

# Thermal and osmotic deswelling of poly(NIPAM) microgel particles

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The effects of temperature and added free polymer on the swelling of poly(NIPAM) (NIPAM = *N*-isopropylacrylamide) microgel particles cross-linked with *N,N'*-methylene bisacrylamide have been investigated. The microgel particles were characterized by photocorrelation spectroscopy (PCS), TEM and SEM measurements. Particle sizes determined by TEM were invariably larger than those measured at 50 °C by PCS. SEM data suggest that dried particles have an oblate spheroid shape. The rate at which poly(NIPAM) particles collapse and swell in response to cycling of the temperature between 28 and 60 °C was examined and some hysteresis was observed. Excluded free polymer [PEG, where PEG = poly(ethyleneglycol)] also caused deswelling of the poly(NIPAM) particles at 25 °C due to osmotic pressure effects. Osmotic deswelling occurred in the presence of monodisperse PEG when the molecular weight of the latter was  $\geq 1470$  g mol<sup>-1</sup>. Higher molecular weight PEG polymers caused a general decrease in the extent of deswelling (at a fixed concentration of PEG).

The study of microgels based on poly(NIPAM) (NIPAM = *N*-isopropylacrylamide) is attracting growing interest in the literature.<sup>1-8</sup> A microgel particle is a cross-linked latex particle which is swollen by a good solvent. Microgels are of interest to the surface coatings industry since they can provide rheological control for high-solids formulations.<sup>6</sup> However, a variety of dissolved polymers are also generally present in most surface coatings formulations. The primary aim of this work is to investigate the effect of free polymer (*i.e.*, a polymer that does not have the tendency to adsorb at the particle surface) on the swelling of poly(NIPAM) microgel particles.

Pelton and Chibante<sup>1</sup> were the first workers to report the preparation of poly(NIPAM) microgel particles. They used an emulsifier-free emulsion polymerization route and found that colloiddally stable particles were produced, provided the total solids content did not exceed 2.5 wt.%. Poly(NIPAM) microgel particles have a lower critical solution temperature (LCST) in water around 31 °C and collapse when heated above the LCST.<sup>3</sup> This effect has been attributed to a thermally induced disruption of the hydrogen bonding between water and the amide groups of poly(NIPAM).<sup>5,9</sup> Kawaguchi *et al.*<sup>5</sup> examined the absorption of proteins by poly(NIPAM) microgel particles as a function of temperature and found that the particles behaved essentially as hydrophilic substrates in the swollen state, but as hydrophobic ones in the collapsed state. Poly(NIPAM) microgels have been studied in these laboratories [in collaboration with Dr. Snowden (Greenwich University)] by photon correlation spectroscopy (PCS) and electrophoretic mobility measurements.<sup>4,8</sup> The flocculation/stability thresholds of the poly(NIPAM)-poly(styrene-sulfonate)-water system were also examined and it was suggested that flocculation occurred as a result of charge screening and depletion forces within the system.

The study of deswelling of macrogels in the presence of free polymers has been active for at least fifty years.<sup>10</sup> It is well known that excluded free polymer induces deswelling of a swollen polymeric network.<sup>10-18</sup> Inomata *et al.*<sup>16</sup> and Ishida *et al.*<sup>17</sup> have recently investigated the effect of poly(ethyleneglycol) (PEG) on the swelling of poly(NIPAM) macrogels. The latter workers found that the extent of deswelling increased with increasing molecular weight of PEG and have proposed a thermodynamic model which provides a semi-quantitative description of their data.<sup>18</sup> In the present study, we examine the effects of temperature and added free polymer on the swelling of poly(NIPAM) microgel particles.

## Experimental

### Materials

NIPAM (Kodak Eastman) and BA (*N,N'*-methylene bisacrylamide) (Aldrich, 99%) were recrystallized from hexane and methanol, respectively. Azobiscyanopentanoic acid (Fluka, 98%) was used as received. 'Milli-Q' grade water was used exclusively.

