temperatures are required to confirm this. Additionally, the apparent controlled aggregation is very interesting, as it shows the particle size can be easily manipulated which has applications in many fields, such as drug delivery. However further experiments are required to study this phenomenon, and determine the level of control.

This project aimed to look at the size and structure of poly(N-isopropyl acrylamide) (PNIPAM) functionalised silica nanoparticles, and how it changed with temperature. Using contrast matching, we focussed specifically on the polymer corona, aiming to identify changes therein. Based on DLS data, we see interesting size changes in PNIPAM-silica with increase in temperature, which appears to decrease in size initially, followed by an increase. The decrease was hypothesised to be due to changes in the hydration shell, and the increase due to particle aggregation.

Preliminary experiments found that a 20:80 % D_2O:H_2O mixture was needed to contrast match the silica core of nanoparticles (Fig 1)

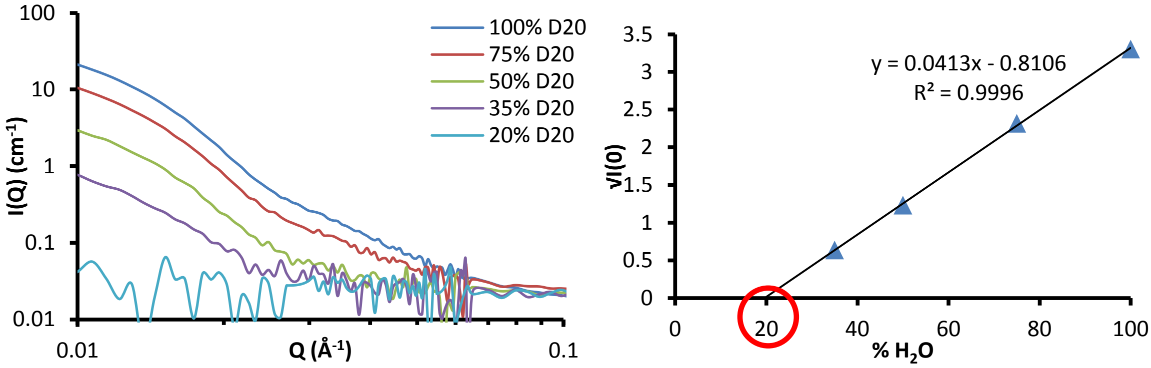

Fig 1 Preliminary experiments to determine the contrast match point of unfunctionalised silica nanoparticles

However, following data acquisition of the contrast-match scattering profiles, no contrast could be found, and the scattering profile remained flat with no structural features evident (Fig 2).

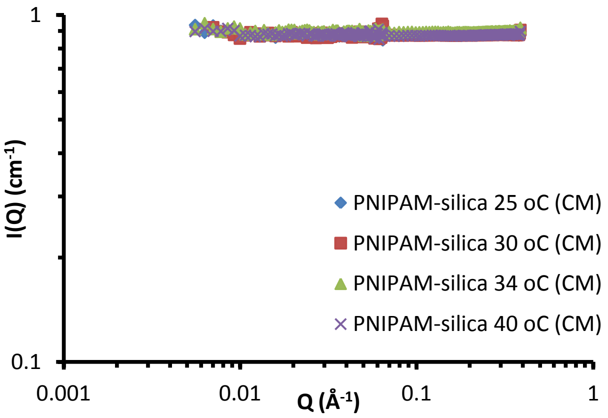

Fig 2 Scattering from contrast-matched PNIPAM-silica nanoparticles at different temperatures

Despite this, the particles were measured in 100% D_2O as well as the contrast matched data (Fig 3). These spectra did reveal information regarding the particles, which could be successfully fitted to a sphere model, Fig 3) revealing a particle diameter of 30 nm. The following fitting information was used; core SLD = 3.2×10^{-6} Å^{-1}, scale factor = 0.008, and PDI 0.39. No core-shell information could be derived to the highly hydrated corona, offering no contrast between that and the D_2O background.

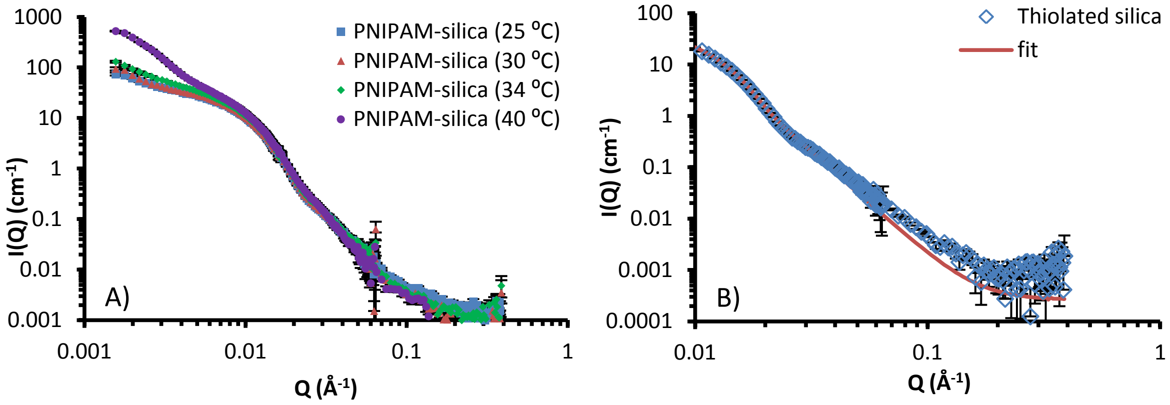

Figure 3 A) Raw scattering data for PNIPAM-silica nanoparticles at different temperatures, and B) fitting of unfunctionalised silica nanoparticles to a sphere model

Due to the high levels of hydration in the polymer corona is not possible to conclude if any structural changes are occurring; as the shell is not visible by SANS, and therefore any changes are undetected.

