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The rheology of deformable and thermo-responsive microgel particles

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This paper describes the preparation and characterization of two monodisperse, hydrophilic polymer latices, with different particle diameters, of poly-*N*-isopropylacrylamide crosslinked with *N*,*N*′-methylenebisacrylamide. The uncrosslinked polymer is water soluble and non-ionic and exhibits a lower consolute solution temperature of about 31–32°C. The latex was prepared via a surfactant-free dispersion polymerization route using water as a solvent at a polymerization temperature of 70°C. The physical properties of the resulting latex were strongly dependent on temperature. At high temperatures (65°C), the particle diameters were 23 and 50 nm, whilst at 25°C they were 130 and 470 nm. This five- to ten-fold increase in the particle diameter corresponds to a 100- to 1000-fold increase in volume. Consequently, the rheological properties, both continuous and oscillatory shear, of these systems are strongly dependent on temperature. Volumetric and particle size changes observed by photon correlation spectroscopy and differential scanning calorimetry thermal analysis were in agreement, confirming that the volume phase transition is controlled and influenced by the same factors observed in the swelling/deswelling behaviour of microgels. The viscoelastic properties of these systems and the elasticity of the dispersion decreased as the temperature was increased and the fluid changed from a predominantly elastic to a viscous material. In addition, at lower temperatures, all the studies showed an increase in the storage modulus of the dispersion with increasing particle concentrations. The rheology of the dispersions as a function of the volume fraction of the particles was monitored and the viscosity and shear-thinning increased as volume fraction increased.

(Keywords: swelling; microgels; rheology)

INTRODUCTION

Colloidal microgels are of great interest and importance to many industrial disciplines such as the pharmaceutical, paints, ink, textile and cosmetic industries. There has been considerable effort in determining and understanding the rheological properties of dense suspensions and the majority of this work has concentrated on hard, non-deformable particles which are simple to deal with experimentally and theoretically[1–3]. Polystyrene and silica particles are good models for the more complex industrial formulations; several studies have shown that the viscoelastic properties of ordered latices are very dependent upon volume fraction[3–7]. Any increase in volume fraction naturally leads to a decrease in mean particle separation and consequently to a more elastic dispersion. Interparticle separation can also be modified if one changes the particle size at the same time, keeping the volume fraction constant. However, in industrial formulations, soft particles are frequently encountered. Starch granules (corn flour) in foods, for example, swell up as hydrogel particles at high volume fractions, which may be attained at relatively low solids fractions; such particles modify the rheological properties of foods such as tomato ketchup. Crosslinked poly-*N*-isopropylacrylamide (polyNIPAM) has characteristics analogous to corn flour, exhibiting a swelling/deswelling behaviour in aqueous solutions[8,9]. This system swells and deswells in response to changes in temperature and solvent composition. On cooling, the solubility of the polymer increases and the particles swell, as shown schematically in *Figure 1*. Thus at room temperature, particles swollen with solvent (water in this case) are formed; in effect, we have a colloidal hydrogel. On heating, the particle contracts back to a hard sphere. Thus the rheological properties of these materials should prove to be a model for the rheology of soft deformable and compressible particles frequently encountered in industrial formulations.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (CH_2:CHCONHCH(CH_3)$_2$) was obtained from Eastman Kodak Company (Rochester, USA) in flaked and dry form and was used without further purification. *N*,*N*′-Methylenebisacrylamide (MBAAm) ((H_2C.CHCONH_2).CH_2) and potassium persulfate ($K_2S_2O_8$), both in dry form, were purchased

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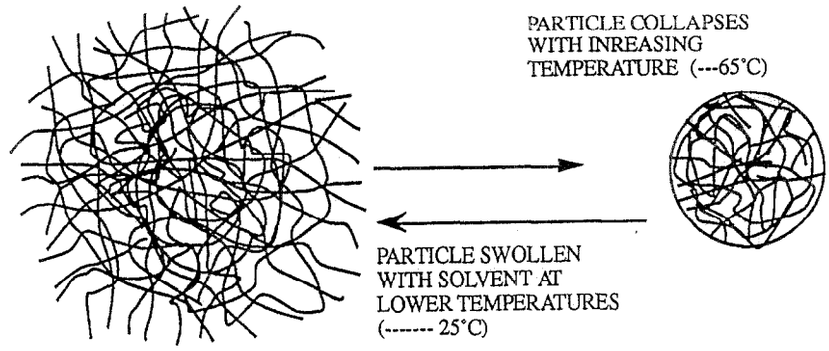