### PEG polymers

Two sets of PEG polymers were employed in the study: 'reagent' and 'calibration standard' grades. The latter were more 'monodisperse'. The molecular weights of the polymers were determined by gel permeation chromatography (by RAPRA and Polymer Laboratories for the reagent and calibration standard grade polymers, respectively) and appear in Table 1.

### Microgel synthesis

The synthetic method given below is for poly(NIPAM/9.0BA). The microgel was prepared using 9.0 wt.% BA based on the total mass of monomers added. A similar method was employed in the preparation of poly(NIPAM/4.5BA).

Water (600 ml) containing NIPAM (8.40 g, 74.2 mmol) and BA (0.84 g, 5.45 mmol) was adjusted to a pH of 9 (with aqueous NaOH), added to a 1000 ml reactor, and stirred (using a Teflon stirrer blade) at 350 rpm. The reactor (a five-

Table 1 Molecular weight data for PEG polymers

PEG grade	$M_{w,P}^a$	$M_w/M_n$
reagent	220	1.2
	1080	1.13
	2010	1.12
	3490	1.15
	8350	1.08
calibration	194	1
	440	1.1
	620	1.05
	1080	1.04
	1470	1.03
	4120	1.02
	7100	1.02
	8650	1.03

<sup>a</sup> Peak molecular weight.

necked, round-bottomed flask) was contained in a constant-temperature oil-bath maintained at  $70 \pm 1^\circ\text{C}$ . Water (13 ml) was added to finely ground azobiscyanopentanoic acid (0.516 g, 1.84 mmol) and the pH of the mixture adjusted to 11 using aqueous NaOH. Nitrogen gas was passed through the monomer solution for 20 min prior to the addition of the initiator solution. The latter was added under anaerobic conditions and a nitrogen atmosphere maintained over the surface of the latex throughout the reaction (total of 16 h). The cooled latex was filtered through glass wool. The total solids content and polymer conversion were typically 1.5 wt.% and 96% respectively. The microgel was cleaned using ten centrifugation cycles with water and stored at  $5^\circ\text{C}$  in the absence of light.

### Physical measurements

Total solids contents were determined gravimetrically by drying pre-weighed samples of latex at  $70^\circ\text{C}$ . Particle size measurements were obtained using a Hitachi HS7S TEM instrument which was calibrated with a diffraction grating. SEM was performed using a Hitachi S-2300 instrument. Optical spectra were recorded at  $25^\circ\text{C}$  over the range 400–625 nm using a UVIKON 940 spectrophotometer.

