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ORIGINAL CONTRIBUTION

B.R. Saunders
B. Vincent

Osmotic de-swelling of polystyrene microgel particles

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Dr. B.R. Saunders · Prof. B. Vincent (✉)
School of Chemistry
University of Bristol
Cantock's Close
Bristol BX8 1TS, United Kingdom

Abstract The effects of added free polymer on the swelling and stability of polystyrene microgel particles dispersed in ethylbenzene have been investigated. The microgel particles were characterized by photon correlation spectroscopy (PCS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) measurements. TEM measurements showed that particles deposited on grids from ethylbenzene (a good solvent for polystyrene) were invariably larger than the same particles deposited from water. SEM data revealed that removal of ethylbenzene favoured the collapse of the particles to a deformed oblate spheroid shape. The stability of the microgel particles in the presence of free (i.e. non-adsorbing) polystyrene was investigated by turbidity – wavelength measurements, and the stability thresholds established. Osmotic de-swelling of the swollen particles was observed in the presence of free polystyrene using PCS. The extent of de-swelling increased with an increase of the molecular weight and concentration of the free polystyrene. A thermodynamic model, based on Flory's theory of network swelling, is presented which, in the presence of excluded free polystyrene, provides a qualitative description of the de-swelling of the microgel particles. The results are also compared to the predictions of scaling theory.

Key words Microgel – polystyrene – swelling – and flocculation

Introduction

The study of microgels occupies an important niche in the field of colloid science [1–5]. A microgel particle is a cross-linked latex particle that is swollen by a good solvent. Microgels can provide rheological control for high-solids surface coatings formulations. Dissolved polymers are usually present in surface coatings formulations and their influence on microgel particles requires elucidation. The aim of this study is to investigate the effect of free polymer (i.e., a polymer that does not adsorb onto the particle surface) on the swelling of polystyrene microgel particles.

Shashou et al. [6] were the first workers to systematically study microgel particles. They measured the viscosities of a range of microgel dispersions and found that the intrinsic viscosity was inversely proportional to the mole ratio of cross-linking monomer used during synthesis. This implies that the size of the swollen microgel particles decreases with increasing concentration of cross-linker in the particles. Sieglaff [7] subsequently studied the swelling of polystyrene microgels in a range of solvents and concluded that swelling of microgel particles mirrors the changes in dimensions of the analogous linear polymers in solution, both effects reflecting similar thermodynamic solvent–segment interactions. The stability boundaries of poly(styrene-co-divinylbenzene) [PS-DVB] microgel

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particles, dispersed in toluene, in the presence of free polystyrene were also investigated by Sieglaff [8]. Interestingly, Sieglaff suggested that excluded free polymer could lead to de-swelling of microgel particles [8]. An extensive study of the stability thresholds of the PS-DVB/ethylbenzene/free polystyrene system was performed by Clarke and Vincent [9]. These authors invoked depletion effects to account for the observed flocculation at high free polymer concentration; three-component stability diagrams were constructed. Racquois et al. [10] recently investigated the rheology of concentrated polystyrene microgel/toluene/free polystyrene systems and found that the presence of the free polymer caused a decrease in the overall viscosity of the suspension. It was suggested that osmotic de-swelling of the particles occurred and that the extent of de-swelling increased with increasing free polymer molecular weight.

We recently studied the swelling of poly(NIPAM) [NIPAM = *N*-isopropylacrylamide] microgel particles dispersed in aqueous PEG [(PEG = poly(ethylene glycol)] solutions [11]. Osmotic de-swelling of the microgel particles occurred in the presence of PEG with a molecular weight above a minimum value. The extents of de-swelling observed, in some instances, approached that of the fully collapsed particle.

De-swelling of *macrogels* in the presence of free polymers was first reported [12] in 1945. Boyer proposed a method for determining the number average molecular weight of the free polymer based on the effect. Since 1945, the de-swelling of *macrogels* in the presence of free polymer has been studied by a number of authors [13–18]. Bastide et al. [18] investigated the de-swelling of polystyrene *macrogel* in the presence of free polystyrene/benzene solution. They developed a scaling theory which provided a good fit to their experimental data.

In the present work we have systematically examined the effect of free polystyrene molecular weight and concentration on the swelling of PS-DVB *microgel* particles dispersed in ethylbenzene. A thermodynamic model based on Flory's model for the swelling of polymer networks is applied to the experimental data.