Figure 1 Schematic representation of the swelling of microgel particles with decreasing temperature

Table 1. A summary of the conditions used to prepare the polyNIPAM latex, and their final particle size at room temperature

Sample no.	Size at (25°C nm)	NIPAM (g)	$NaHCO_3$ (g)	pH	MBAAm (g)	$K_2S_2O_8$ (g)	H_2O distilled (ml)	Solids (% w/w)	Cloud point (°C)	NIP:MB ratio	Stirring time (h)	Synth. temp. (°C)
1	130	12.5	0.25	9.0	2.5	1.0	1000	12.5	31.9	10:1	24	70
2	470	12.5	0.00	8.0	2.5	0.8	1000	17.5	34.5	10:1	21	70

from Aldrich and were used without further purification. The water was distilled and passed through a water polishing unit to remove trace organic impurities and particulate materials prior to use.

Preparation of polyNIPAM microspheres

Two monodisperse polyNIPAM latices of different particle diameters (sample nos 1 and 2) were prepared under similar specified and controlled conditions as indicated in *Table 1*. The method adopted is similar to that used by Goodwin *et al.*[1] for the preparation of polystyrene latices. Each sample had $12.5\,g\,l^{-1}$ of the monomer polyNIPAM. The monomer for each sample was dissolved in 1000 ml of doubly distilled water (at 20°C) in a 5 l round-bottomed flask equipped with a condenser, a nitrogen inlet and a stirrer. It was necessary that nitrogen should be bubbled into this mixture to remove oxygen, which acts as a radical trap to terminate polymerization, and for the reaction to be subsequently kept under a blanket of nitrogen. The temperature of the flask was raised to 70°C. Into the same flask, a measured amount of MBAAm was added (see *Table 1*) 30 min after the reactor vessel had equilibrated at 70°C. After a thorough mixing of both NIPAM and MBAAm, potassium persulfate (as given in *Table 1*) was added to initiate polymerization. This mixture began to develop turbidity after heating for a short period of time. At this stage, a seed polymer developed and hence polymerization continued to the point where the whole mixture became milky. The reaction was continued for 24 h under mild stirring. The latex was then filtered through glass wool and poured into dialysis tubing. The latex was then dialysed against pure water for at least two weeks, with daily water changes, to remove any small molecular impurities in the latex.

For the rheology measurements, the latex was first concentrated by placing the dialysis bags under a hydrostatic pressure. This procedure could only concentrate the latex to ~5% solids fractions of latex. For higher solids fractions, the dispersion was centrifuged at $15\,000\,rev\,min^{-1}$ to isolate free water from the latex. Latex dispersions produced in this way attained a solids concentration of around 15%; more dilute dispersions were produced by dilution. In all cases, the final volume fractions were determined gravimetrically.

Photon correlation spectroscopy

Photon correlation spectroscopy (p.c.s.) was used to determine particle size as a function of temperature for polyNIPAM microgel particles. The technique measures the Brownian motion of particles and directly measures the diffusion coefficient, from which the hydrodynamic particle size may be estimated. In this work a Malvern 4700 correlator was used.

A second measurement was done using a Malvern mastersizer S3.01, which uses laser diffraction for determining the particle size, and a comparison of the results from the two instruments did not show significant difference. A temperature range of 20–65°C was covered and care was taken at high temperatures to ensure that there were no heat convection currents in the sample.

Differential scanning calorimetry

The differential scanning calorimetry (d.s.c.) experiments were performed by placing a small sample of the latex (~10 mg, typically at a solids fraction of 0.1) dispersed in water into a d.s.c. pan. The pans were hermetically sealed, placed into a Perkin–Elmer DSC and scanned over a temperature range of 5–105°C, held isothermally for 5 min and then cooled over the same temperature range.

Rheological measurements

Steady state, shear stress (τ)–shear rate ($\dot{\gamma}$) curves were obtained using a Bohlin rheometer (Bohlin Reologi, Lund, Sweden), interfaced with an IBM PC. From the shear rate sweep ranges ($0–600\,s^{-1}$) the $\tau–\dot{\gamma}$ curves were

obtained. A Bingham model was applied, where:

$$\tau = \tau_B + \eta_{pl}\gamma \quad (1)$$

From equation (1) the yield value τ_B was obtained by extrapolation of the linear portion of the shear stress–shear rate curve to $\dot{\gamma} = 0$, and the plastic viscosity, η_{pl}, was obtained from the linear portion of the curve.