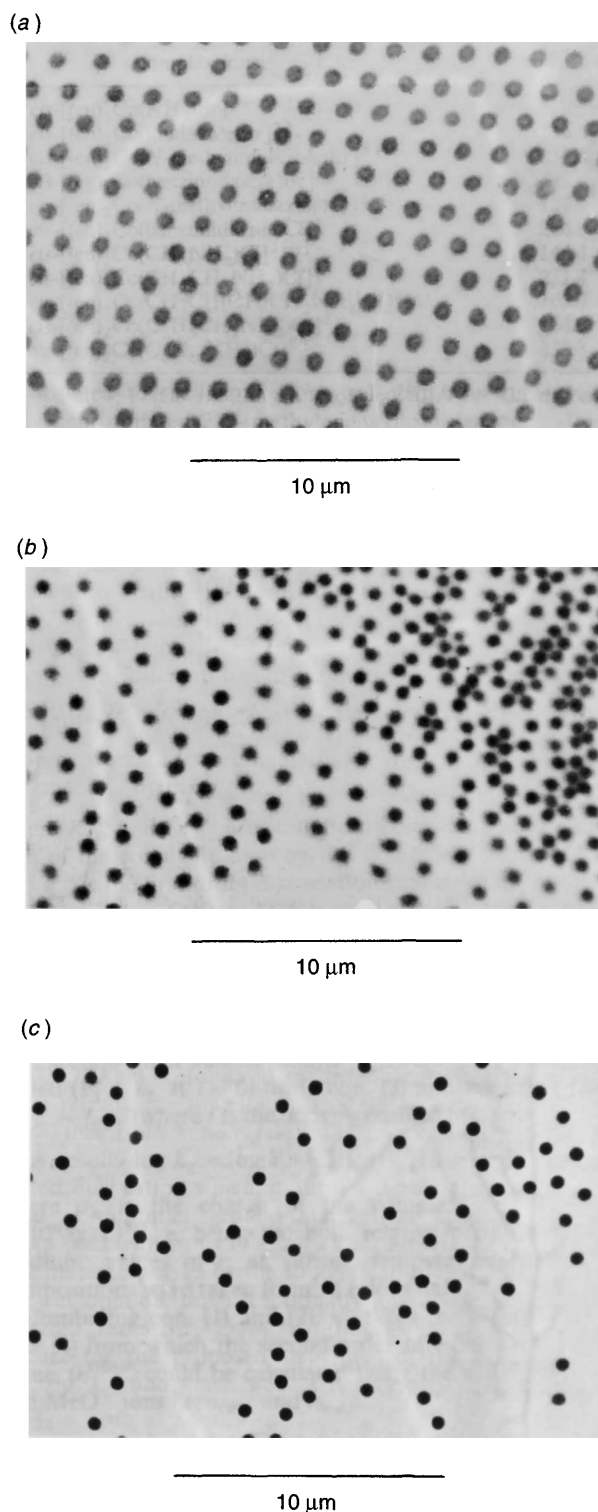
PCS data were obtained using a Brookhaven 'Zeta Plus' instrument. All samples, containing microgel particles and free polymer, were allowed to mix under rotation for ca. 24 h and stand for another 24 h, prior to measurement. The PCS measurements were made at  $25^\circ\text{C}$  unless stated otherwise. The values for the hydrodynamic diameter ( $d$ ) reported are the average of at least five measurements using a data acquisition time of 5 min per measurement. We express the changes in the swelling of the microgel particles in terms of the deswelling ratio,  $\alpha = (d/d_0)^3$ , where  $d_0$  is the value measured for the control sample [pure poly(NIPAM) microgel at  $25^\circ\text{C}$ ]. The coefficient of variation of the deswelling ratio was 10%. All data obtained in the presence of PEG were obtained using a microgel concentration of 0.050 wt.%.

The viscosities and refractive indices of the parent-free polymer solutions were measured at  $25^\circ\text{C}$  using a calibrated Cannon–Fenske U-type capillary viscometer and an Abbé refractometer, respectively. The viscosity–shear rate characteristics of several of the polymer solutions were investigated over the shear rate range  $1\text{--}40\text{ s}^{-1}$  using a Bolin Rheometer CS, and found to be Newtonian.

## Results and Discussion

### Characterization of poly(NIPAM) by particle size measurements

Transmission electron micrographs of poly(NIPAM/4.5BA) particles deposited at room temperature (*i.e.*, from the swollen state) appear in Fig. 1(a) and (b). The particles appear to have deposited in a two-dimensional array. Similar micrographs were reported by Pelton and Chibante.<sup>1</sup> They attributed the ordered particle arrangement to surface tension which, combined with interparticle repulsion, causes the swollen particles to form a two-dimensional close-packed array within the droplets. During solvent evaporation the particles pack in an ordered manner in the remaining wet part of the film on the grid, *i.e.*, in advance of the three-phase (air/water/surface) contact line. The spacing between the particles shows that the particles have shrunk somewhat after drying. In those parts of the film which dry first, the particles do not form an array. Such disordered arrangements of particles may be seen in the upper right-hand region of Fig. 1(b). The three-phase contact line appears to have advanced from right to left in this micrograph.



