

The preparation and physico-chemical properties of poly(*N*-ethylacrylamide) microgels

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The preparation and physico-chemical characterisation of a novel thermosensitive microgel dispersion of anionic poly(*N*-ethylacrylamide), poly(NEAM), is reported. Dispersions were prepared by the single-step emulsion polymerisation of *N*-ethylacrylamide in water, in the presence of *N,N'*-methylenebisacrylamide as a cross-linking agent and ammonium persulfate as the initiator. Transmission electron micrographs of the microgel dispersions showed that the reaction time greatly influenced the physical characteristics of the resultant microgel particles, with monodisperse spheres, having a mean diameter of 414 ± 21 nm, being obtained following a 24-h preparation. Using high sensitivity differential scanning calorimetry (HSDSC) a kinetically limited phase transition was observed for a 2.6% (w/w) dispersion, having an excess specific heat capacity maximum at 78.2°C (at a scan rate of 60 K h⁻¹). The thermodynamic parameters and turbidimetric changes (as a function of temperature, pH and electrolyte concentration) associated with this transition are reported. In the presence of 1 mol dm⁻³ sodium chloride, the temperature at which this conformational transition occurs decreases with a corresponding increase in the calorimetric enthalpy of the transition. A reversible aggregation of the microgel particles was also observed on heating a 0.7% (w/w) dispersion to 80°C in the presence of 3 mol dm⁻³ sodium chloride. Experimental measurements of the reduced viscosity, η_{red} , of a 3% (w/w) dispersion, as a function of temperature and electrolyte concentration, provided further evidence of a temperature-induced conformational change with respect to the poly(NEAM) chains, resulting in a more compact conformation. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Colloidal microgels are intramolecularly cross-linked polymeric particles, usually dispersed in an aqueous solvent, with particle diameters in the range of 100 nm to 1 μ m. They behave like micro-sponges, allowing solvent molecules to enter the interstitial spaces within their porous structure causing them to swell. The preparation, characterisation and applications of these systems have been described in a comprehensive review by Murray and Snowden¹. The physico-chemical properties of microgels are related to conformational changes that occur in response to changes in environmental conditions such as pH, temperature and ionic strength. An example of a thermosensitive microgel is the aqueous based poly(*N*-isopropylacrylamide), poly(NIPAM) system. This is prepared by the free radical emulsion polymerisation of NIPAM in water at 70°C, in the presence of *N,N'*-methylenebisacrylamide as a cross-linking agent, using the method first described by Pelton and Chibante². Poly(NIPAM) undergoes a fully reversible conformational change on heating, in water, with the particles shrinking and swelling in response to changes in temperature. The thermodynamic parameters and turbidimetric changes associated with this transition have been reported by Murray et al.³. Recently, copolymers of NIPAM and acrylic acid have been prepared which are also thermosensitive⁴, however, the transition temperature at which the particles shrink is greatly influenced by the pH of

their solvent environment due to the introduction of ionisable carboxyl groups. Copolymer-type microgels offer opportunities for utility in applications over a much wider range of transition temperatures than the homopolymer poly(NIPAM) microgels. Due to their unique properties, microgels have found use in a large number of applications including controlled flocculation, a property exploited by the field of enhanced oil recovery⁵. Further, as a result of their sponge-like nature they have also been considered as potential uptake and release systems for metal and other ion impurities in water⁶. The aim of the present study is to increase the range of applications of such materials even further by attempting to prepare an aqueous-based, thermosensitive microgel having a higher phase transition temperature than that of poly(NIPAM). The hydrogel, poly(*N*-ethylacrylamide), has been synthesised and characterised by Ito et al.⁷, and has been shown to have a transition temperature of 72°C. The work presented here is believed to be the first reported preparation of a poly(NEAM) microgel system. The physico-chemical properties of this microgel are discussed with direct comparisons being made to poly(NIPAM).

EXPERIMENTAL

N-Ethylacrylamide, NEAM, was obtained from Dajac laboratories inc. (Feasterville, PA, USA) and was used without further purification as were *N,N'*-methylenebisacrylamide, BA (BDH, Electran, Molecular Biology Grade) ammonium persulfate, APS (BDH, AnalaR) and NaCl (Aldrich, A.C.S.).

