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Swelling behavior of poly-*N*-isopropylacrylamide microgel particles in alcoholic solutions

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Abstract It has been shown that the swelling of poly-*N*-isopropylacrylamide (poly-NIPAM) microgel particles can be controlled by the addition of alcohols, in addition to the previously observed effect of temperature. The degree of swelling is also controlled by the amount of cross-linker within the microgel particles. At 25 °C, poly-NIPAM microgel particles collapse upon the addition of MeOH, EtOH and 2-PrOH to a minimum size and then,

reswell again as the alcohol-rich region is approached. This trend was also observed for poly-NIPAM microgel particles dispersed in 2-PrOH/water mixtures upon heating to 50 °C. The particles, dispersed in either water or alcohol/water mixtures were found to be stable to flocculation between 25 °C and 50 °C.

Key words Microgel – poly-NIPAM – deswelling – cononsolvency

Introduction

A microgel particle is a cross-linked latex particle which can swell and contract as a result of the application of an environmental trigger, e.g., temperature, pH, ionic strength or electric field [1]. In 1986 Pelton and Chibante [2] synthesized microgel particles from *N*-isopropylacrylamide (NIPAM) and *N*, *N*-methylenebisacrylamide (BA) using free-radical emulsion polymerization. Since then studies have been made on the kinetics of the polymerization [3] and the properties of the particles formed [4, 5]. Poly-NIPAM particles, when cross-linked with BA, are thermo-shrinking. At room temperature the microgel particles are in their swollen form, but as the temperature is increased, above the lower critical solution temperature (LCST), around 31 °C [2], the microgel particles collapse. This has been explained by a decrease in the hydrogen bonding between the amide groups of the polymer and the water molecules [6], i.e., the solvent changes from “good” to “poor”.

Preliminary investigations have already been undertaken in this laboratory to investigate the effect of mixed solvents on the swelling properties of microgel particles [7]. McPhee et al. [3] briefly commented on the effect of methanol added to an aqueous solution of poly-NIPAM microgel particles, although limiting their study to a maximum of 35%(v/v) methanol. They observed a decrease in the particle diameter with increasing methanol content up to this concentration. Zhu and Napper [8] recently observed deswelling with an initial increase in alcohol concentration, and re-entry swelling at higher alcohol concentrations, for poly-NIPAM chains grafted to polystyrene latex particles in alcohol/water mixtures at 25 °C.

Pure water and pure alcohol are both good solvents for poly-NIPAM but are not apparently for mixtures of the two over a certain concentration range. This phenomenon is known as “cononsolvency”. In terms of Flory’s interaction parameter χ : $\chi \rightarrow 0$ for the pure solvents, but $\chi > 0.5$ for a cononsolvent.

In this study, the work of Zhu and Napper [8] has been extended to examine the effect of methanol (MeOH),

ethanol (EtOH) and 2-propanol (2-PrOH) at various concentrations in water, on the swelling behavior of poly-NIPAM microgel particles between 25 °C and 50 °C.

Most previous work has looked at the effect of aqueous solutions of the lower alcohols [6, 9–13], other small organic molecules [10, 14] and free polymer [15, 16] on poly-NIPAM *macro*gels. It is important to note that there are several differences between *macro*gels and *micro*gels. *Micro*gels have much larger interfacial areas than *macro*gels due their respective sizes. *Micro*gels are typically 1 nm–1 µm in diameter [1], whereas *macro*gels have dimensions greater than 1 mm [7]. *Micro*gels also have an ability to flow (in the dispersed phase). *Micro*gels are synthesized above their LCST in order to produce stable, monodisperse particles via free-radical polymerization. Despite these differences, *macro*gels and *micro*gels show similar trends upon changes in solution conditions, although discontinuous deswelling is observed for *macro*gels [12], whereas in the case of *micro*gels deswelling is gradual and continuous.

Experimental

Materials

NIPAM (Eastman Kodak), BA (Aldrich) and ammonium persulfate (Aldrich) were used as received. Water was Milli-Q grade. MeOH (Tennants), EtOH (Haymans) and 2-PrOH (Merck) were also used as received.

