1. Background

- Thermoresponsive self-assemblies have shown potential for a wide range of applications.
- Poly(N-isopropyl acrylamide) (pNIPAM) is one of the most widely studied thermoresponsive polymers and shows a lower critical solution temperature (LCST) close to body temperature (~32 °C).
- One limitation of pNIPAM is that it exhibits slow reversibility (hysteresis) upon cooling in certain systems.
- This phenomenon is not fully understood and numerous reports show seemingly contradictory data.

2. Aims and Objectives

- To synthesise a series of micelles with thermoresponsive pNIPAM coronas and varying core hydrophobicity by copolymerising varying amounts of a hydrophilic monomer (dimethyl acrylamide, DMA) into the core-forming hydrophobic block composed of poly(n-butyl acrylate) (nBA).
- To study the macroscopic and nanoscale behaviour using a combination of variable temperature DLS and SLS, turbidimetry and microcalorimetry in order to understand how these behaviours change with small changes in the micellar structure.

3. Polymer Synthesis and Micelle Preparation

- pNIPAM-b-pnBA-co-DMA diblock copolymers were synthesised by RAFT polymerisation from a pNIPAM macroCTA (mCTA) to yield polymers with varying mol % of a hydrophobic monomer (nBA) in the second block (1-5).
- The diblock copolymers were self-assembled into micelles in aqueous solution using a solvent switch technique.
- The micelles were analysed by multi-angle dynamic and static light scattering (DLS and SLS) at 20 °C and were shown to have increasing Nagg values with mol % nBA in the core-forming block.

4. Variable Temperature DLS and SLS

- The micelles were analysed by multi-angle DLS and SLS at temperatures ranging from 10-25 °C.
- Partial Zimm analysis revealed the core radii, which when combined with Ragg from DLS, allowed the coronal chain length across the temperature range to be calculated.
- The pNIPAM chains began to respond by collapsing at temperatures well below the known LCST.
- The trend in the coronal chain collapse was independent of Nagg in the regime investigated.

5. Microcalorimetry and Turbidimetry Analysis

- The micelles were heated above the LCST of pNIPAM and the change in turbidity was measured.
- Macroscopic precipitation of the micelles lead to a decrease in the transmitted light.
- The cloud point (the temperature at which the transmittance reaches half of the original transmittance at T<LCST) was shown to be independent of Nagg when heating the sample.
- The change in heat capacity with varying temperature, measured by microcalorimetry, also showed the same transition temperature for all the micellar systems studied.
- The thermal hysteresis, (the difference between the cloud points from turbidimetry, obtained from heating and cooling the sample) was shown to increase with increasing core hydrophobicity.
- Micelles with higher Nagg took longer to resuspend upon cooling.

6. Conclusions

- Micelles of tunable Nagg were synthesised by controlling the ratio of hydrophobic to hydrophilic monomer in the core-forming block of well-defined amphiphilic diblock copolymers.
- Collapse of the pNIPAM coronal chains was observed by variable temperature light scattering prior to the cloud point, however the degree of coronal collapse over the temperature range investigated was not dictated by Nagg.
- The transition temperatures observed by turbidimetry and microcalorimetry were independent of Nagg. However, the thermal hysteresis showed a positive correlation with core hydrophobicity, and therefore Nagg
- These results demonstrate that consideration of the macroscopic and molecular behaviour of responsive polymers at both the unimer and particle level must be considered for real-world applications.

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8. References