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Typically, for a 1 l preparation, NEAM (6.0 g) and BA (0.6 g) were dissolved in deionised water (800 ml) and placed into a 2 l, three-necked, round-bottom flask. The reaction flask was immersed in a water bath, heated to 80°C and the monomer solution was stirred under a nitrogen atmosphere. On reaching this temperature, APS (0.65 g), dissolved in 200 ml water, was added to the monomer solution. The reaction mixture was then heated to 90°C for 24 h with continuous stirring. The solution was then cooled and kept refrigerated at 5°C prior to use. A small sample was removed before refrigeration and concentrated for transmission electron microscope analysis.

Calorimetric measurements made on the dispersions were carried out using a MicroCal, MC-2D ultrasensitive differential scanning calorimeter (MicroCal Inc., Northampton, MA, USA) interfaced to an IBM 486/SX computer for instrumental control and data acquisition. Samples were run against the appropriate reference sample (H₂O or H₂O containing NaCl). Reference samples in both cells were used to obtain the baselines which were subsequently subtracted from the sample scans. During scanning all samples were kept under an atmosphere of nitrogen to suppress bubble formation. Calorimetric data was obtained at scan rates of 10, 30 and 60 K h⁻¹. Data acquisition and analysis was carried out using the DA2 software package, supplied by the instrument manufacturer.

The turbidity of the microgel dispersions was measured as a function of temperature, pH and electrolyte concentration using a Lambda 2 (Perkin-Elmer) spectrophotometer, interfaced to an IBM 486/SX computer for data acquisition and also connected to a programmable temperature scanning water bath which was used at a scan rate of 1 K min⁻¹. The temperature in the sample cell was monitored using a platinum thermocouple temperature probe. The turbidity of the dispersions was measured against distilled water in the range 40–90°C.

The temperature-induced flocculation of a 0.7% (w/w) poly(NEAM) dispersion in the presence of 3 mol dm⁻³ sodium chloride was studied by visual inspection of the samples prepared in glass vials, heated in a water bath to 80°C, with photographs being taken of the destabilised dispersion.

Experimental measurement of the reduced viscosity, η_{red} , of both a 3% (w/w) poly(NEAM) and 2% (w/w) poly(NIPAM) dispersion, as a function of temperature and also electrolyte concentration for the poly(NEAM) dispersion, was carried out using a 'size A' Ostwald viscometer. All measurements were made in a thermostatically controlled water bath, regulated to at least $\pm 0.02^\circ\text{C}$. The efflux times measured were kept long, i.e. greater than 100 s, by the use of a capillary of appropriate size. The poly(NIPAM) dispersion was pre-concentrated by centrifugation at 50 000 rpm for 30 min using a Beckman L8-70 ultracentrifuge.

RESULTS AND DISCUSSION

The physical appearance of the poly(NEAM) microgel at 90°C was turbid, resulting from the scattering of light from the hard sphere-like microgel particles. At room temperature, however, the particles are in an extended conformation, swollen with solvent and therefore have an almost clear appearance. This is due to the refractive index of the swollen particles being closely matched to the continuous solvent medium. Transmission electron microscopy was used to analyse the dispersions in relation to the