Finally, the particle-particle interactions were investigated in order to assess the low PDI seen with DLS. Here, data were fit to a linear-pearls model (at 25, 30, and 34 °C, Fig 4A-C), followed by a fractal model (40 °C, Fig 4D). Fitting parameters; core SLD $3.2\ \text{x}10^{-6}$ Å^{-1}, scale factor = 0.008, and PDI 0.42. These are found in Fig 4.

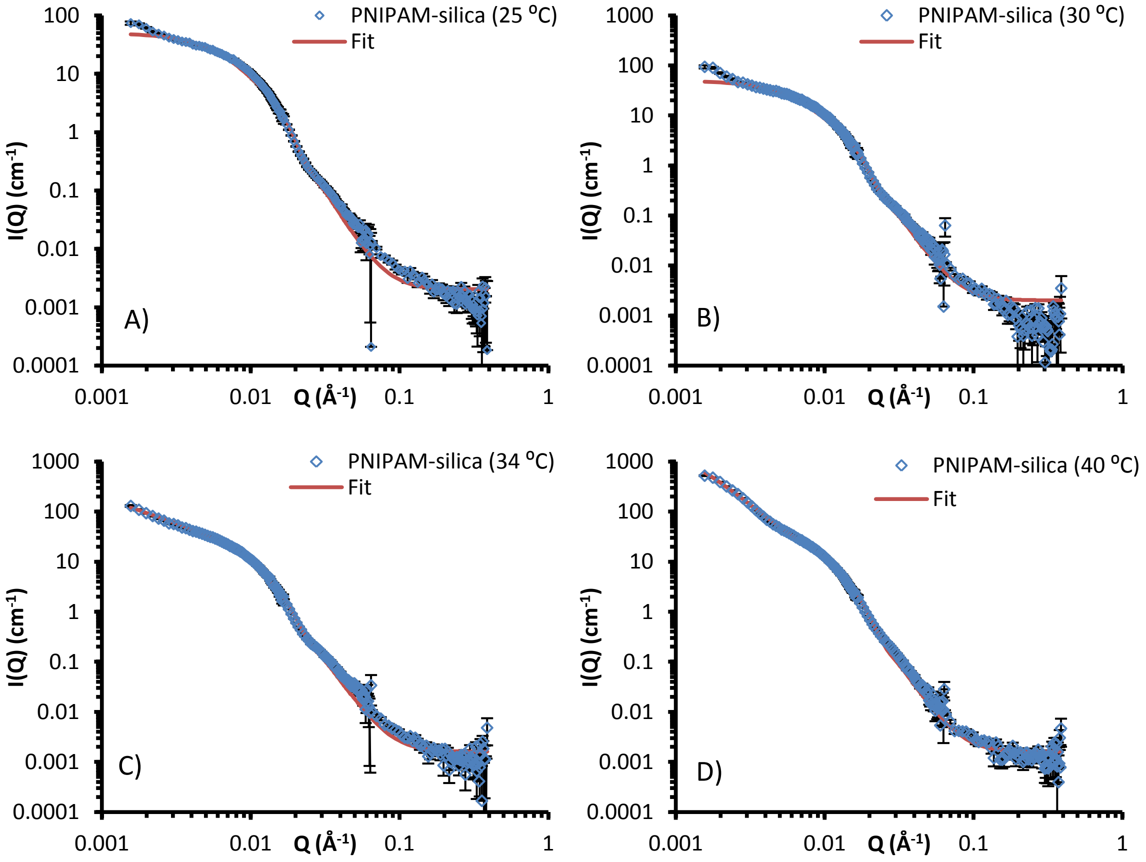

Figure 4 Fits to a linear pearls model (at 25, 30, and 34 °C, A-C, respectively), and fit to a fractal model (at 40 °C, D)

From these data, it is possible to conclude that at lower temperatures (i.e. below 30 ^{o}C) the particles are randomly distributed. This is represented by a very close proximity of particles to each other.

It should be noted that in fitting, the value representing number of pearls did not affect the fit, and changing this number did not alter the Chi^{2} of the fit, further suggesting particle agglomeration. However, at 34 ^{o}C, the point at which the particles undergo phase-transition, the particles become less tightly aggregated, but the number of particle interactions increases. This time, changing the number of pearls does alter the fit, suggesting only a limited number of particles are interacting with each other, confirming the equilibrium hypothesis discussed earlier. Finally, at 40 ^{o}C, the particles no longer fitted to a linear-pearl model, and instead were fitted to a fractal model. Here, it is possible to conclude that the final agglomeration have a well-defined structure (due to a fractal dimension of 2), with a defined size, as predicted by DLS. Given that the particle radius is 14 nm (diameter 28 nm), and the overall size of the aggregate is 84 nm, 3 nanoparticles are interacting to form this 3D structure. Depending on the special orientation of these particles, this data is corroborated by DLS. The 84 nm aggregate size predicted by SANS fits the DLS size of 106 nm at the same temperature (when one takes into consideration the addition of a hydration shell around the aggregate which is not detected by SANS).

The SANS data demonstrated here is in good agreement with the DLS data, and confirms the hypothesis that at higher temperatures, the functionalised nanoparticles are forming small clusters with a very uniform overall size. It is likely that the temperature will dictate how tight the interactions between the particles are given the changes observed in DLS. At high temperatures, the shrinking of the stabilizing corona (as detected using DLS and literature data; as it is not visible to SANS) induces the clustering, causing the proposed interactions.