Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information

Reversible temperature-controlled gelation in mixtures of pNIPAM microgels and non-ionic polymer surfactant

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Figure 1 contains the NMR spectrum for d7-NIPAM used to synthesise deuterated pNIPAM microgels. NMR revealed that the d-NIPAM monomer had become partially hydrogenated, where the peak at 1.16 ppm would not been seen for the fully deuterated d7-NIPAM sample. As a result, the d-NIPAM is assumed to be d5-NIPAM for the scattering length density calculations.

Figure 1: NMR spectrum for d7-NIPAM monomer used to synthesise deuterated pNIPAM microgels. The predicted structure of d7-NIPAM is also included in the figure. The integration of the peak at 1.16 ppm was used to predict the degree of deuteration in the d-NIPAM monomer.

Figure 2 shows the deswelling data for all of the particles used in this investigation, measured using dynamic light scattering (DLS) (section 2.6 main text). The key information taken from this data is summarised in Table 1 (main text). All of the particles used in this investigation have a similar deswelling ratio. The rhodamine B labelled particles have a significantly larger diameter than the unlabelled and fluorescein labelled particles.

Figure 3 shows the fluorescence emission intensity measured for samples containing Nile red dye. Fluorescence intensity measurements were carried out using a Horiba Scientific

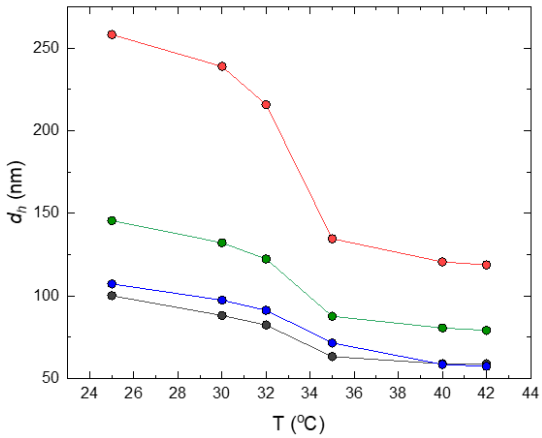

Figure 2: Dynamic light scattering data for all the microgels used as part of this investigation. Unlabelled pNIPAM 1 (blue), unlabelled pNIPAM 2 (black), rhodamine B labelled, uniformly cross linked pNIPAM (red), fluorescein labelled pNIPAM (green).

FluoroMax-4 spectrofluorimeter. The excitation wavelength used was 530 nm and slit width 1 nm. A Peltier device was used to achieve temperature control. Nile red is a solvatochromic dye, with an environmentally dependent emission wavelength. The fluorescence measurements were taken at 25°C and 45°C, to see where the dye preferentially resides for the range of environments used in this investigation. It can be observed that the emission of Nile red is different when comparing pure pNIPAM (λ_{max}=640 nm) and triblock-copolymer samples (λ_{max}=620 nm). It can also be observed that the emission in the mixed samples is similar to that of the pure triblock-copolymer emission (λ_{max}=620 nm).

Figure 4 contains DLS data of the supernatant surrounding the gels. The supernatant was collected from a sample that forms an incomplete gel (blue, 2 wt% pNIPAM, 10 wt% triblock-copolymer) and a complete gel (green, 6 wt% pNIPAM, 8 wt% triblock-copolymer), chosen to represent example behaviours from the phase diagram for the mixtures (Figure 3 main text). The DLS results show that the supernatant surrounding the incomplete gels contains both pNIPAM and triblock co-polymer, as indicated by the increase in hydrodynamic radius above the volume phase transition temperature, a feature for low concentration mixtures of pNIPAM and triblock-copolymer (Figure 4a main text). DLS was also used to look at the supernatant surrounding samples that form complete gels, the results show that the

