

The Temperature-controlled Flocculation of Crosslinked Latex Particles

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Aqueous dispersions of poly(*N*-isopropylacrylamide) latex are shown to be stable at 25 °C in the presence of simple electrolytes and non-adsorbing polymers; at 40 °C, however, flocculation of the particles takes place as a result of charge screening and depletion forces operative in the system; this process is shown to be reversible, with the particles redispersing on cooling to 25 °C.

The flocculation of hard sphere particles in the aqueous environment by the addition of simple electrolytes is a well-established phenomenon in colloid science.¹ Similarly, flocculation, brought about by the presence of non-adsorbing polymer^{2,3} has been reported for particulate dispersions both in the aqueous⁴ and non-aqueous⁵ environments. The critical aggregation temperature of microgel particles of poly(*N*-isopropylacrylamide) (NIPAM) copolymerised with acrylamide has been studied by Pelton and Chibante⁶ using CaCl₂. Measurements were made as a function of the fraction of acrylamide incorporated in the polymerisation process and it was found that the temperature at which aggregation was first observed increased linearly with increasing acrylamide concentration. The critical aggregation temperature of a homopolymer sample of poly(NIPAM) as a function of electrolyte is discussed in this paper and the reversibility of the process with respect to temperature is illustrated. We further report the stability behaviour of poly(NIPAM) in the presence of a non-adsorbing polyelectrolyte in an attempt to illustrate the unique characteristics of the poly(NIPAM) latex.

Poly(NIPAM) particles were prepared by the free radical polymerisation of NIPAM in water at 70 °C, in the presence of *N,N'*-methylenebisacrylamide, following the procedure des-

cribed by Pelton and Chibante.⁶ Following dialysis against distilled water, transmission electron micrographs showed the particles to be monodisperse spheres having a mean diameter of 450 nm. Poly(styrene sulfonate) M_w 46 000, (M_w/M_n 1.05; M_w = weight average mol mass, M_n = number average mol mass) was purchased from Polymer Laboratories Ltd, Shropshire. The temperature dependency of the particle diameter of poly(NIPAM) latex was determined by photon correlation spectroscopy using a Malvern instrument type 7027 dual LOGLIN digital correlator equipped with a krypton-ion laser (λ = 530.9 nm). The intensity of scattered light was measured at 90°. Particle size was measured from 25 to 50 °C in increments of 5 °C both on heating and cooling using an external water bath.

Stability experiments were carried out using dispersions containing 0.1% microgel particles and various amounts of sodium chloride made up to a total volume of 5 cm³. The samples were placed in a water bath at 25 °C and allowed to stand overnight. The extent of any aggregation in the dispersion was estimated from the wavelength dependence of the turbidity of the dispersions⁷ where $n = -[d(\log \text{turbidity})/d(\log \text{wavelength})]$. The same experiment was repeated by placing the samples in a water bath 40 °C, and also at both

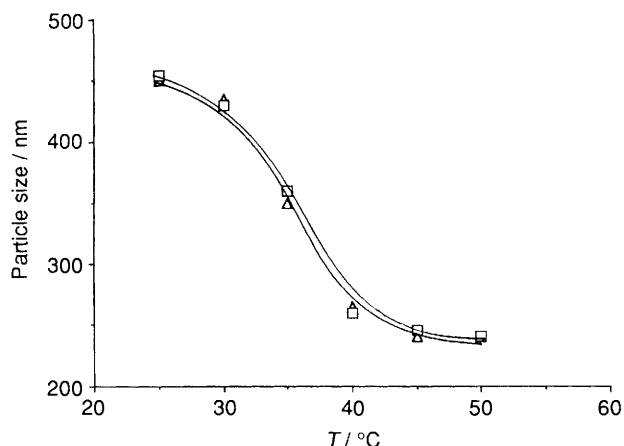


Fig. 1 A plot of particle size against temperature for a 0.01% dispersion of poly(NIPAM) latex in water (Δ : heating; \square : cooling)