**Fig. 1** Transmission electron micrographs of poly(NIPAM/4.5BA) particles. The particles shown in (a) and (b) were deposited from aqueous dispersions at room temperature. The particles shown in (c) were deposited at  $50^\circ\text{C}$ .

It is usually the case that the average diameter of those particles in the more ordered regions of the TEM grid is greater than for the more concentrated, random regions. Improved uniformity of the particle size of poly(NIPAM/4.5BA) could be achieved by depositing the particles at  $50^\circ\text{C}$  onto the TEM grid [Fig. 1(c)]. The particles also appear to be more spherical than those shown in Fig. 1(a) and (b). However, the average particle diameter obtained from the TEM micrographs for these particles exceeds that obtained from PCS measurements at  $50^\circ\text{C}$  (see Table 2).

Table 2 Particle size data for poly(NIPAM) microgels<sup>a</sup>

microgel	particle diameter TEM/nm <sup>b</sup>		particle diameter PCS/nm		$\alpha^c$
	25 °C	50 °C	$d_o/25\text{ °C}$	$d_c/50\text{ °C}$	
poly(NIPAM/4.5BA)	610 ± 61	530 ± 27	685 ± 23	355 ± 12	0.140
poly(NIPAM/9.0BA)	420 ± 18	—	590 ± 19	325 ± 11	0.170
poly(NIPAM/9.1BA) <sup>d</sup>			393	217	0.170

<sup>a</sup> The ± numbers represent one standard deviation. <sup>b</sup> Particles deposited at room temperature and 50 °C. <sup>c</sup> Deswelling ratio of the particles at 50 °C. <sup>d</sup> Data taken from ref. 7.

Perusal of the data shown in Table 2 reveals that the deswelling ratio of poly(NIPAM/9.0BA) at 50 °C is the same as that measured by Wu *et al.*<sup>7</sup> for a similar microgel. However, Wu *et al.* prepared poly(NIPAM/9.1BA) in the presence of SDS (sodium dodecyl sulfate, 0.41 mmol l<sup>-1</sup>). SDS stabilizes the growing particles at an earlier stage of the polymerization and results in smaller particles [*cf.* poly(NIPAM/9.0BA)]. The similarity of the deswelling ratios of poly(NIPAM/9.0BA) and poly(NIPAM/9.1BA) suggests that the presence of 0.41 mmol l<sup>-1</sup> SDS does not significantly affect the distribution of BA within the microgel particles. It is also evident from Table 2 that the deswelling ratios of poly(NIPAM/4.5BA) and poly(NIPAM/9.0BA) are comparable. This is despite the latter being prepared using twice the BA concentration of the former, and may be ascribed to an inhomogeneous distribution of BA throughout the microgel particles.<sup>7</sup>

Pelton and Chibante<sup>1</sup> suggested that poly(NIPAM) microgel particles formed discs during solvent removal. Fig. 2 shows an SEM micrograph of poly(NIPAM/4.5BA) particles viewed at an angle of 30° to the sample plane. The particles appear to have formed oblate spheroids upon drying. This is the most likely reason for the particle diameters measured by TEM being larger than those measured on the same microgel at 50 °C by PCS. It was therefore decided to use the hydrodynamic diameter measured by PCS at 50 °C (Table 2) to represent the collapsed particle diameter ( $d_c$ ) and not the TEM value.

Response of poly(NIPAM/4.5BA) particles to temperature cycling

An important property of poly(NIPAM) microgel particles is their ability to respond to changes in temperature. A study of the rate at which the particle size changes in response to temperature variation was undertaken in order to obtain information about the molecular processes involved in the temperature-induced phase transition. Fig. 3 shows the change in the deswelling ratio induced by cycling the temperature of the dispersion between 28 and 60 °C. (The temperature of the

dispersion was measured *in situ* using a calibrated thermocouple.) The data show significant scatter (particularly at 28 °C), which arises primarily from the necessity of employing short data acquisition times (30 s) during these measurements. However, the data shown in Fig. 3 reveal that the particles are able to swell and deswell fairly rapidly in response to the temperature variations imposed.