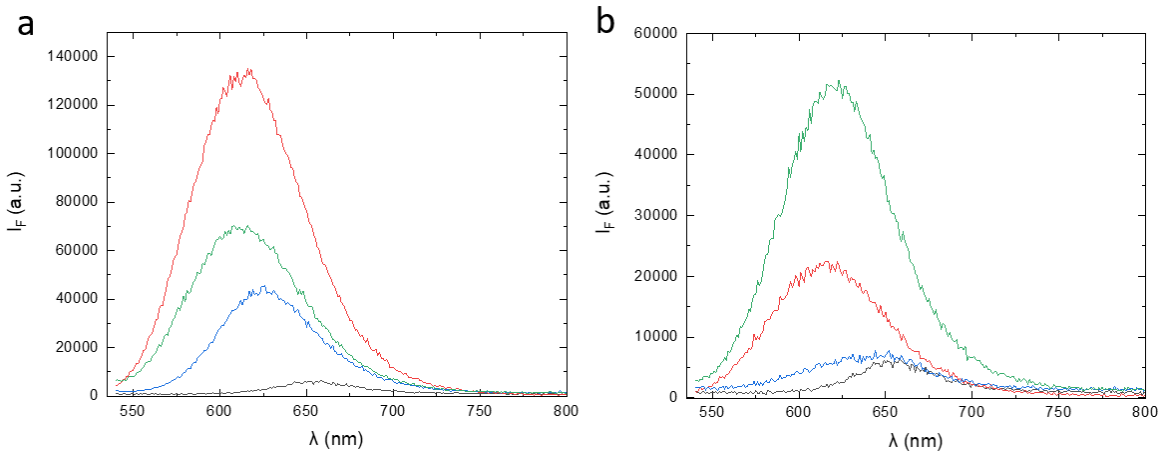

Figure 3: Fluorescence emission spectra for samples, pure water (black), pNIPAM (blue), triblock-copolymer (red), pNIPAM and triblock-copolymer (green). Polymer concentrations were 0.1 wt%, Nile red concentration 8.3 mM, data collected at 25°C (a) and 45°C (b).

supernatant contained no microgels, only the triblock-copolymer micelles.

Figure 5 shows the phase diagram for poly-ethgylcol (PEG) and pNIPAM microgels mixtures. The PEG used has a Mw of 100,000 (Sigma Aldrich), with a radius of gyration of 15.9 nm,[1] comparable to the size of triblock-copolymer micelles. The phase diagram looks similar to that of pNIPAM and triblock-copolymer, where there is evidence of a macroscopic gel forming at high concentrations of pNIPAM and PEG. However, a complete gel network is not observed over the concentration range studied. This indicates that the interaction between pNIPAM and PEG is weaker than that between pNIPAM and triblock-copolymer, illustrating that the driving force for gelation is enhanced due to the presence of the hydrophobic poly-propyleneoxide region. The poly-propyleneoxide block is what causes the polymer micelles to form, due to the polymer being insoluble in water. This aggregation results in a dense poly-ethylene oxide layer to interact with the NIPAM, hence the increased ability of the poly-propyleneoixde block to form gels compared with the linear polymer. When looking at the gels they also appear stable to dilution, where a 5 wt% pNIPAM and 3 wt% PEG sample was diluted by a factor of five, and remained a gel at elevated temperatures. This data indicates that the PEG group does interact with pNIPAM, and is capable of associating to the pNIPAM microgels resulting in gelation. This shows that the PEG

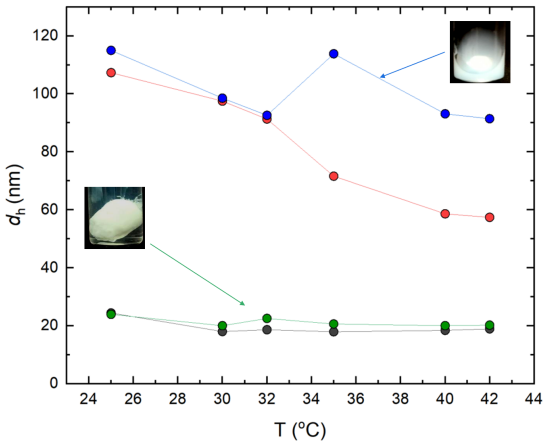

Figure 4: Dynamic light scattering data of the supernatant surrounding a gel sample, pure triblock-copolymer (black), pure pNIPAM (red), supernatant of a sample containing 2 wt% pNIPAM and 10 wt% triblock-copolymer (blue), supernatant of sample containing 6 wt% pNIPAM and 8 wt% triblock-copolymer (green). The supernatant was removed with a pipette after the samples were held above the T_{VPT} for several minutes to allow syneresis to occur, by submerging the sample into freshly boiled water. Supernatant was taken from 0.5 g mixtures of pNIPAM and triblock-copolymer, and diluted with deionised water to obtain a large enough volume for dynamic light scattering.

blocks on the polymer are responsible for bridging the particles.