Theory

A cross-linked microgel particle swells when dispersed in a good solvent. The swelling continues until the swelling force (resulting from attractive polymer–solvent interactions) balances the restraining elastic force (due to the cross-links). In the discussion that follows the subscripts 1, 2, and 3 refer to the solvent, the polymer network of the microgel particle, and the free polymer, respectively. The average volume fraction (ϕ_2) of the polymer in the swollen state is the ratio of the volume of the collapsed (unswollen) particle (V_c) to that of the swollen particle. Flory [19] derived the following expression for ϕ_2:

$$\phi_2 = \left\{\frac{2XV_1}{V_c(\frac{1}{2} - \chi_{12})}\right\}^{3/5} \tag{1}$$

where X is the number of moles of cross-links, V_1 the molar volume of solvent, and χ_{12} the solvent/polymer interaction parameter. If we consider a chemically cross-linked copolymer comprised of monomers A and B (where A is the difunctional monomer) and the amount of A is much less than B, it may be shown that the average cross-link density in the unswollen particle is given by,

$$\frac{X}{V_c} = \frac{\rho_B}{M_A + (\frac{1}{x_A} - 1)\,M_B} \tag{2}$$

where ρ_B, M_A, M_B, and x_A are the density, molecular weight, and mole fraction of monomer A or B, as indicated. If the values of M_A and M_B are assumed to be the same then, Eq. (2) reduces to:

$$\frac{X}{V_c} \simeq \frac{x_A\rho_B}{M_B}\,. \tag{3}$$

We now consider a microgel particle suspended in a polymer solution. It is assumed that free polymer is excluded from the microgel particle interior. The chemical potential of the solvent (μ_1) in the free polymer solution is given by the standard Flory–Huggins expression [19]:

$$\frac{\mu_1 - \mu_1^0}{RT} = -\left\{\left(\frac{1}{2} - \chi_{13}\right)\phi_3^2 + \frac{\phi_3\rho_3V_1}{M_3}\right\} \tag{4}$$

where μ_1^0 and ϕ_3 are the chemical potential of the pure solvent and the volume fraction of the free polymer, respectively.

On the other hand, the chemical potential of the solvent within the swollen microgel particle is given by [19],

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln(1 - \phi_2) + \phi_2 + \chi_{12}\phi_2^2$$
$$+ 2V_1\left(\frac{x}{V_c}\right)\left(\phi_2^{1/3} - \frac{\phi_2}{2}\right) \tag{5}$$

which may be simplified (when $\phi_2 \ll 1$) to:

$$\frac{\mu_1 - \mu_1^0}{RT} \cong -\phi_2^2\left(\frac{1}{2} - \chi_{12}\right) + 2V_1\left(\frac{x_A\rho_B}{M_B}\right)\phi_2^{1/3}\,. \tag{6}$$

The chemical potential of the solvent surrounding the microgel particle and that contained within the particle interior must be equal at equilibrium. Combining Eqs. (4)

and (6) leads to:

$$\left(\frac{1}{2}-\chi_{13}\right)\phi_3^2+\frac{\phi_3 M_1 \rho_3}{\rho_1 M_3}$$
$$=\phi_2^2\left(\frac{1}{2}-\chi_{12}\right)-2\left(\frac{M_1}{\rho_1}\right)\left(\frac{x_A \rho_B}{M_B}\right)\phi_2^{1/3}. \qquad (7)$$

Equation (7) predicts that the microgel particle will deswell if the volume fraction of free polymer is increased, or if the molecular weight of the free polymer is decreased. Equation (7) cannot be solved explicitly for ϕ_2; it does give the implicit dependence of ϕ_2 on M_3 and ϕ_3. However, the following analytical expressions for ϕ_3 and M_3 may be derived,

$$\phi_3=-\frac{M_1\rho_3}{2\rho_1 M_3(\frac{1}{2}-\chi_{13})}+\left\{\left(\frac{M_1\rho_3}{2\rho_1 M_3(\frac{1}{2}-\chi_{13})}\right)^2\right.$$
$$\left.-\left(\frac{2M_1 x_A \rho_B \phi_2^{1/3}}{\rho_1 M_B(\frac{1}{2}-\chi_{13})}\right)+\frac{\phi_2^2(\frac{1}{2}-\chi_{12})}{(\frac{1}{2}-\chi_{13})}\right\}^{1/2} \qquad (8)$$

and

$$M_3=\frac{\dfrac{\phi_3 M_1 \rho_3}{\rho_1}}{\phi_2^2(\frac{1}{2}-\chi_{12})-\dfrac{2\phi_2^{1/3}M_1 x_A \rho_B}{\rho_1 M_B}-(\frac{1}{2}-\chi_{13})\phi_3^2}. \qquad (9)$$

Experimental

Materials

Styrene (Aldrich, 99%) was purified by vacuum distillation and stored in the dark under a nitrogen atmosphere at −10 °C. DVB (Aldrich, 55%) and ethylbenzene (Lancaster, 99%) were used as received. Azobiscyanopentanoic acid (Fluka, 98%) was also used as received and the water was "Milli-Q" grade.

