Experimental report

25/11/2020

Proposal:	**9-11-1968**	**Council:**	10/2019
Title:	Temperature responsive binary gelation of pNIPAM microgels and a neutral triblock-copolymer surfactant		
Research area:	Chemistry		

This proposal is a new proposal

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Samples:	d7-NIPAM Synperonic PE/P105

Instrument	Requested days	Allocated days	From	To
D11	2	0		
D33	2	2	02/09/2020	04/09/2020

Abstract:

SANS will be used to study the structure of an adsorbed triblock-copolymer (PEO-PPO-PEO type) surfactant on pNIPAM microgels. It has been observed that when mixtures of pNIPAM microgels and triblock-copolymer surfactant are heated above the volume phase transition temperature of pNIPAM, the sample transitions from a liquid to a gel. This transition is fully reversible. We have demonstrated that the gelation is a result of the association of the polymers at elevated temperatures, however the nature of the association is unclear. We aim to use SANS to reveal the structure of the adsorbed polymer, to elucidate whether the gel network results from polymer micelles bridging the microgel particles, or whether the surfactant penetrates inside the microgel periphery and this results in gelation. This study will ultimately lead to a greater understanding of this binary gelation and aid with future design of these systems.

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Instrument: D33

Dates: 02.09.20-04.09.20

Introduction

Microgels are soft, cross-linked polymer particles that form stable colloidal suspensions. Due to their polymeric composition, microgels are responsive to external stimuli including light, pH and temperature, with the result being a change in the particle size. Poly(N-isopropylacrylamide) (pNIPAM) is a temperature responsive polymer which can be synthesised to form microgels. pNIPAM has a volume phase transition temperature (VPTT) at 32°C where the particles collapse and expel water from the interior. This VPTT is constant for pure pNIPAM systems, irrespective of concentration, molecular weight or architecture, but can be altered by the presence of additives such as salt and surfactant.

It was recently discovered that at temperatures in excess of the VPTT, mixtures of pNIPAM and a triblock-copolymer surfactant undergo a transition from liquid to solid gel, this transition is fully reversible and can be repeated several times with temperature cycling. The gelation is also accompanied by a change from transparent liquid to opaque white solid. The gels that result are initially space spanning but contract over a time scale much greater than the collapse of the individual pNIPAM microgels. During this collapse, the gels retain the shape of the container that they form in.

Our previous investigations indicated that the gelation results from the association of the two species in solution, rather than that of the common gelation regime due to depletion, where non-adsorbing polymer causes colloidal aggregation. This association is highlighted by an increase in the hydrodynamic radius of the pNIPAM particles in the presence of the surfactants above the VPTT at low concentrations. Confocal microscopy of fluorescently labelled polymers showed that both species are present in the gel network. We here use SANS to investigate the structure of the aggregates formed at elevated temperatures to provide further evidence of the polymer associating.

Experiment

We measured the scattering from mixtures of deuterated pNIPAM microgel particles in two contrasts: contrast matched with the solvent (D_2O:H_2O mixture) in order to look in detail at the structure of the triblock-copolymer surfactant, and in H_2O to see the particles and if there is evidence of an adsorbed surfactant layer. The microgel particles are 100 nm in diameter when swollen in water, and 50 nm in diameter when collapsed, measured using dynamic light scattering. The polymer micelles are 20 nm in diameter. When these polymers are mixed and heated, the size of the objects observed using dynamic light scattering are approximately 110 nm in diameter.

We investigated the effect of temperature on the behaviour of these mixtures, running the experiment at 25°C and 40°C to see if there was any evidence of a temperature responsive association. The temperature responsive behaviour of pure pNIPAM and triblock-copolymer we characterised in both solvents, along with mixtures of the two species. The concentration of pNIPAM was fixed at 0.3 wt% in all samples and the concentration of triblock-copolymer was varied. The concentrations of triblock-copolymer investigated were 0.5, 0.65 and 0.75 wt%, to see how concentration effected the interaction between the components.

In total, 7 samples were run at two temperatures (25°C and 40°C) and in two contrasts (H_2O:D_2O (35:65 by weight) and H_2O).

Sample	**Concentration**
pNIPAM	0.3 wt%
Triblock-copolymer	0.5 wt%
	0.65 wt%
	0.75 wt%
pNIPAM + triblock-copolymer	0.3 wt%, 0.5 wt%
	0.3 wt%, 0.65 wt%
	0.3 wt%, 0.75 wt%

Results and discussion

The SANS data is still being fitted, but the initial conclusions from the results are summarised below.

The pure triblock-copolymer samples have been fit using the polymer micelle model available in SASview. The fits obtained are comparable to ones included in the literature for these samples. The pure pNIPAM microgel samples have been fit using the Lorentz model at all temperatures and the sphere model at 40°C, both available in SASview. The Lorentz model indicated that the correlation length inside the microgels decreased with temperature as the microgels collapsed. The sphere model was only used the fit the samples at 40°C as below this temperature the microgels are fuzzy and do not fit well to a spherical form factor. The sphere fit indicated the radius of the particles was approximately 28 nm at 40°C, comparable to DLS data for the particles.

