Temperature and pH responsive micelles from the controlled polymerization of NIPAM

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We have synthesised a series of temperature responsive poly(N-isopropylacylamide) [polyNIPAM] amphiphiles, and studied their self-assembly behaviour as a function of molecular weight, temperature and pH.

The temperature responsive polymer polyNIPAM undergoes a phase separation in aqueous solutions at a lower critical solution temperature (LCST) of approximately 33°C. This stimulus responsive property creates a host of possible applications, and a great deal of effort has been expended on the synthesis and study of polyNIPAM based microgels, films, membranes and block copolymer micelles. This last group has received particular attention in recent years with the advent of easily controlled block lengths and compositions using controlled polymerization techniques such as RAFT. However, precise control of the stimuli-response is still elusive, and argument still abounds in the literature as to the exact mechanism of the LCST.

Using a RAFT control agent with a well defined dodecyl-based hydrophobic tail, we have synthesised a series of single block polyNIPAM amphiphiles with a range of molecular weights. By using a short, well-defined hydrophobic block we fix two of three packing parameter constraints (i.e. the critical length and the volume per tail) and just study the effect of the area per head group as a function of both molecular weight and temperature. By addition of a pH responsive end group to the polyNIPAM block, we are able to switch the amphiphiles between non-ionic and charged by a simple change in solution pH.

The LCST was found to decrease with a decrease in the molecular weight. This is in contrast to the behaviour of single block polyNIPAM which has an increase in its LCST with decreasing molecular weight. Using small-angle neutron scattering (SANS) we show that the amphiphiles form micelles up to their LCSTs, and that the micelles undergo morphological changes prior to phase separation.