The data from Fig. 3 have been replotted in Fig. 4 to show the variation of the deswelling ratio with temperature. Hysteresis is now clearly evident. This may originate from ‘entanglements’ formed during collapse, after heating.<sup>19</sup> An additional explanation is that the collective diffusion of the polymer network and the associated bulk counterflow of water through the microgel particles occurs at a slower time-scale than that of the temperature variation.<sup>20</sup> Work performed on similar microgel particles<sup>21</sup> revealed that hysteresis is absent when the particles are allowed sufficient time to equilibrate at each temperature (*ca.* 10 min). Therefore, the hysteresis observed in Fig. 4 has a kinetic origin and most likely involves network diffusion. Matsuo and Tanaka<sup>22</sup> observed hysteresis in poly(NIPAM-co-sodium acrylate) gel beads and reported a hysteresis gap of 3 °C. This value is consistent with the data shown in Fig. 4.

Stability of poly(NIPAM/4.5BA) microgel particles in the presence of PEG

The addition of free polymer (*i.e.*, non-adsorbing polymer) to a colloidal dispersion may lead to depletion flocculation.<sup>23,24</sup> It was therefore necessary to test if this was occurring in the systems studied in this work. Turbidity–wavelength measurements provide a useful method for detecting aggregation in dispersions,<sup>25</sup> and Snowden and Vincent<sup>4</sup> have shown that the method is applicable to poly(NIPAM) microgels. Flocculation is detected by a decrease in the magnitude of *n*, where

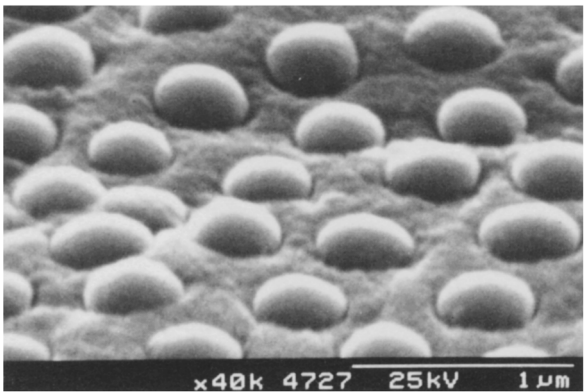


Fig. 2 Scanning electron micrograph of poly(NIPAM/9.0BA). Particles deposited at room temperature and viewed at an angle of 30° to the sample plane.

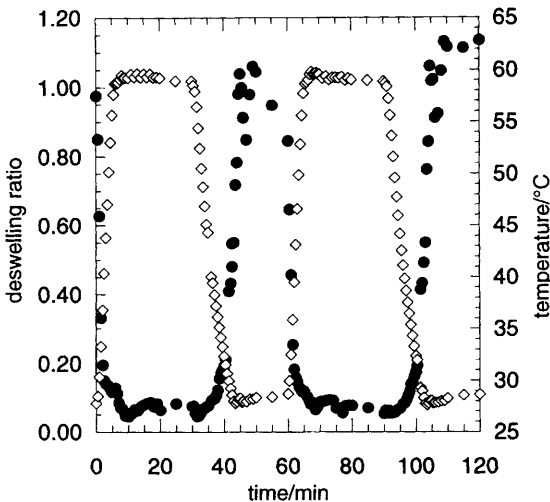
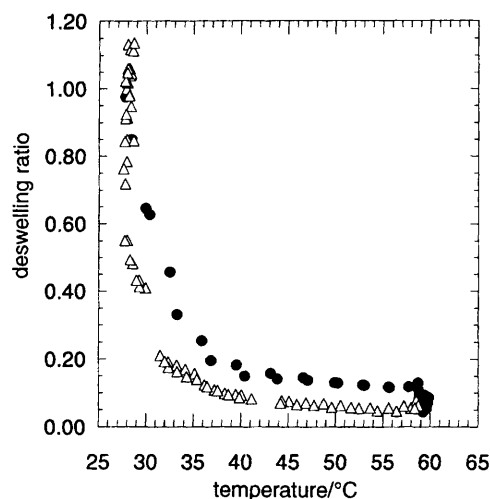