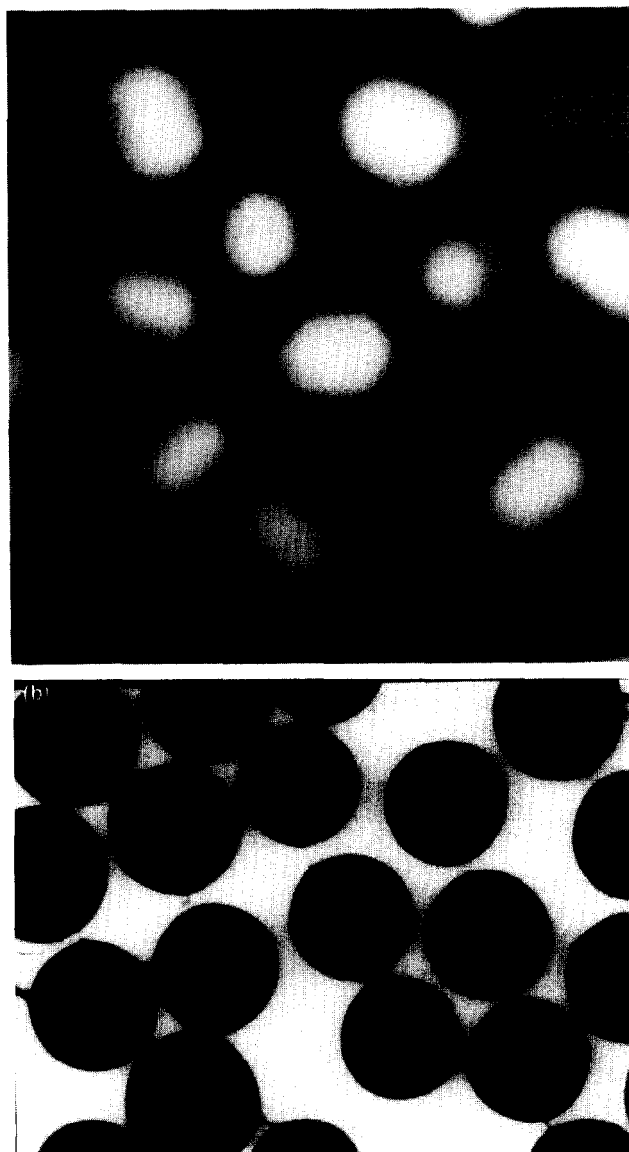


Figure 1 A transmission electron micrograph of a pre-dialysed poly(NEAM) microgel dispersion from (a) a 6-h preparation and (b) a 24-h preparation

distribution of sizes and shape of the particles. *Figure 1(a)* shows a micrograph of a pre-dialysed poly(NEAM) microgel dispersion from a 6-h preparation. This illustrates that a reaction time of 6 h was not sufficient to produce spherical particles, hence subsequent dispersions were prepared with increases being made to the reaction time. An improvement in the appearance of the particles resulted with monodisperse spheres being obtained from a 24-h preparation (see *Figure 1(b)*). Measurements taken from the micrographs of this preparation gave a mean particle diameter of 414 ± 21 nm. On altering the ratio of monomer to crosslinker and/or increasing the quantity of initiator used in the 6-h preparations, no improvement in the appearance of the particles was observed. Also with the inclusion of sodium dodecyl sulfate, a method reported by McPhee *et al.*⁸, for enhancing the stability of poly(NIPAM) microgel dispersions, for a 6-h preparation, again no improvement was observed.

Poly(NIPAM) dispersions do not readily facilitate bacterial growth under normal laboratory conditions. The poly(NEAM) dispersions prepared were found however, to behave in a similar way to some copolymer-NIPAM gels in that the transmission electron micrographs of a dialysed

sample, kept at room temperature, showed the presence of bacterial growth which, following microscopic analysis of a culture of the bacteria, was found to be a single strain of the genus *Bacillus stearotherophilus*. Sodium azide was therefore added as a bactericide prior to dialysis in order to prevent any microbial degradation of the polymer. However, sodium azide was found to adversely affect the system with the transition temperature of the microgel particles being increased to greater than 90°C. This increase was attributed to a possible hydrolysis of the acrylamide groups to acrylic acid thus increasing the hydrophilic character of the polymer, hence increasing its affinity with water. All dispersions subsequently prepared were therefore refrigerated at 4°C to prevent/delay bacterial growth as much as possible.

Figure 2 shows the HSDSC output at a scan rate of 30 K h⁻¹ for the heating cycle of a 2.6% (w/w) poly(NEAM) dispersion. This figure also illustrates the effect of adding electrolyte to a poly(NEAM) microgel dispersion. The thermodynamic parameters associated with the observed transition are given in Table 1. The phase transition observed in the absence of electrolyte is a consequence of the increase in the Flory⁹ interaction parameter (χ) for poly(NEAM) in water with increasing

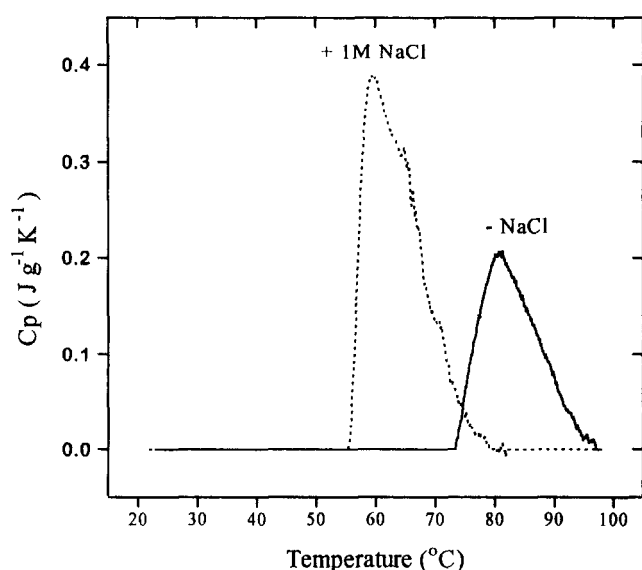


Figure 2 Temperature dependence of the partial specific heat capacity of the colloidal poly(NEAM) microgel system in double deionised water at a concentration of 2.6% (w/w). The HSDSC recording shows the heating, endothermic scan of the microgel in the absence of electrolyte and in the presence of 1 mol dm⁻³ NaCl at a scan rate of 30 K h⁻¹