Figure 6 highlights how the measured polydispersity (PDI) changes with temperature for mixtures of pNIPAM microgels and triblock-copolymer surfactant, and compares the change in PDI to the pure pNIPAM microgel samples. The PDI data is taken from the DLS data summarised in Figure 4 (conventional pNIPAM) and Figure 6 (UCL pNIPAM) in the main text. It can be seen that above the T_{VPT} for pNIPAM, there is a decrease to the recorded polydispersity for mixtures of pNIPAM and triblock-copolymer surfactant. This provides evidence for the polymers associating above these temperatures.

Figure 7 contains the SANS data collected for mixtures of pNIPAM and triblock-copolymer surfactant at 25°C (left) and 40°C (right). The data is taken from Figure 5 in the main text but with the error bars included. The raw SANS data can be accessed through the following link, DOI: 10.5286/ISIS.E.RB1910080.

Figure 8 contains the deswelling data for the d-pNIPAM particles synthesised as part of this work. The temperature at which pNIPAM is fully deswollen is shifted to higher

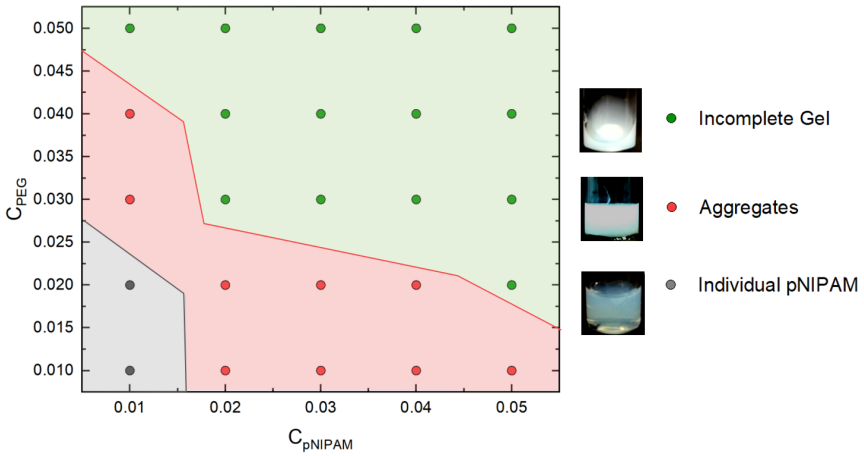

Figure 5: Phase diagram for mixtures of pNIPAM and 100,000 MW PEG. All data was collected after samples were held above the T_{VPT} for several minutes to allow syneresis to occur, by submerging the sample into freshly boiled water. Grey circles indicate where no obvious interaction was observed, red circles represent liquid samples with macroscopic aggregates, green circles represent gels without all of the pNIPAM incorporated in the network. Coloured regions of the phase diagram are to guide the eye. All concentrations are expressed as weight fractions.

temperatures for the d-pNIPAM sample, therefore the SANS experiment was conducted at 25°C and 40°C, to ensure the measurement was run above temperatures where the polymers associate, which occurs above the T_{VPT} of pNIPAM.

Figure 9 contains a Guinier plot for mixtures of pNIPAM and triblock-copolymer surfactant at 40°C. The Guinier region was assumed to be $\mathrm{q}R_g < \sqrt{3}$. This resulted in a radius of gyration for the sample of 55 nm. The radius of a collapsed microgel is approximately 25 nm and the diameter of the triblock-copolymer micelle is approximately 20 nm at 40°C. It is assumed that the scattering signal is from the triblock-copolymer surfactant, as the pNIPAM microgels are contrast matched with the solvent. Therefore, this radius of gyration is consistent with a slightly swollen pNIPAM microgel decorated with triblock-copolymer surfactant micelles, rather than aggregates of pNIPAM microgels.