Synthesis of microgel particles

The method of synthesis described here is for a poly-NIPAM microgel prepared using 9% BA, although a similar method was employed for those microgels prepared using lower proportions of BA. Microgel synthesis was carried out in a 11, three-necked, round-bottomed flask, thermostatted at 70 ± 1 °C. The monomers, NIPAM (4.2 g, 37 mmol) and BA (0.42 g, 2.7 mmol), were dissolved in water (300 ml) and stirred (20 min at 350 rpm). The stirring was stopped and the solution purged with nitrogen (10 min). Ammonium persulfate (0.21 g), dissolved in water (7 ml), was added to the reaction vessel and stirring was restarted (350 rpm). Within 5 min the solution had turned a turbid white. The reaction was allowed to proceed for 16 h under a nitrogen atmosphere, with stirring (350 rpm). After this, the reaction mixture was cooled to 25 °C whilst maintaining the stirring and nitrogen flow. The microgel dispersion was “cleaned” by 10 centrifugation/redispersion cycles (10000 rpm for 45 min at 15 °C). The solids content

was typically 1.5%(w/w) and samples were stored in the dark at room temperature.

Particle characterization

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies were made using a JEOL “JEM-100CX” instrument calibrated with a diffraction grating. Particle size measurements were made with a Brookhaven “Zeta-Plus” photon correlation light-scattering apparatus. The required viscosities and refractive indices were obtained from the literature [17, 18]. 0.025% (w/w) Dispersions of the poly-NIPAM particles were used for all the photon correlation spectroscopy (PCS) experiments, which were tumbled for 12 h prior to measurement. The standard deviation in the values obtained for the hydrodynamic diameter (d) was typically 5%. The deswelling ratio is defined as $(d/d_0)^3$, where d_0 is the diameter of the microgel particles in pure water at 25 °C. Optical spectra were obtained over the range 450–600 nm at either 25 °C or 50 °C using a thermostatted “UVIKON-940” spectrometer. Samples were equilibrated for 1 h prior to measurement.

Results and discussion

Particle characterization

TEM micrographs were similar to those obtained by other authors [2, 4]. It has also been suggested that solvent evaporation leads to the particles having an oblate-disk-shape in electron micrographs and this is confirmed by the SEM micrograph shown in Fig. 1. The grid was prepared at 50 °C and taken at an angle of 60 ° to the sample. This shows the particles are oblate-disk-shaped. The SEM data obtained for the microgel heated at 50 °C reveal that particle deformation occurs during deposition onto the substrates. This is consistent with the presence of water within the particles prior to evaporation. McPhee et al. [3] calculated the change in weight fraction of polymer in the particles as a function of temperature which showed significant water content above the LCST. Further evidence of the retention of water at 50 °C will be presented below.

Influence of cross-linker concentration on the deswelling properties of poly-NIPAM microgel particles in water as a function of temperature

Figure 2 compares the deswelling properties of poly-NIPAM microgel particles prepared using different

Fig. 1 SEM micrograph of cleaned poly-NIPAM (4.5% BA) taken at 60° to the sample (prepared at 50 °C)