Fig. 3 Variation of the deswelling ratio (●) of poly(NIPAM/4.5BA) with time in response to temperature (◇) cycling. The data have been smoothed.



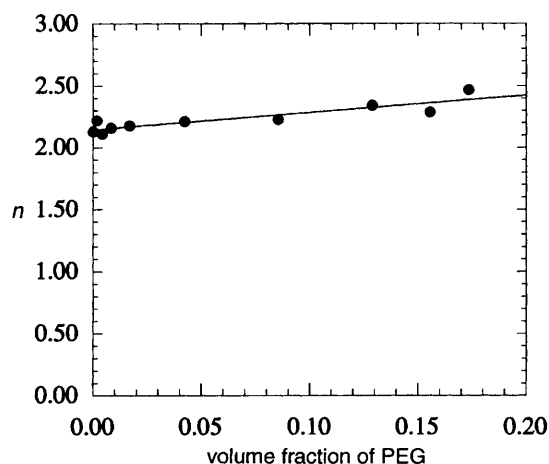


**Fig. 4** Deswelling ratio of poly(NIPAM/4.5BA) vs. temperature during heating (●) and cooling (△) cycles. The data have been smoothed.

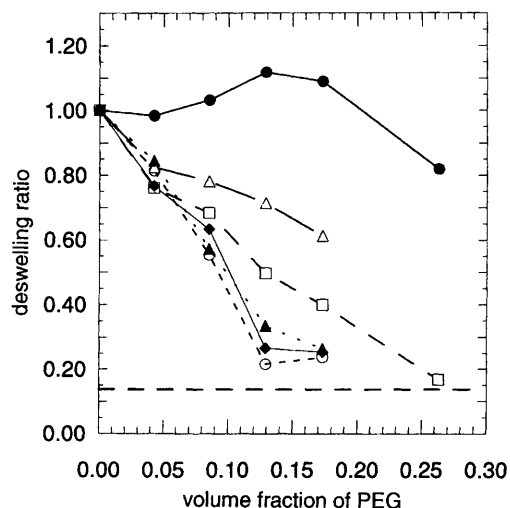
$n = -d \log(\text{O.D.})/d \log(\lambda)$  (O.D. and  $\lambda$  are the optical density and wavelength, respectively).<sup>25</sup> The values of  $n$  measured for poly(NIPAM/4.5BA) in the presence of PEG 3490 are shown in Fig. 5. The magnitude of the  $n$  value tends to increase with increasing volume fraction of PEG 3490. These data support the view that the microgel particles do remain stable throughout the entire range of PEG volume fractions studied. The change in the  $n$  value may be due to particle shrinkage and/or an increase in the refractive index of the polymer solution. The other systems discussed below were routinely examined using the above method and were also found to be stable.

#### Osmotic deswelling of poly(NIPAM/4.5BA) in the presence of PEG

Fig. 6 shows the variation of the deswelling ratio of poly(NIPAM/4.5BA) with the volume fraction of PEG, for the range of PEG molecular weights available in the more poly-disperse 'reagent' grade series. The trends observed generally agree with the results of Ishidao *et al.* for macrogels.<sup>17</sup> It is evident from Fig. 6 that no deswelling occurs in the presence of PEG 220, at least for volume fractions of free PEG less than *ca.* 0.2. This is presumably because these low molecular weight PEG chains can freely enter the microgel particles. To some extent this low molecular weight PEG may be regarded as a co-solvent (*i.e.*, with water). There is some evidence of shrinkage at higher PEG volume fractions ( $> 0.2$ ) which may