Figure 10 contains a scheme highlighting the difference in interaction between UCL pNIPAM and conventional pNIPAM microgels. The triblock-copolymer surfactant cannot penetrate the periphery of the UCL microgels due to the increased density of cross links near the particle surface. Next to each scheme is a picture of a high temperature sample of a

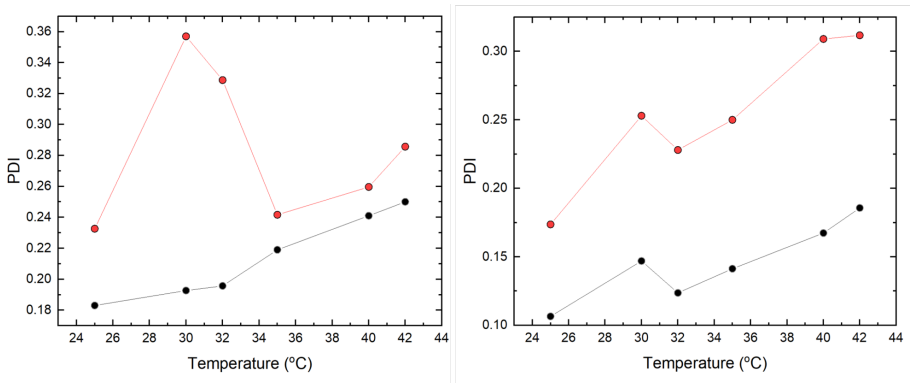

Figure 6: Polydispersities taken from the dynamic light scattering data for mixtures of pNIPAM and triblock-copolymer surfactant. Pure pNIPAM sample (black), pNIPAM mixed with triblock-copolymer (red). Conventional pNIPAM (left), uniformly cross linked pNIAM (right). The concentration used for this study was 0.3 wt% pNIPAM, 0.75 wt% triblock-copolymer.

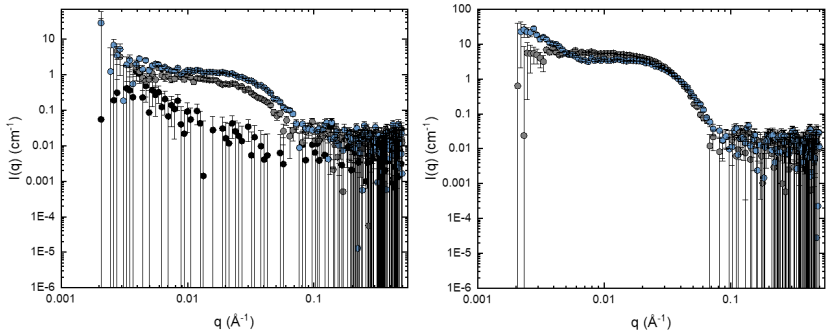

Figure 7: SANS data collected for mixtures of pNIPAM and triblock-copolymer surfactant. The left is data collected at 25°C, the right data collected at 40°C. The black plot is pure d-pNIPAM (0.3 wt %), the grey plot is pure triblock-copolymer (0.75 wt%) and the blue plot is a mixture of d-pNIPAM (0.3 wt%) and triblock-copolymer (0.75 wt%).

mixture of triblock-copolymer and pNIPAM. It can be seen that mixtures of conventional pNIPAM and triblock-copolymer form the gels described throughout this work, however the UCL particle samples remains a liquid at concentrations far above the concentration gels are expected to form. The conventional pNIPAM has been labelled with a fluorescein monomer and the UCL labelled with a rhodamine B monomer. Microgels using both of these fluorophores were found to form gels with conventionally synthesised particles, highlighting that the presence of the dye is not responsible for this observation.

Figure 11 shows a comparison between the turbidity of pNIPAM particles with a hetero-

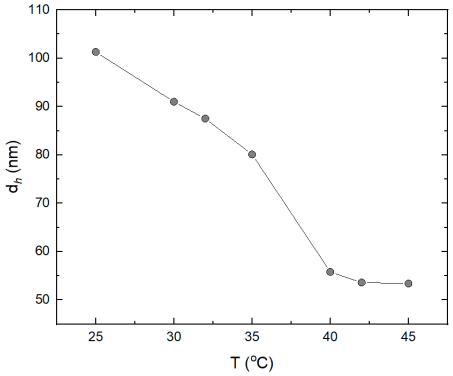

Figure 8: Dynamic light scattering data collected for the d-pNIPAM microgels used as part of the SANS investigation.