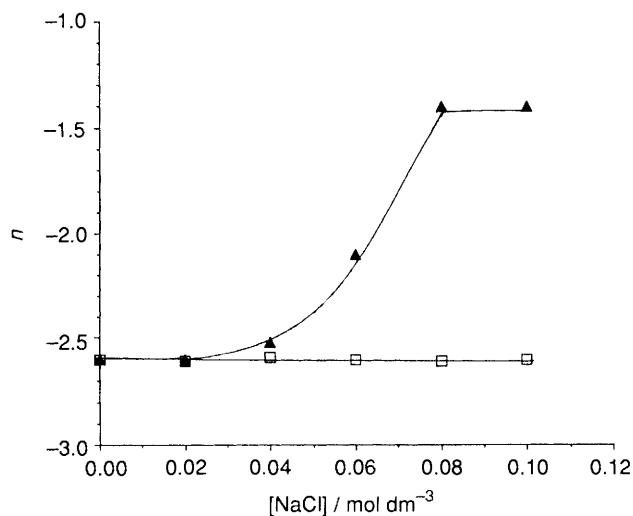


Fig. 2 A plot of $d(\log \text{absorbance})/d(\log \text{wavelength})$ (n) for a 0.1% dispersion of poly(NIPAM) latex at increasing concentrations of NaCl at 25 (\square) and 40 °C (\blacktriangle)

temperatures using poly(styrene sulfonate) in water and a background electrolyte of 0.01 mol dm^{-3} NaCl.

Fig. 1 illustrates the decrease in particle diameter of the poly(NIPAM) latex particles on heating. The initial diameter of 450 nm at 25 °C decreased to 240 nm at 50 °C resulting in an eightfold decrease in the volume of the particle. On cooling, however, the particles expanded and adopted their original particle size. This procedure was found to be fully reversible over a number of heating and cooling cycles with no hysteresis taking place between the heating and cooling curves. The particles remained dispersed in water over the temperature range (25–50 °C) studied.

In the presence of 0.1 mol dm^{-3} NaCl at 25 °C the dispersion remained stable, however, on repeating the same experiment at 40 °C, aggregation of the poly(NIPAM) latex takes place. This is illustrated in Fig. 2. The flocculated sample in 0.06 mol dm^{-3} NaCl at 40 °C redispersed on cooling to 25 °C, with the value of n decreasing to -2.6 which is consistent with the particles becoming fully redispersed. This process of heating the samples, inducing flocculation, then cooling and allowing the particles to redisperse can be repeated many times with the process remaining fully reversible on each occasion. Fig. 3 illustrates the change in absorbance of the dispersion at 592 nm with increasing temperature. It can clearly be seen that the onset of

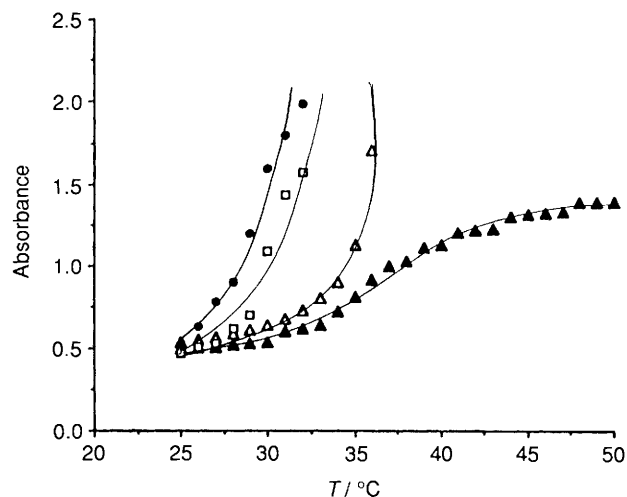


Fig. 3 A plot of turbidity at 592 nm against temperature for 0.1% dispersion of poly(NIPAM) in different solutions of NaCl (\blacktriangle : in water; \triangle : in 0.1 mol dm^{-3} NaCl; \square : in 0.5 mol dm^{-3} NaCl; \bullet : in 1 mol dm^{-3} NaCl)