The same rheometer was also used in the oscillatory shear mode. For the present measurements a frequency range of 0.01–5 Hz was chosen. In oscillatory shear measurements, one initially fixes the frequency (0.1 Hz) and measures the rheological parameters as a function of the strain amplitude. This enables one to obtain the linear viscoelastic region, where the complex modulus (G^*), the storage modulus (G') and the loss modulus (G'') are independent of applied strain at any frequency. Once this linear region is established, then measurements are made as a function of frequency at a fixed amplitude. In these experiments, a strain of 0.002 or less ensured operation in the linear elastic region. The rheometer performs the test by running the cup back and forth in a sinusoidal manner. The phase angle shift, δ, is automatically computed from the time displacement between the sine wave of the stress and the strain (Δt), i.e. $\delta = \omega\Delta t$, where ω is the frequency (in radians). The moduli are calculated from the stress and strain amplitudes (τ_0 and γ_0, respectively) and from the phase angle shift (δ) by the following equations:

$$G^* = \tau_0/\gamma_0 \quad (2)$$

$$G' = G^* \cos\delta \quad (3)$$

$$G'' = G^* \sin\delta \quad (4)$$

RESULTS AND DISCUSSION

In *Figure 2* the particle size of the polyNIPAM latex particles is plotted as a function of temperature. It may be seen that as the temperature increases above 30°C the particle size decreases and becomes constant above 60°C. It may be noted that for both latices the particle diameters decrease by a factor of five to six, which corresponds to a 100- to 200-fold increase in particle volume. The temperature range over which there is a drastic change in particle size (30–50°C) corresponds closely to the θ temperature of polyNIPAM (35°C).

Figure 3 shows a d.s.c. curve for a 10% solids fraction polyNIPAM latex in water. An endothermic, reversible

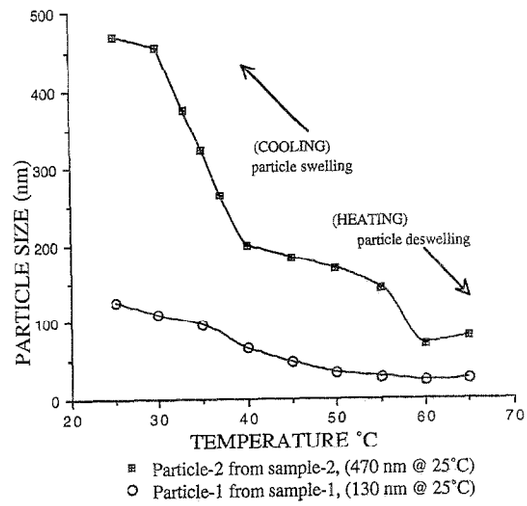

Figure 2 Particle size of the polyNIPAM particles plotted as a function of temperature