**Fig. 5** Variation of  $n [= -d \log(\lambda)/d \log(\text{O.D.})]$  of poly(NIPAM/4.5BA) with volume fraction of PEG 3490

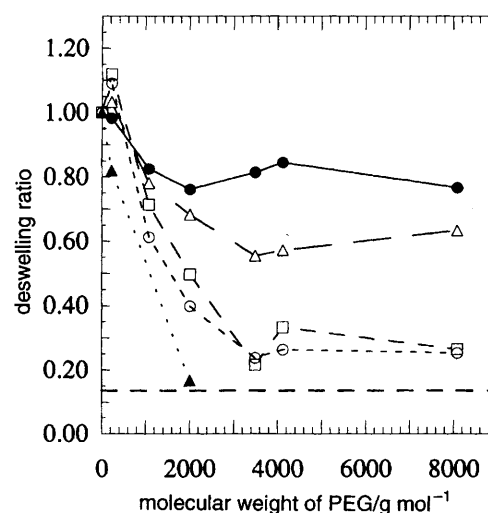


**Fig. 6** Effect of the volume fraction of reagent grade PEG on the deswelling ratio of poly(NIPAM/4.5BA). The PEG peak molecular weights are 220 (●), 1080 (△), 2010 (□), 3490 (○), 4120 (▲) and 8350 (◆). The horizontal line shows the value of the deswelling ratio of pure poly(NIPAM/4.5BA) at 50°C.

be due to the net solvency for the poly(NIPAM) becoming slightly worse. Zhu and Napper<sup>26</sup> found that poly(NIPAM) chains at latex interfaces collapsed and then reswelled in alcohol–water blends as the alcohol volume fraction was increased. The collapse of the polymer chains in a mixture of good solvents was termed 'co-non-solvency', and may be responsible for the shrinkage of poly(NIPAM/4.5BA) noted above. An alternative explanation is that the microgel particles become saturated with PEG 220 at volume fractions  $> 0.2$  leading to osmotic compression.

It is evident from the data shown in Fig. 6 that deswelling occurs at low PEG volume fractions for PEG molecular weight  $\geq 1080 \text{ g mol}^{-1}$ , when the free chains are effectively excluded from the interior of the microgel particles.

The data shown in Fig. 6 have been replotted in Fig. 7 to show the variation of deswelling ratio with molecular weight, at fixed free PEG volume fraction. It is noteworthy that, for a given volume fraction of PEG, the deswelling ratio effectively becomes independent of molecular weight above some value and only depends on volume fraction. If all the free chains are

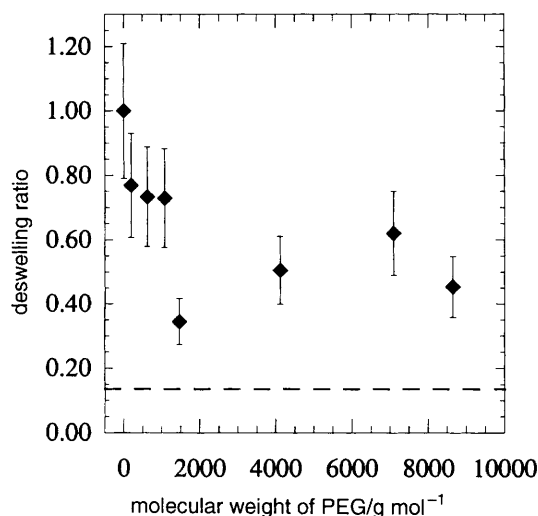


**Fig. 7** Effect of the molecular weight of reagent grade PEG on the deswelling ratio of poly(NIPAM/4.5BA). The volume fractions of PEG are 0.0424 (●), 0.085 (△), 0.129 (□), 0.173 (○) and 0.263 (▲). The horizontal line shows the value of the deswelling ratio of pure poly(NIPAM/4.5BA) measured at 50°C.

indeed excluded from the microgel particles (above some molecular weight), this is what one would expect to observe if an osmotic compression mechanism is operating.