temperature. The higher temperatures promote more polymer-polymer contacts, thus the soft sphere-like microgel particles contract becoming more rigid, simultaneously forcing out solvent from the interstitial spaces. On cooling, the particles return to their swollen state. As previously mentioned, the hydrogel (i.e. the bulk gel) of poly(*N*-ethylacrylamide) has been synthesised and characterised by Ito et al.⁷ and has been shown to have a phase transition at 72°C with a calorimetric enthalpy of transition of 0.4 J g⁻¹. For the phase transition of the poly(NEAM) microgel, at a scan rate of 30 K h⁻¹, the T_m (the temperature at the maximum value of the excess specific heat capacity, $C_{p,max}$ was 79.4°C and the ΔH_{cal} (the calorimetric enthalpy of the transition) was found to be 1.97 J g⁻¹ (see Figure 2 and Table 1). The transition exhibited by the poly(NEAM) microgel was not perfectly reversible indicating the involvement of a kinetically limited conformational change. The effect of a heat-cool-heat cycle on the thermodynamic parameters of a 2.6% (w/w) poly(NEAM) microgel dispersion, when using scan rates of 60 and 30 K h⁻¹, is shown in Table 1. It can be seen that the T_m increases and ΔH_{cal} decreases on heating the sample for a second time. This is quite unlike the behaviour exhibited by a poly(NIPAM) microgel dispersion, as it has been shown that the first and second heating scans of the same sample are superimposable for this system. It should also be noted that the HSDSC profile for the heating scan of a poly(NEAM) dispersion, shown in Figure 2, is asymmetrical with the asymmetry arising from the sharp increase in the excess specific heat capacity in the region approaching the T_m . However, in contrast the transition exhibited by a Poly(NIPAM) microgel dispersion has been found to be quite symmetrical³. Further, for poly(NIPAM)³, the T_m has been shown to remain constant as a function of concentration of microgel between 0.05 and 0.5% (w/w) and with varying scan rates between 10 and 60 K h⁻¹. For the poly(NEAM) system the T_m was found to be dependent on both the concentration of microgel and the scan rate used, as shown in Table 1. This gives support to the suggestion that the phase transition of the poly(NEAM) microgel involves kinetic limitations which may explain the discrepancy between the thermodynamic parameters reported for a hydrogel⁷, and those we outline here. In the presence of 1 mol dm⁻³ sodium chloride, at a scan rate of 30 K h⁻¹, the T_m was found to decrease by 20°C and the ΔH_{cal} increased by a factor of approximately 2.5, when comparing with data recorded for the dispersion in the absence of electrolyte also at a scan rate of 30 K h⁻¹ (see Figure 2 and Table 1). Similar behaviour has been observed for the poly(NIPAM) system¹⁰.

Table 1 Microcalorimetrically recorded thermodynamic parameters^a for a 2.6% (w/w) poly(NEAM) microgel dispersion

Solvent	Heating run no.	Scan rate (k h ⁻¹)	ΔH_{cal} (J g ⁻¹ , ± 0.08)	T_m (°C, ± 0.05)	$\Delta T_{1/2}$ (°C, ± 0.1)	$C_{p,max}$ (J g ⁻¹ K ⁻¹ , ± 0.01)	T_o (°C)
H ₂ O	1st	60	3.35	78.2	9.9	0.293	69
H ₂ O	2nd	60	1.67	81.6	12.1	0.126	71.5
H ₂ O	1st	30	1.97	79.4	7.82	0.197	71.1
H ₂ O	2nd	30	1.21	80.1	9.5	0.126	73.2
1 M NaCl _(aq)	1st	30	5.02	59.3	11.0	0.377	52
H ₂ O ^b	1st	10	—	86.1	—	—	78.2

^a ΔH_{cal} is the calorimetric enthalpy of the transition; T_m is the temperature at which the excess heat capacity of the transition is a maximum ($C_{p,max}$); $\Delta T_{1/2}$ is the width of the transition in °C at $1/2C_{p,max}$; and T_o is the temperature at which the transition begins.

^bThe concentration of the microgel dispersion was increased to 10% (w/w) when using this scan rate. Due to the nature of the phase transition exhibited, only a value for the T_m was obtainable.