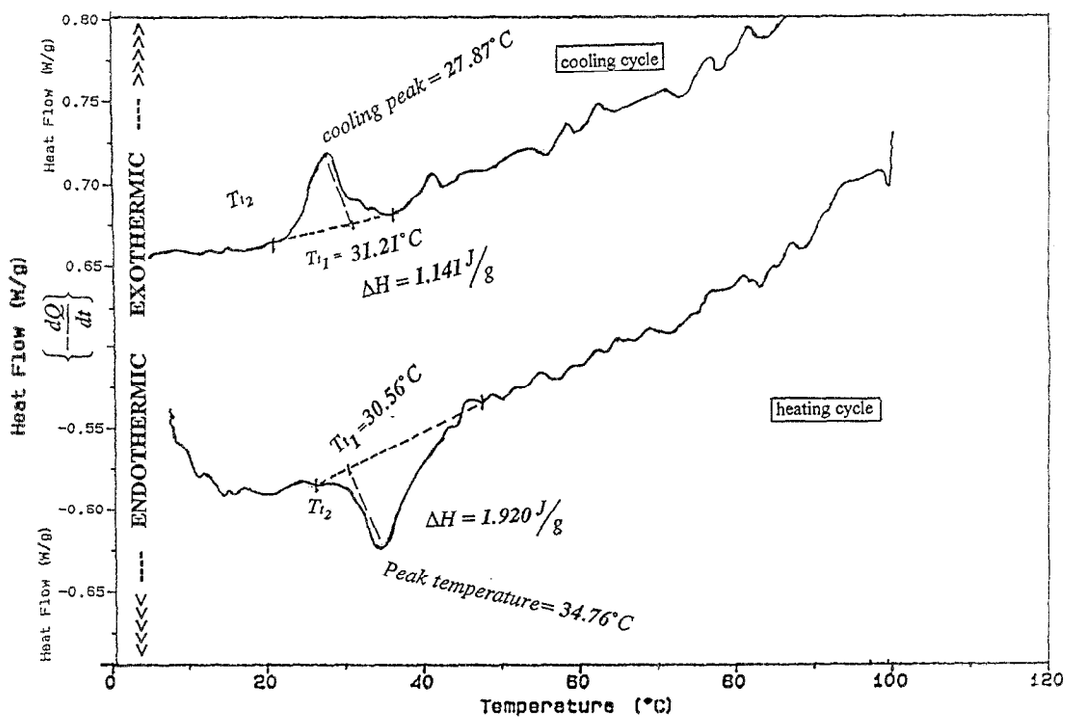

Figure 3 D.s.c. curve for heating and cooling of polyNIPAM latex: sample no. 1 with specimen weight of 10.606 mg heated from 5 to 105°C at a heating rate of 10°C min^{-1}

peak is noted at 30–45°C. This corresponds to the temperature region where the particle size is changing and hence to the region where the polyNIPAM particles are undergoing their swelling–deswelling transition.

For the rheology experiments, the NIPAM latex was concentrated. *Figure 4* is a plot of the viscosity of this latex at 28°C. The latex is clearly shear-thinning, with the viscosity falling by some four orders of magnitude over the shear rate range studied. A yield value of 0.4 Pa was noted for this dispersion. The data in *Figure 4* show a high shear limiting viscosity, i.e. a region where the viscosity is independent of the shear rate. In *Figure 5* this high shear limiting viscosity is plotted as a function of the solids fraction of the polyNIPAM. It can be seen that at low solids fractions the viscosity increases drastically, for example the viscosity is three orders of magnitude greater than that of water at the higher solids fractions, and is also around three orders of magnitude greater than the viscosity of, say, a polystyrene latex at a similar volume fraction. The explanation for this enhanced viscosity is that the particles are swollen with water such that their effective volume fraction is much higher than the solids fraction would suggest. Indeed, from their rheological properties, these microgel particles are perhaps more akin to a polymeric gel, such as xanthan, than to colloidal particles. However, in *Figure 5* it is clear that the viscosity of the smaller particles, at a given solids fraction, is greater than that of the larger particles. This is in agreement with studies on hard colloidal dispersions such as polystyrene latex particles.

Materials with shear-thinning flow curves of this type are frequently viscoelastic and in *Figure 6* elastic and storage moduli data are presented. The elastic modulus, particularly at higher frequencies, is considerably larger than the loss modulus. This is ascribed to the strong interactions between the swollen microgel particles at this temperature, 20°C (note that at this solids fraction of particles, the volume fraction of swollen particles is going to be greater than the close-packed limit for rigid spheres, i.e. 0.74). The moduli values are also high, again indicating that strong particle interactions are present in this system.

Figures 7 and *8* show the variation in the viscosity and moduli with temperature, respectively. At low shear rates

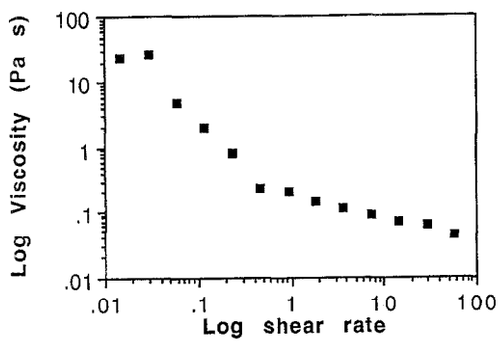

Figure 4 Viscosity *versus* shear rate (s^{-1}) for 12.5% polyNIPAM dispersions at 28°C