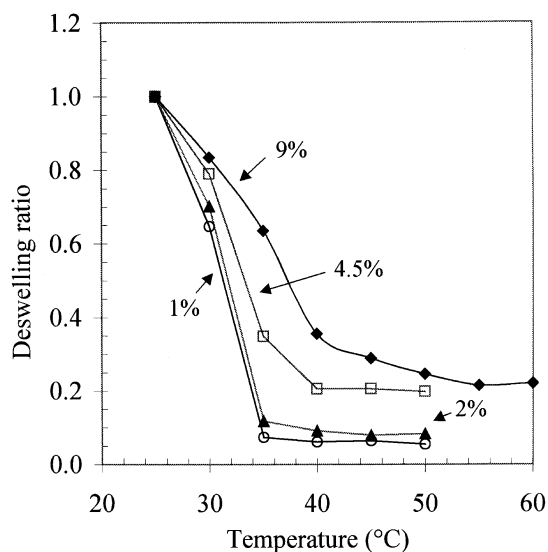
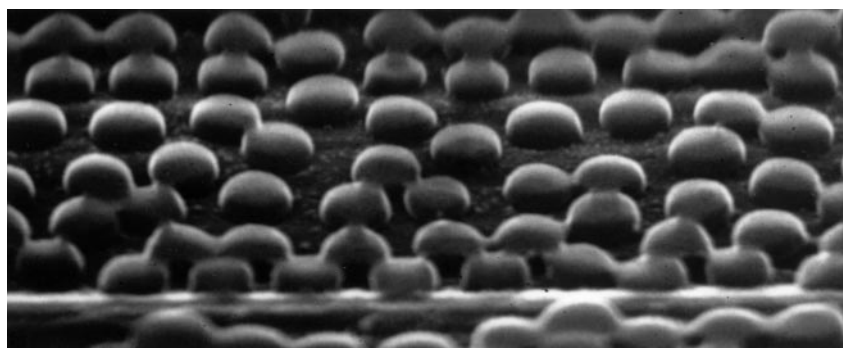


Fig. 2 The effect of the amount of cross-linker used on the deswelling ratio of poly-NIPAM microgel particles (♦ 9%; □ 4.5%; ▲ 2%; ○ 1%)

amounts of cross-linker. The data show that all of the microgel particles deswell as the temperature is increased. As expected, a decrease in cross-linker concentration leads to a greater degree of collapse as has been observed by other authors [3, 4]. The LCST of poly-NIPAM microgel particles is estimated as 31 °C [2] and the deswelling data for poly-NIPAM microgel particles prepared using 1% and 2% BA are consistent with this value. However, increasing the amount of BA used during the synthesis appears to broaden the deswelling transition and raise the average LCST. Poly-NIPAM (4.5% BA) and poly-NIPAM (9% BA) are essentially copolymer microgels and the interaction of the BA units with water is significant. It appears as though the incorporation of BA produces copolymer regions which have a greater affinity for water (and a raised local LCST) than that of pure poly-NIPAM.

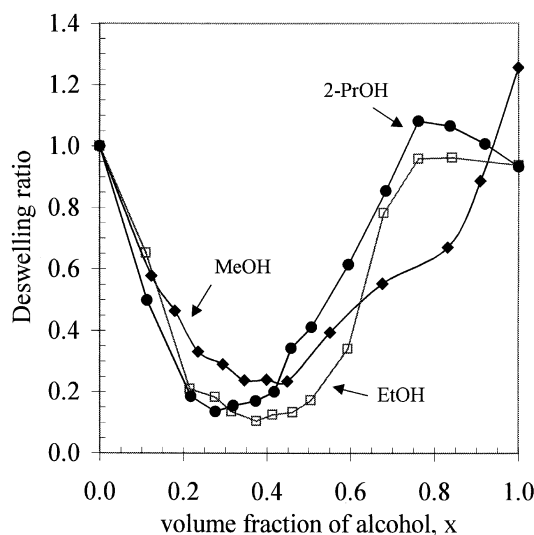


Fig. 3 Change in the deswelling ratio of poly-NIPAM (9% BA) microgel particles as a function of increasing volume fraction of three alcohols. The alcohols investigated are MeOH (♦), EtOH (□) and 2-PrOH (●)

Influence of alcohol/water mixtures on the deswelling properties of poly-NIPAM microgel particles at 25 °C

The variation of the deswelling ratio, as a function of the volume fraction of MeOH, EtOH and 2-PrOH is shown in Fig. 3. In all the cases the microgel particles collapse to a minimum size in the water-rich region and then reswell on increasing the alcohol concentration further. As the alcohol chain length is increased, the minimum deswelling ratio is achieved at a lower volume fraction of alcohol (Table 1). The x_{\min} values reported here are similar to those reported by Zhu and Napper [8], who investigated the effect of alcoholic solutions on poly-NIPAM homopolymer chains grafted onto nonswelling polystyrene latex-particle cores. From Table 1 and Fig. 3 there is evidence to suggest that increasing the alcohol chain length causes greater deswelling (at x_{\min}) and a “sharper”