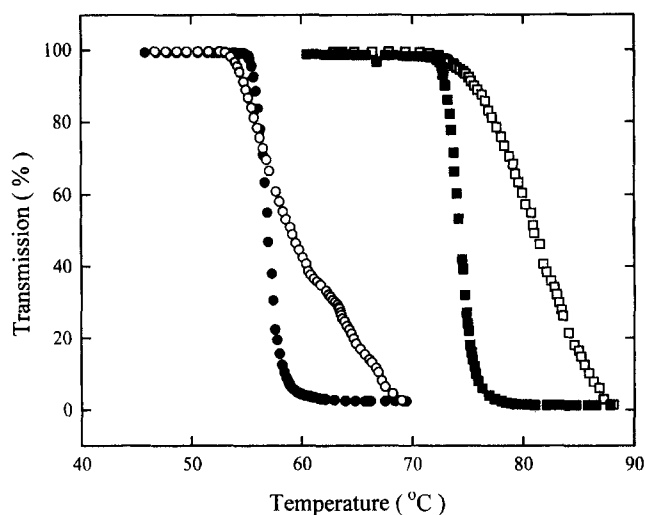


Figure 3 The turbidity of a 2.6% (w/w) dispersion of poly(NEAM) at 547 nm as a function of temperature. (a) In water: (■) heating and (□) cooling scans at 60 and -60 K h^{-1} , respectively. (b) In 1 mol dm^{-3} NaCl: (●) heating and (○) cooling scans at 60 and -60 K h^{-1} , respectively

We observe this decrease in T_m because the electrolyte decreases the solvency of the microgel and increases the Flory interaction parameter of the poly(NEAM) in water, leading to a decrease in the polymer-solvent interaction, thus resulting in a contraction of the particles as described previously.

Figure 3(a) shows the change in turbidity at 547 nm of a poly(NEAM) dispersion in water (a 24-h preparation, 2.6% (w/w)) as a function of temperature, for both a heating and cooling cycle. A shift in the transition is observed on going from the heating to the cooling scan. The maximum transition temperature obtained from a first derivative plot of the heating curve is 74.5°C , however, for the cooling cycle this was found to be 80.9°C . There is clearly some hysteresis taking place within this system further suggesting that the transition is macroscopically kinetically limited. This behaviour is significant with respect to poly(NIPAM) which has been shown, by turbidimetric analysis, to exhibit a fully reversible phase transition with the heating and cooling scans being superimposable³. Further, for poly(NIPAM) systems, excellent correlation exists between the transition temperatures measured by turbidimetric analysis (34.2°C) and HSDSC (34.5°C). This is not the case for the poly(NEAM) system, with the transition temperature measured turbidimetrically being lower than that obtained from HSDSC. However, the transition temperatures from turbidity measurements correspond more closely with the T_0 values (the temperature at which the transition begins) from calorimetric measurement (see Table 1). This difference may be due to the nature of the turbidimetric technique as minimal conformational changes in the microgel particles will alter the percent transmission of the dispersion, whereas the HSDSC technique is sensitive to the major macroscopic transition. As for the HSDSC study of poly(NEAM), the presence of sodium chloride was found to decrease the transition temperature observed from turbidity measurements, this is also the case for the poly(NIPAM) systems¹¹. Figure 3(b) shows the change in turbidity at 547 nm of a poly(NEAM) dispersion in the presence of 1 mol dm^{-3} sodium chloride as a function of temperature, for both a heating and cooling cycle. The maximum transition temperature obtained from a first derivative plot of the heating curve is 57°C , however, in

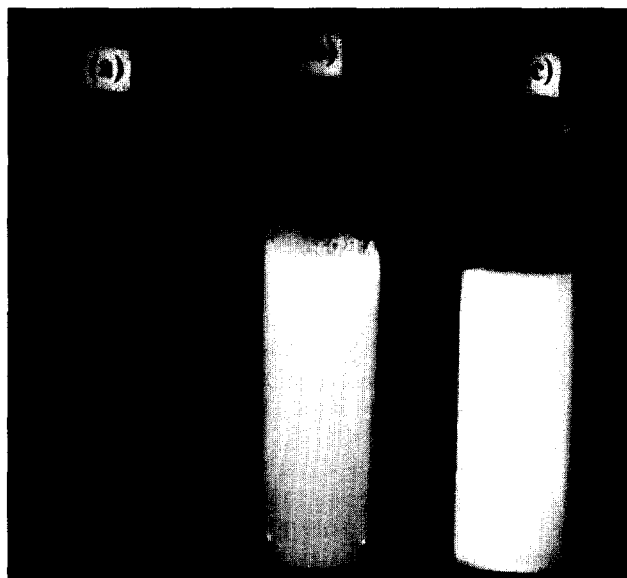


Figure 4 A photograph showing the temperature-controlled flocculation of a 0.7% (w/w) poly(NEAM) dispersion: (a) in the presence of 3 mol dm^{-3} NaCl at 19°C ; (b) in the presence of 3 mol dm^{-3} NaCl at 80°C ; and (c) in the absence of electrolyte at 80°C