The dotted line in Fig. 6 and 7 corresponds to the deswelling ratio obtained on heating the microgel particles to 50 °C ( $\alpha = 0.140$ ) in the absence of free PEG and is the minimum obtainable value. It is clear from the trends in Fig. 6 and 7 that this value would be reached if the volume fraction range of free PEG had been extended beyond those reported. Unfortunately, flocculation of the particles became evident at higher PEG concentrations. Nevertheless, it would seem that with the poly(NIPAM) microgels sufficient PEG may be added (in principle) to remove the water from the microgel particles, in a similar way to changes in solvency caused by raising the temperature (see above). It is also of interest to compare the time-scale of the two mechanisms; with the PEG 3490 sample (at  $\alpha = 1.0$ ), it took *ca.* seven minutes for the final value of the deswelling ratio to be attained, after adding the polymer to the microgel dispersion. The thermally induced deswelling reported (see Fig. 3) on changing the temperature between 28 and 50 °C was also on a similar time-scale.

Fig. 8 shows the variation of the deswelling ratio of poly(NIPAM/4.5BA) with molecular weight for the more monodisperse 'calibration grade' PEG samples. The data obtained for molecular weights of PEG > 1400 g mol<sup>-1</sup> show considerable deswelling. The deswelling ratio also appears to increase as the molecular weight of PEG approaches 9000 g mol<sup>-1</sup>. These data are broadly in agreement with those obtained using the less monodisperse grade PEG (Fig. 7). The latter data are less sensitive to changes in molecular weight due to the presence of a range of polymer coil sizes, which is reflected by the absence of a distinct minimum of the deswelling ratio. Conversely, the data obtained using the more monodisperse, calibration grade, PEG (Fig. 8) show evidence of a minimum when the PEG molecular weight is 1470 g mol<sup>-1</sup>. Thus, obstruction to the migration of monodisperse PEG into the microgel interior (and hence osmotic deswelling) occurs when the molecular weight is 1470 g mol<sup>-1</sup>. The radius of gyration of PEG may be estimated from<sup>27</sup>  $\langle r^2 \rangle^{1/2} = 0.060M^{0.5}$  where  $M$  is the molecular weight (g mol<sup>-1</sup>). Therefore, the minimum pore size of the poly(NIPAM/4.5BA) particles is approximately 2.0 nm.



**Fig. 8** Effect of the molecular weight of monodisperse calibration grade PEG (volume fraction = 0.129) on the deswelling ratio of poly(NIPAM/4.5BA). The horizontal line shows the value of the deswelling ratio of pure poly(NIPAM/4.5BA) measured at 50 °C. The error bars represent  $\pm$  two standard deviations.

## Conclusions

The work presented above allows the following conclusions to be made. (1) Transmission electron microscopy does not yield accurate values of the collapsed particle diameter of poly(NIPAM/4.5BA) and poly(NIPAM/9.0BA). These particles do not completely deswell upon removal of the solvent and deform under gravity to an oblate spheroid shape. (2) Poly(NIPAM) microgel particles swell and deswell rapidly when cycled between 28 and 60 °C. However, some hysteresis is present. This probably originates from a limiting collective diffusion rate of the polymer network. (3) Deswelling of poly(NIPAM/4.5BA) occurs in the presence of monodisperse PEG with a molecular weight of greater than or equal to 1470 g mol<sup>-1</sup>. Above this limiting value, the extent of deswelling generally decreases with increasing molecular weight of monodisperse PEG. The minimum pore size of poly(NIPAM/4.5BA) is estimated as 2 nm from the deswelling data.

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