Included in Fig. 1 is an example of the scattering obtained for samples containing 0.75 wt% triblock-copolymer and 0.3 wt% pNIPAM. The scattering from 0.65 wt% and 0.5 wt% triblock-copolymer samples looked similar except for the intensities being lower due to the lower concentrations. The data indicates that at low temperatures (25 °C), there is no interaction between the triblock-copolymer and the pNIPAM microgels. In H_2O, the scattering looks almost identical to pure pNIPAM for the mixtures (b) and the object is of comparable size to pure pNIPAM. In the D_2O:H_2O mixture the curve looks almost identical to pure pNIPAM, with some evidence of a larger object a low Q, this object is of comparable size to the pure pNIPAM microgels so it was concluded this was due to pNIPAM scattering as the particles are not perfectly contrast matched (a).

At elevated temperatures there is evidence of an interaction between pNIPAM and triblock-copolymer. In the H_2O contrast, there is evidence of a large object forming, much larger than pure pNIPAM at this temperature. Little can be concluded about the triblock-copolymer scattering in this contrast. Fitting the object using the sphere model (SASview) indicated it was approximately 160 nm in diameter, which is larger than a swollen pNIPAM particle (110 nm) (d). In the D_2O:H_2O contrast more can be concluded about the triblock-copolymer behaviour. There is evidence that a larger object forms again in this contrast, approximately 160 nm like seen in H_2O. Free triblock-copolymer micelles remain in solution as there is still a strong signal for the micelles in the scattering, however, this scattering has a lower intensity than for the pure triblock-copolymer at equivalent temperature and concentration (c). From the absolute intensity of the scattering signal for the micelles, approximately 35% of the triblock-copolymer is absorbed inside the pNIPAM microgels causing the scattering from the larger object. The percentage of absorbed surfactant increased with decreasing triblock-copolymer concentration.

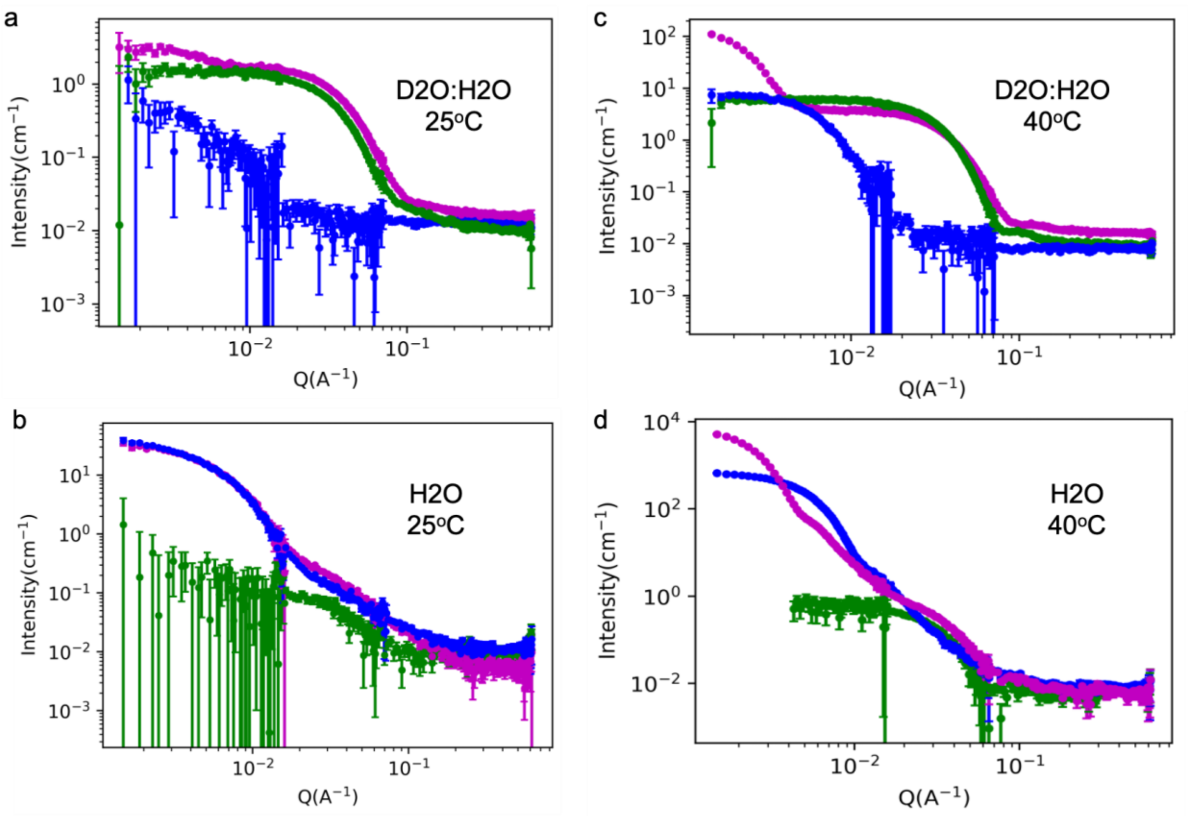

Figure 1: SANS curves obtained for mixtures of pNIPAM (0.3 wt%) and triblock-copolymer (0.75 wt%). The green curve is the scattering from pure triblock-copolymer, the blue curve is the scattering from pure pNIPAM and the purple curve is the scattering from mixtures.

From this data, it is concluded that the triblock-copolymer absorbs inside the microgels, preventing the particles from fully deswelling. At higher concentrations this results in the particles undergoing gelation at elevated temperatures, due to the increased van der Waals attractions between these larger, more hard sphere-like microgel particles. The scattering data indicates that this association only occurs at elevated temperatures, hence the gelation only occurs at elevated temperatures.