the absence of electrolyte this was found to be 74.5°C , as discussed earlier. This decrease in the transition temperature of almost 20°C , on going from water as the solvent to 1 mol dm^{-3} sodium chloride, agrees with the results from the calorimetric measurements. Once again, some hysteresis is observed between the heating and cooling processes. Microgels of homopolymer poly(NIPAM) do not display any conformational changes with respect to the pH of the aqueous environment⁴. This was also found to be the case for the poly(NEAM) microgel system. The turbidimetric analysis of a poly(NEAM) microgel dispersion in water, as a function of pH, showed that the transition temperature was independent of the pH of the aqueous environment.

Figure 4 shows a photograph taken of the three vials prepared in the flocculation study. In the presence of 3 mol dm^{-3} sodium chloride at 19°C (Figure 4(a)), the dispersion remained clear indicating that the particles were largely unaffected, however, on heating to 80°C (Figure 4(b)), aggregation of the particles was observed. The dispersion became turbid with at first a 'gritty' appearance being noted, characteristic of an aggregation, with larger flocs forming with time, sticking to the walls of the glass vial. On cooling the flocculated dispersions and gently inverting the glass vial several times, the flocculated particles redispersed. This temperature-induced aggregation of the particles and subsequent redispersion on cooling was repeated several times with the process remaining fully reversible. On heating to 80°C in the absence of electrolyte (Figure 4(c)), the dispersion became turbid, however, no aggregation was observed. The temperature-controlled flocculation of poly(NIPAM) microgels has been studied by Snowden and Vincent¹¹, their observations, made at 25°C , were attributed to the microgel particles being swollen with solvent and therefore having a very low Hamaker constant which is closely matched to the continuous solvent medium and, as a result, the van der Waals attraction energy is very small. At that temperature, steric repulsive forces, arising from an extended conformation of the outer polymer chains, also stabilise the particles via a steric mechanism and thus further prevent aggregation. On heating, the extended polymer chains collapse to the

surface as the particles shrink to become hard sphere-like in nature, with the Hamaker constant of the particles correspondingly increasing as the composition of the solvent within the structure decreases, thus allowing aggregation of the particles to occur. With respect to the poly(NEAM) dispersions, electrolyte concentrations of the order of 3 mol dm^{-3} sodium chloride far exceed those usually associated with a contraction of the electrical double layer. The aggregation observed is therefore likely to be attributable to an incipient mechanism arising from a very poor polymer-solvent interaction at such high electrolyte concentrations. A destabilisation resulting from a compression of the electrical double layer is not observed for this system, probably as the greater solvency of the NEAM monomer leaves the particle surface slightly 'hairy', even above the T_m , some steric repulsion exists until a point is reached when the solvency, on increasing the electrolyte concentration, becomes so poor the 'hairy' chains collapse onto the surface. Clearly this process is not taking place until an electrolyte concentration approaching 3 mol dm^{-3} is reached. On cooling, the solvency of the dispersion improves and the particles swell and simultaneously redisperse. The physico-chemical properties of poly(NIPAM) have been widely studied and have been found to be highly dependent upon temperature. Linear poly(NIPAM) is water soluble and has a lower critical solution temperature (LCST) of $31\text{--}32^\circ\text{C}$, at which point it undergoes a phase separation. This phase separation has been studied by using various techniques including viscosity measurement. Pelton *et al.*¹² have observed a change in viscosity with temperature for the linear polymer, reaching a maximum value at the LCST. It was suggested by the authors that this increase in viscosity at the LCST was due to the collapsing chains undergoing intermolecular association. On increasing the temperature beyond the LCST the polymer completely phase separated and the viscosity decreased. Figure 5 illustrates the change in the reduced viscosity, η_{red} , of both a poly(NIPAM) and poly(NEAM) microgel dispersion in water, with increasing temperature. The reduced viscosity of a poly(NEAM) dispersion in the presence of 0.5 mol dm^{-3} sodium chloride is also shown.