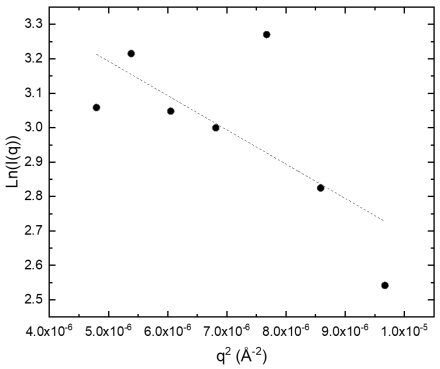

Figure 9: Guinier plot for low q region of pNIPAM (0.3 wt%) and triblock-copolymer (0.75%) mixtures at 40°C, taken from SANS data collected for the mixtures.

geneous cross link distribution and uniformly cross linked pNIPAM particles. The particles are labelled with equivalent amounts of rhodamine B dye. In the literature, uniformly cross linked particles are evidenced by the sample being more transparent than the conventionally synthesised particles. The uniformly cross linked particles have a lower turbidity than the conventionally cross linked particles, indicating a uniform cross link distribution in the sample.[2,3] The particles are smaller than those synthesised in the literature, therefore, the difference in turbidity is more subtle. The particles used in this work are similar in diameter, with the conventionally synthesised particles being slightly smaller (uniformly cross linked 260.0 nm, conventional pNIPAM 181.5 nm at 25°C). Due to the feeding method used to synthesise the particles, the uniformly cross linked particles (0.11 PDI) also show a smaller polydispersity than the conventionally synthesised particles (0.25 PDI), measured using DLS.

Figure 10: Photograph comparing turbidity of conventional pNIPAM particles (181.5 nm, left) and uniformly cross linked (260.0 nm, right). Concentration 0.5 wt%. The particles are labelled with rhodamine B dye.

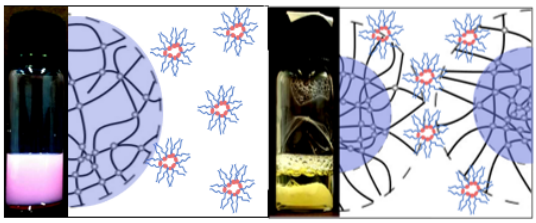

Figure 11: Comparing samples of uniformly cross linked pNIPAM particles (bottom) with pNIPAM microgels synthesised using precipitation polymerisation (top). The concentration of the samples imaged are 4 wt% pNIPAM and 4 wt% triblock-copolymer. Images of microgels are taken after being held above the T_{VPT} of the NIPAM by submerging the sample into freshly boiled water for several minutes, to allow syneresis of the samples to occur. Next to each image of the macroscopic gel is an scheme representing the behaviour of the species in solution. The UCL particles and the pNIPAM are labelled with Rhodamine B and fluorescein respectively to provide clarity.

This again indicates that the particles are uniformly cross linked.[2]

Figure 12 highlights how the addition of triblock-copolymer to collapsed microgels, does not cause aggregation. Triblock-copolymer and pNIPAM samples were preheated in boiling water prior to mixing, to ensure the pNIPAM microgels were collapsed before interacting with the polymer. Once the samples were mixed there was no evidence of gel networks forming, showing that penetration of the triblock-copolymer into the microgel particles is key to the gelation mechanism (Figure 12, center). The sample was then cooled to room temperature and again submerged into boiling water (Figure 12, right), the sample formed a gel, showing that the concentration used for this investigation is capable of forming gel networks. A pure pNIPAM microgel sample was also submerged into boiling water and the sample remains liquid, showing that the presence of the triblock-copolymer is necessary for

gelation to occur (Figure 12, left).

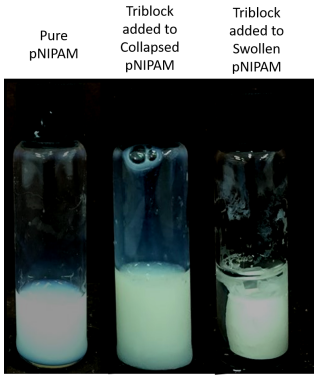

Figure 12: Images of pNIPAM microgel samples. The samples have been placed in boiling water to dewell the pNIPAM particles. Pure pNIPAM particles (6.45 wt%), to highlight how the sample remains a liquid at high temperatures and concentrations (left), pNIPAM and triblock copolymer preheated before mixing, remains a liquid (middle), pNIPAM and triblock copolymer not preheated before mixing (right), the sample concentration used was 3 wt% pNIPAM, 10 wt% triblock-copolymer.

References

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