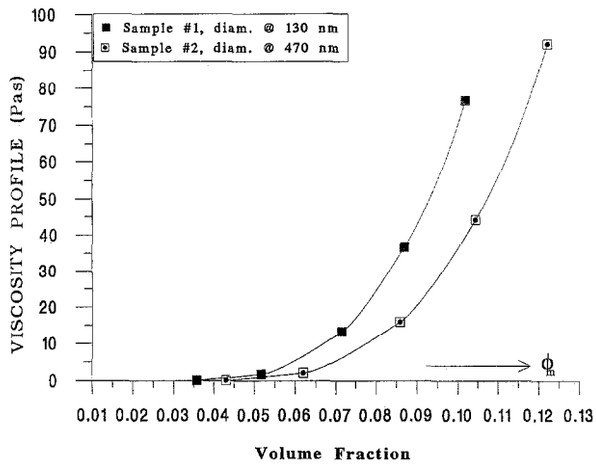

Figure 5 High shear limiting viscosity plotted as a function of solids fraction of polyNIPAM latex at 28°C, for two different particle sizes

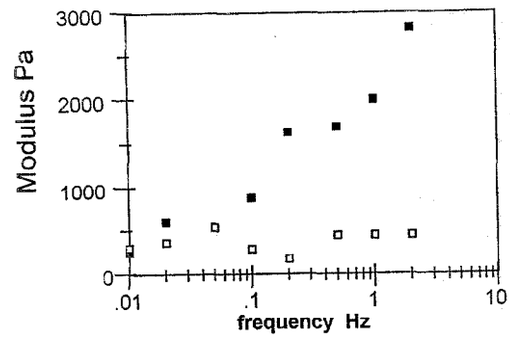

Figure 6 Elastic modulus (solid symbols) and loss modulus (open symbols) plotted as a function of frequency for polyNIPAM latex at 28°C

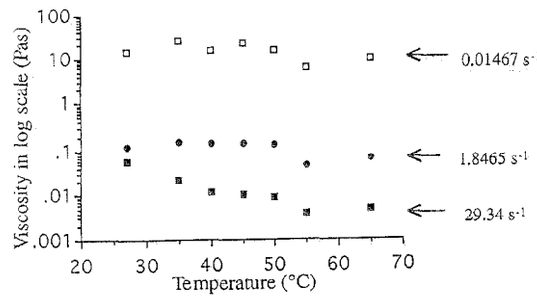

Figure 7 Plot of viscosity *versus* temperature at three shear rates for polyNIPAM latex: □, 0.01467 s^{-1}; ●, 1.846 s^{-1}; ■, 29.34 s^{-1}

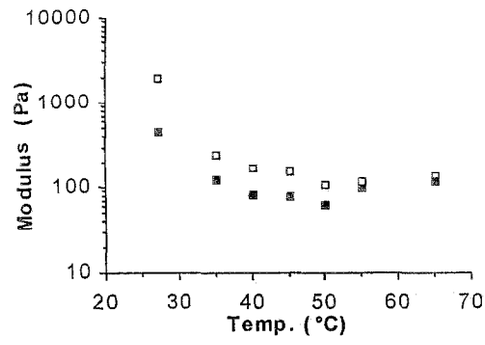

Figure 8 Plot of the elastic modulus (□) and loss modulus (■) at a frequency of 1 Hz, and as a function of temperature for the polyNIPAM latex particles

there is little temperature dependence (*Figure 7*), but at higher shear rates it may be noted that the viscosity gradually decreases with increasing temperature and comes to a limiting value at around 55°C (*Figure 7*). This temperature effect is more marked in the moduli data (*Figure 8*). Here the elastic modulus, which is expected to be the most sensitive rheological parameter to any change in structure in the dispersion, decreases by an order of magnitude between 28 and 50°C and thereafter becomes constant. Similar trends are also observed in the loss moduli data.

Thus it is clear that increasing temperature decreases the 'rheology' of the dispersions and, moreover, this may be directly related to the shrinkage of the particles which occurs on increasing the temperature, as shown in *Figure 2*.

Note that the particles remained colloidally stable over the entire temperature range during these experiments owing to the presence of the sulfate groups on the surface of the particles.

CONCLUSIONS

The decrease in diameter of polyNIPAM particles when heated (25–65°C) is a consequence of the solubility for the *N*-isopropylacrylamide and water system. The θ temperature for the uncrosslinked polymer is around 30°C, thus the polyNIPAM particles also collapse at around this temperature. The existence of this phase change is confirmed by the d.s.c. results. Not surprisingly, this swelling/deswelling phenomena gives rise to significant rheological changes. The elastic modulus was the most sensitive to temperature and was observed to decrease by an order of magnitude between 28 and 50°C.

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