The reduced viscosity, η_{red} , is defined as:

$$\eta_{\text{rel}} = \frac{\eta_{\text{rel}} - 1}{c}$$

where η_{rel} is the relative viscosity and c is the concentration expressed in g dl^{-1} . It can be seen that they both exhibit a decrease in η_{red} as the temperature is increased. A critical point is reached in each case where the rate of decrease changes dramatically, this is an indication of the pronounced conformational changes that are occurring in both systems. It should be noted that the temperatures at which these changes occur are very similar to the phase transition temperatures (LCSTs) measured for these microgels by turbidimetric analysis. A significant difference is observed in the behaviour of the poly(NIPAM) microgel to that of the linear polymer reported by Pelton *et al.*¹². In the case of the microgel system the viscosity is observed to almost reach a minimum value in the region of the LCST of the polymer, however, the opposite is true for the linear system as discussed earlier. This phenomena clearly demonstrates one of the interesting physico-chemical differences which take place on going from one physical form to another for the same polymeric material. On increasing the temperature further, beyond the LCST, the viscosity of the dispersion decreases only slightly. This may be interpreted, by considering physical changes taking place during the swelling and shrinking behaviour of the microgel particles in response to temperature changes. The temperature dependency of the particle diameter of a poly(NIPAM) microgel has been studied by photon correlation spectroscopy¹³. The mean particle diameter was observed to decrease from approximately 550 nm at 25°C to 150 nm at 50°C . This four-fold decrease in particle diameter corresponds to a 60-fold decrease in the overall volume of the particle. The particles may thus be clearly envisaged as shrinking with increasing temperature. We therefore suggest that the decrease in the viscosity of the poly(NIPAM) microgel dispersion with increasing temperature can be directly related to this progressive decrease in the hydrodynamic volume of the particles. This conclusion has also been reported by Kiminta *et al.*¹⁴ who measured the

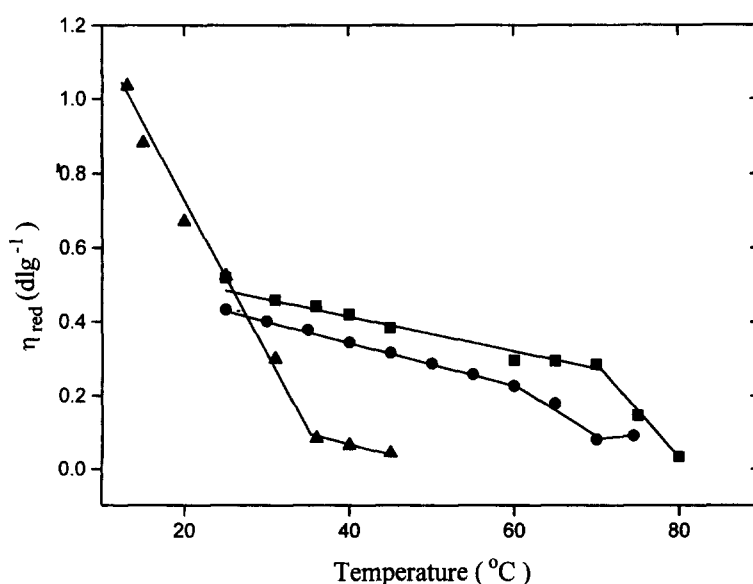


Figure 5 The reduced viscosity, η_{red} , of (■) poly(NEAM) and (▲) poly(NIPAM) dispersion in water, and (●) a poly(NEAM) dispersion in 0.5 mol dm^{-3} NaCl, as a function of temperature

