

Aggregation of PNIPAM microgels During the Coil-Globule transition

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Abstract

Aqueous solutions of the cross-linked thermally responsive polymer poly(N-isopropylacrylamide) (pNIPAM) have been studied extensively in recent years [1]. This polymer has been particularly well-studied because it has a volume phase transition temperature (VPTT) just below body temperature and is thus thought to have potential bio-medical and cosmetic applications.

Below the VPTT, water is a good solvent for pNIPAM and the polymers in solution behave as soft colloids. At these temperatures, the cross-linked polymer coils swell and, even at concentrations as low as 4% w/w, exhibit viscoelastic behaviour and may form colloidal crystals. In contrast, above the VPTT, water is a poor solvent and the polymer coil collapses to form a globular latex. The volume excluded by these collapsed particles at high temperature is much reduced, and so the suspension viscosity lies close to that of water.

At low ionic strength (< 10 mM NaCl), the coil-globule transition is thought to proceed without aggregation. However just above the VPTT, when the coils have nearly completely collapsed, there is a jump in both solution viscosity and intensity of scattered light, indicating particle aggregation. The increase in both properties is small and they pass through a maximum over a few °C (this contrasts with the behaviour at high ionic strength, when macroscopic gelation occurs and persists over a wide range of temperatures). This behaviour is exhibited even in the absence of added salt and at polymer concentrations down to 0.2% w/w. On cooling, no such unusual behaviour was found and the changes with temperature are monotonic.

Results from viscosity, dynamic light scattering and microelectrophoresis will be presented for homo-pNIPAM microgels with a range of cross-link density.

The conjecture is that polymer chain entanglement may occur during particle collapse, leading to weak flocculation. The tendency of pNIPAM microgels to aggregate on heating may present significant challenges in applications of these that require complete colloidal stability.

[1] Saunders B. R. and Vincent B., *Advances in Colloid and Interface Science* 1999, 80, 1-25.
Pelton R., *Advances in Colloid and Interface Science* 2000, 85, 1-33.