Table 1 Comparison of the deswelling ratios and x_{\min} for the different alcohols. Included is the deswelling ratio for water at 50 °C

Alcohol	Deswelling ratio	x_{\min}
MeOH	0.24	0.40
EtOH	0.11	0.37
2-PrOH	0.14	0.28
Water	0.21	—

minimum (i.e., the minimum is much “sharper” for 2-PrOH than either MeOH or EtOH).

The data presented in Fig. 3 may be explained in terms of the formation of a hydrated clathrate structure [19] in alcohol/water mixtures. It is thought that water molecules form a disordered tetrahedral structure around an alcohol molecule [21]. Onori [22] found that a greater number of water molecules was required to form such clathrate structures around 2-PrOH than around either EtOH or MeOH. In water alone, the water molecules form cage-like structures around the hydrophobic groups of the poly-NIPAM chains [23] and also form hydrogen bonds with the amide groups. It is the removal of water molecules, solvating the poly-NIPAM chains to form these clathrate hydrates that causes the microgel particles to collapse, since both the hydrogen and hydrophobic bonding are disrupted. This effect has been termed “cononsolvency”. The observation that x_{\min} decreases with increasing chain length is consistent with the clathrate-hydrate mechanism discussed above, since the encapsulation of the alcohol breaks down at lower alcohol volume fractions with increasing size of the alcohol molecules [8]. The collapse of the microgel particles implies that intramolecular hydrogen bonding between the amide groups and hydrophobic interactions of the iso-propyl groups are increased which in turn may promote further collapse of the microgel particles. However, hydrophobic interactions between the alcohol molecules and the polymer chains may oppose complete collapse. Indeed, Mukae et al. [11] have shown that EtOH is more concentrated within poly-NIPAM *macro*gels than in bulk solution even at x_{\min} .

Table 1 also shows the deswelling ratio of poly-NIPAM microgel particles in water at 50 °C. Greater collapse of the microgel is achieved in both EtOH and 2-PrOH than just heating alone. It has been suggested that even in the collapsed form, above the LCST, the microgel particles contain around 10%/wt water [24]. Dong and Hoffman calculated a similar value (20%) for poly-NIPAM gels [25]. Therefore, at these alcohol/water compositions, the water appears to have been more extensively removed from the core of the particle. The data shown in Table 1 represent further evidence that heating poly-NIPAM microgel particles above the LCST is insufficient

to remove all of the solvated water. It is not yet clear why the overall collapse is more pronounced for EtOH and 2-PrOH than that observed for MeOH.

It is also evident from Fig. 3 that, as the volume fraction of alcohol is increased above x_{\min} , the microgel particles show re-entrant swelling to give the same, or even slightly larger, particle size than that in pure water. Swelling occurs when the volume fraction of alcohol molecules exceeds the critical concentration (x_{\min}), such that the alcohol molecules can no longer be encapsulated in the clathrate structure. Hence, the alcohol molecules now interact directly with the poly-NIPAM chains through hydrogen bonding and hydrophobic interactions. Evidence for direct hydrogen bonding between alcohol molecules and poly-NIPAM chains has recently been reported [8].

Since the microgel particles contain surface-charge groups originating from the initiator, electrostatic effects cannot necessarily be ignored. However, the surface-charge density is low [3] and the addition of salt has no effect on the particle size [26]. Saunders et al. [7] compared charged microgel particles and poly-NIPAM microgel particles in alcohols and found significant differences in their deswelling behaviors. Therefore, we believe that electrostatic effects play no significant part in the deswelling behavior of poly-NIPAM microgel particles.