viscosity of poly(NIPAM) microgels at various shear rates. At higher shear rates, the viscosity was found to gradually decrease with increasing temperature, reaching a limiting value at approximately 55°C. From this study and the measurement of the particle size of the microgel, as a function of temperature, it was concluded that the swelling/deswelling phenomena of the particles gives rise to significant changes in the viscosity and other rheological properties of the system. In the present study the behaviour of the poly(NEAM) microgel dispersion was found to differ from the poly(NIPAM) system. It can be seen from the viscosity profile in *Figure 5* that the viscosity decreases only very slightly with increasing temperature until a point, within the region of the LCST of the polymer, where it begins to fall rapidly. On considering the previous discussion this would suggest that little shrinkage of the particles occurs prior to the LCST, however, on increasing the temperature beyond the LCST the particles appear to shrink rapidly. Unfortunately reproducible dynamic light scattering data could not be obtained for the poly(NEAM) system in order to try and correlate the viscometric studies with changes in particle size. In the presence of 0.5 mol dm⁻³ sodium chloride, the viscosity profile of the poly(NEAM) dispersion is shifted with the transition occurring approximately 5°C lower than in the absence of electrolyte. This decrease in the transition temperature is obviously less severe than that observed in the presence of 1 mol dm⁻³ sodium chloride (i.e. 20°C) as discussed earlier. This is comparable with HSDSC studies of a poly(NIPAM) microgel dispersion in the presence of various concentrations of sodium chloride reported by Murray et al.¹⁰. The transition temperature of the poly(NIPAM) microgel was observed to gradually decrease with increasing quantities of electrolyte. Due to the use of a capillary viscometer a viscometric study of a poly(NIPAM) microgel dispersion in the presence of sodium chloride solutions was not performed due to the ease at which the particles aggregate. Turbidimetric studies of a poly(NIPAM) microgel in the presence of varying quantities of sodium chloride have been performed by Snowden and Vincent¹¹ and it was observed that the latex was flocculated in 0.06 mol dm⁻³ sodium chloride, hence any attempt at obtaining a viscosity profile would be meaningless.

Centrifugation of poly(NIPAM) dispersions at 50 000 rpm for 30 min resulted in a clear supernatant with an iridescent packed bed of particles, characteristic of monodisperse ordered packing. Poly(NEAM) under identical conditions will not centrifuge out, in fact after 5 h at 50 000 rpm only a very small number of particles were observed to have formed a plug. This suggests that the particles have a density very similar to that of the continuous solvent medium. The particles are therefore highly swollen with water, suggesting that the polymer-solvent interaction is more favourable than in the poly(NIPAM) system, most probably due to the less hydrophobic nature of the *N*-ethyl side chain relative to

the *N*-isopropyl group. The much higher phase transition temperature further supports this hypothesis.

CONCLUSIONS

Solution polymerisation of *N*-ethylacrylamide in water in the presence of a cross-linking agent does produce monodisperse colloidal microgels. The transition temperature of the particles was found to be of the order of 78°C, a value far higher than that for similar microgel particles of the homologous poly(*N*-isopropylacrylamide), this being 34°C. This is readily explained by virtue of the less hydrophobic side chain. Further differences exist between poly(NEAM) and poly(NIPAM) in that the conformational change associated with the transition is kinetically limited therefore giving rise to hysteresis between the heating and cooling process. The vulnerability of the poly(NEAM) dispersions to microbial contamination may further limit the practical utility of these particles as they display poor storage characteristics.

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REFERENCES

1. Murray, M.J. and Snowden, M.J., *Adv. Coll. Inter. Sci.*, 1995, **54**, 73.
2. Pelton, R.H. and Chibante, P., *Colloids Surf.*, 1986, **20**, 247.
3. Murray, M.J., Rana, F., Haq, I., Cook, J., Chowdhry, B.Z., Snowden, M.J., *J. Chem. Soc. Chem. Commun.* 1994, 1803.
4. Snowden, M.J., Chowdhry, B.Z., Vincent, B. and Morris, G., *J. Chem. Soc. Faraday Trans.*, 1996, **92**, 5013.
5. Snowden, M.J., Morgan, J., Vincent, B., UK Patent No. GB2262117A, 1993.
6. Snowden, M.J., Thomas, D., Vincent, B.J., *Chem. Soc. The Analyst*, 1993, 3676.
7. Ito, S., Hirasa, O., Yamauchi, A., Fujishige, S., Ichijo, H., *Polymer Gels*, in: ed. D. DeRossi et al. Plenum Press, New York, 1991.
8. McPhee, W., Tam, K.C. and Pelton, R., *J. Colloid Interface Sci.*, 1993, **156**, 24.
9. Flory, P.J., *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953.
10. Murray, M.J., Chowdhry, B.Z., Snowden, M.J., *J. Phys. Chem.* 1997, manuscript in preparation.
11. Snowden, M.J., Vincent, B., *J. Chem. Soc. Chem. Commun.*, 1992, 1103.
12. Pelton, R., Wu, X., McPhee, W., Tam, K.C., *Colloidal Polymer Particles*, in: ed. J.W. Goodwin, R. Buscall. Academic Press, 1995, p. 81.
13. Snowden, M.J. and Chowdhry, B.Z., *Chem. Br.*, 1995, **31**(12), 943.
14. Ole Kiminta, D.M., Luckham, P.F. and Lenon, S., *Polymer*, 1995, **36**(25), 4827.