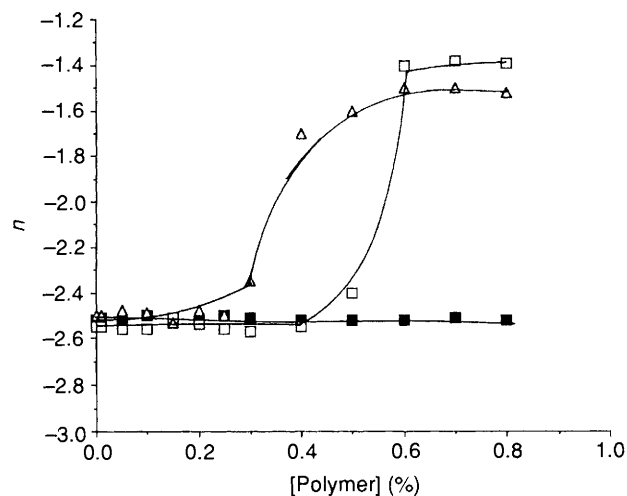


Fig. 4 A plot of $d(\log \text{absorbance})/d(\log \text{wavelength})$ for a 0.1% dispersion of poly(styrene sulfonate) at increasing concentrations of poly(styrene sulfonate) at 25 (\blacksquare) and 40 °C (\square) in water at pH 7 and in 0.01 mol dm^{-3} NaCl (\triangle)

aggregation takes place at lower temperatures as a result of increasing the electrolyte concentration in the dispersion. On cooling all the samples to 25 °C, the particles slowly redispersed.

Fig. 4 shows the stability of the poly(NIPAM) particles in the presence of poly(styrene sulfonate). At 25 °C the particles remained dispersed up to the highest polymer concentration studied at 0.8%. On repeating the same experiment with the dispersions at 40 °C, flocculation was found to take place at a polymer concentration of 0.6% and above. The samples remained flocculated while the temperature was maintained at 40 °C. On cooling the flocculated dispersions to 25 °C and gently inverting the container several times, the flocculated samples redispersed fully with their ' n ' values simultaneously decreasing from -1.3 to -2.7 . This process was also found to be reversible over a number of heating and cooling cycles. Fig. 4 also illustrates that when the same experiment was carried out in a background electrolyte of 0.01 mol dm^{-3} NaCl, an insufficient electrolyte concentration to destabilise the particles at 40 °C, the critical flocculation concentration (CFC) of sodium poly(styrene sulfonate) is reduced to 0.35%.

The decrease in diameter, of the poly(NIPAM) lattices on heating from 25 to 40 °C is a consequence of the increase in the χ parameter for the *N*-isopropylacrylamide–water system. This facilitates more polymer–polymer contacts, hence the particles contract and shrink substantially. At 25 °C the particles can be envisaged as spongy microgels with polymer chains extending away from the surface resulting in a steric barrier and therefore preventing flocculation. Further, the microgels are swollen with solvent and have a very low Hamaker constant, consequently their van der Waals attraction energy would be very small. At 40 °C the particles shrink forcing out any solvent from the interstitial spaces and become very similar to hard spheres in their nature. Aggregation of the particles now takes place as the Hamaker constant increases and screening of the charges at the particle surface allows close enough approach for coagulation to occur. We shall report in the near future a series of calculations confirming the increasing Hamaker constant with increasing temperature.

In the presence of poly(styrene sulfonate) at 40 °C the particles flocculate as a consequence of depletion forces operative in the system. It is believed that the polymer does not adsorb onto the particles from water as both species have negative charges. Other hard sphere colloids have been reported to undergo a depletion flocculation with poly(styrene sulfonate)^{4,8} under similar conditions but at a fixed temperature. The flocculated latex on cooling to 25 °C redisperses, as the very soft nature of the particles at this temperature would require very high polymer concentrations to cause destabilisation. Clarke and Vincent⁹ studying the stability of non-aqueous microgel dispersions of polystyrene in the presence of free polystyrene polymer, reported that the CFC of polymer increased significantly as the microgel became swollen and 'softer'. Similarly in a recent publication Milling *et al.*¹⁰ investigating the effect of grafted chain coverage on the

depletion flocculation of sterically stabilised silica particles demonstrated that the CFC of the polystyrene also increased with increasing surface coverage of grafted polymer *i.e.* 'softness' of the particle.

This behaviour is believed to be unique with no other known examples of temperature-induced depletion flocculation having been reported in the scientific literature. In the presence of 0.01 mol dm⁻³ NaCl the electrostatic repulsive potential is greatly reduced as a result of the charges at the particle surface being screened and, therefore, flocculation into a secondary minimum arising from depletion forces takes place more readily. This behaviour is consistent with the current theories of colloid stability.

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