The PCS data presented above have assumed the particles to be stable and monodisperse. The stability of the particles in these alcoholic solutions was confirmed using optical density measurements. The gradient (n), where $n = -(\log(\text{optical density})/\log(\text{wavelength}))$ is known to be sensitive to the presence of aggregates in a system [27]. An abrupt decrease in the n -value is indicative of flocculation. The n -values for the 2-PrOH/water system were all less than -2.2 and do not show evidence of flocculation. Similar data were obtained for the other systems studied and it can, therefore, be concluded that all samples are stable at 25 °C. It can be inferred that when the microgel particles are deswollen, the Hamaker constant A_H is large and hence the particles are more susceptible to flocculation than when the particles are swollen, i.e., A_H is small.

In the work of McPhee et al. [3] they applied Flory’s theory for the swelling of a nonionic network to one of their poly-NIPAM microgel particles. Our data for the 2-PrOH/water mixtures were substituted into Eq. (3) in this reference. This equation requires a volume for the fully collapsed state. We have already shown (Table 1) that greater collapse is achieved in 2-PrOH/water mixtures than by heating the microgel particles in water to 50 °C. Irrespective of which value is used for the fully collapsed state, we obtained values of $\chi > 0.5$ for poly-NIPAM microgel particles in water below the LCST which is contrary to what is already known about poly-NIPAM in water. This was not only peculiar to the 2-PrOH/water

mixtures. Other authors [28, 29] have found the application of the Flory–Huggins theory not to be applicable to the poly-NIPAM gels in water as the theory does not account for specific interactions (hydrogen bonding). The model does also not account for the clathrate structures proposed.

Influence of temperature on deswelling properties of poly-NIPAM microgel particles in 2-PrOH/water mixtures

Figure 4 shows the hydrodynamic diameters of poly-NIPAM microgel particles in increasing volume fractions of 2-PrOH as a function of temperature. The data show the same general behavior over the temperature range investigated. However, there are three points of interest to note. The minimum diameters observed in the presence of 2-PrOH at all temperatures are lower than that measured for the microgel particles in pure water at 50 °C. Previous authors [3–5, 23] have assumed that at 50 °C the microgel particles are in their fully collapsed state, although here there is evidence to suggest that further collapse has been achieved. This conclusion is consistent with the electron micrographs as discussed above. The position of x_{\min} is shifted to higher volume fractions with increasing temperature ($x_{\min} = 0.417$ at 50 °C). We are not aware of any work in the literature that reports such behavior. The existence of an x_{\min} value suggests that an (partially) ordered structure, possibly the proposed clathrate structure, still exists even at temperatures as high as 50 °C. Computer modelling by Skipper [30] showed that the hydration

structure around methanol molecules is insensitive to temperature, despite the increase in energy required to maintain such a hydration shell. It is tentatively suggested that the consolvency mechanism is enhanced by increasing the temperature to 50 °C.

For comparison, the data from Fig. 4 were replotted in terms of the deswelling ratio and are shown in Fig. 5. At alcohol concentrations above x_{\min} , the cosolvent appears to be a better solvent for the poly-NIPAM chains than water alone. This effect is more pronounced with increasing temperature and is attributed to an increase in the hydrophobic interactions between the poly-NIPAM chains and solvent which become stronger with an increase of temperature [30].

Influence of cross-linker concentration on deswelling of poly-NIPAM microgel particle in alcohol/water mixtures at 25 °C

Finally, we examined the affect of cross-linking monomer concentration on the deswelling behavior of poly-NIPAM microgel particles in alcohols. Table 2 compares the effect on the deswelling ratio in alcohol/water solutions for poly-NIPAM (9% BA) and poly-NIPAM (4.5% BA). The data show that the poly-NIPAM (4.5% BA) particles deswell to a greater extent than poly-NIPAM (9% BA). A similar observation was observed upon heating the microgel particles in pure water (Fig. 2). In addition, the data for poly-NIPAM (4.5% BA) also show smaller deswelling ratios in the presence of alcohol than those that resulted

Fig. 4 Hydrodynamic diameters of poly-NIPAM (9% BA) as a function of temperature in 2-PrOH/water solutions. The horizontal line shows the hydrodynamic diameter measured for the microgel particles in pure water at 50 °C. The data were recorded at 25 °C (◆), 30 °C (□), 40 °C (▲) and 50 °C (○)

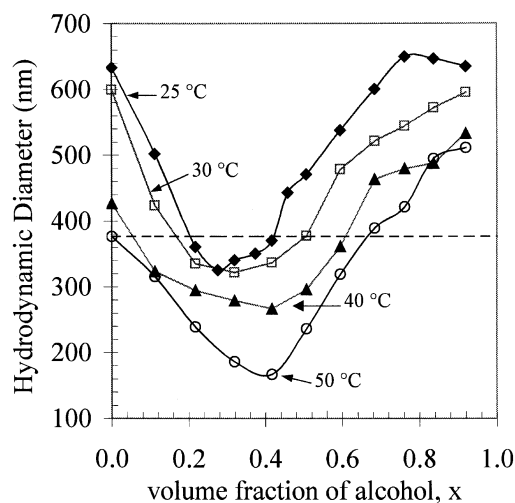


Fig. 5 Deswelling ratios of poly-NIPAM (9% BA) in 2-PrOH/water solutions as a function of temperature. Deswelling ratio at temperature $T = (d_T/d_{H_2O(T)})$. The horizontal line shows the deswelling ratio measured for the microgel particles in pure water at 50 °C. Data taken from Fig. 4 and same symbols used

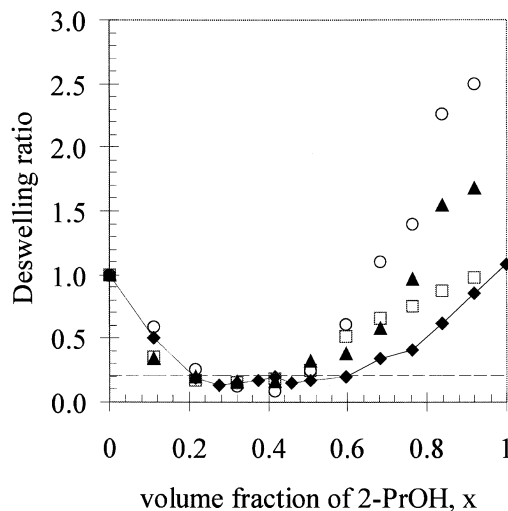


Table 2 Comparison of the deswelling ratio as a function of cross-linker concentration

Alcohol fraction, x	Deswelling ratio at x_{\min}	
	9% BA	4.5% BA
0.27 EtOH	0.11	0.07
0.60 EtOH	0.78	0.44
0.27 2-PrOH	0.16	0.05
0.60 2-PrOH	0.86	0.73

from heating the particles in pure water. These data suggest that the retention of water by poly-NIPAM microgel particles dispersed in pure water at temperatures greater than 50 °C is independent of microgel composition.

Conclusions

From the current work the following conclusions can be made:

1) Poly-NIPAM microgel particles initially deswell upon the addition of MeOH, EtOH and 2-PrOH in water, until a minimum value is reached. On increasing the alcohol concentration of the solution further, reswelling of the microgel occurs. The volume fraction required

for maximum deswelling depends on the length of the alcohol chain, and may be explained in terms of the formation of clathrate hydrates. Increases in the hydrogen bonding and hydrophobic interactions between the polymer chain and solvent molecules have been used to explain this effect.

- 2) Heating poly-NIPAM (9% BA) microgel particles in 2-PrOH/water mixtures to 50 °C collapses the particles to a greater extent than that observed in pure water alone at the same temperature. These data not only broadly support evidence for the presence of an ordered structure (clathrate hydrate) at these temperatures, but also provide evidence that heating alone does not lead to the fully collapsed state of the microgel particles. It is believed that this is due to stronger hydrophobic interactions between the polymer chains and 2-PrOH molecules than at 25 °C.
- 3) The amount of cross-linker used in the initial polymerization affects the swelling properties of the microgel. Greater collapse is obtained in microgel particles prepared using less BA. This is also reflected by the addition of alcohols where a greater overall collapse results for those prepared using less BA.

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