Polystyrene free polymers

Two sets (A and B) of polystyrene polymers were employed in this work: "in-house" (A) and "calibration standard" (B) grades. Those in set B (purchased from Polymer Laboratories) were somewhat more "monodisperse" than those in set A which were prepared [20] in house by the anionic polymerization of styrene in toluene in the presence of butyllithium at 25 °C. The polymerization was terminated by the addition of methanol. The molecular weights of the polymers were determined by gel permeation chromotography (by RAPRA and Polymer Laboratories for A and B, respectively), and appear in Table 1.

Table 1 Molecular weight data for polystyrene polymers

Polystyrene	M_W[a]	M_W/M_N
A	8500	1.77
	42300	1.37
B	600	1.15
	970	1.12
	2050	1.05
	3030	1.04
	4780	1.03
	5450	1.03
	6960	1.03
	9660	1.02
	11280	1.02
	12640	1.02
	17000[b]	1.04
	20300	1.03

[a] Weight average molecular weight (g/mol). [b] Peak molecular weight.

Microgel synthesis

The synthetic method given below is for PS-0.3DVB. The microgel was prepared using 0.30 wt.% DVB based on the total mass of monomers added. A similar method was employed for the preparation of PS-1.4DVB.

Water (265 ml) was adjusted to a pH of 9 (with aqueous NaOH), added to a 500 ml reaction vessel, and stirred (using a Teflon stirrer blade) at 350 rpm. The reaction vessel (a five-necked, round-bottom flask) was contained in a constant-temperature oil-bath, maintained at 70 ± 1 °C. Water (7 ml) was added to finely ground azobiscyanopentanoic acid (0.244 g, 0.871 mmol) and the pH of the mixture adjusted to 11 using aqueous NaOH. Styrene (28.6 g, 0.275 mole) was added to DVB (0.086 g, 0.661 mmol), mixed thoroughly, and then added to the reactor. The initiator solution was added with stirring to the deoxygenated monomer mixture 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 9 wt.% and 92%, respectively. Unreacted styrene was removed using rotary evaporation. The latex was then cleaned using ten centrifugation cycles with water. The latex was stored at 5 °C in the absence of light. Portions of the latex were freeze-dried and redispersed in ethylbenzene. The microgel was subjected to five centrifugation cycles with ethylbenzene in order to remove any uncrosslinked polystyrene.

Physical measurements

The total solids contents of the dispersions were determined gravimetrically by drying pre-weighed samples at

70 °C. Particle size measurements were determined from transmission electron microscopy (TEM) measurements using *Hitachi HS7S* and *JEOL JEM-100CX* instruments. Scanning electron microscopy (SEM) results were obtained using a *Hitachi S-2300* instrument. Particles examined by electron microscopy were deposited on TEM grids at room temperature. Optical spectra were recorded at room temperature over the wavelength range 400–625 nm using a *Perkin Elmer Lambda* 5 spectrophotometer. Carefully matched 10 mm glass cells were employed and the dispersions obeyed the Beer–Lambert law.

Photon correlation spectroscopy (PCS) data were determined at 25 °C using a Brookhaven Zeta Plus instrument. All samples, containing microgel particles and free polymer, were mixed thoroughly prior to measurement. The values of the hydrodynamic diameter (d) reported in this work are the average of at least three measurements, with a data acquisition time of 5 min per measurement. The de-swelling ratio, $\alpha = (d/d_0)^3$ (where d_0 is the diameter of the microgel particles measured in pure ethylbenzene) and the volume fraction, ϕ_2 (defined above), represent the extent of swelling of the microgel particles. (The de-swelling ratio and volume fraction are related by $\alpha = (d_c/d_0)^3/\phi_2$, where d_c is the diameter of the collapsed particles). The coefficient of variation of the de-swelling ratio was found to be less than 4.5%. All the PCS and turbidity data measured in the presence of free polystyrene were obtained using microgel concentrations of 0.090 and 0.180 wt.% for PS-1.4DVB and PS-0.3DVB, respectively. The viscosities and refractive indices of the parent free polymer solutions were measured at 25 °C using a calibrated Cannon-Fenske U-type capillary viscometer and an Abbé refractometer, respectively.

The PCS and turbidity – wavelength measurements of the microgel/ethylbenzene/free polymer systems were generally made after an equilibration time of 48 h. However, the microgel particles flocculated within 48 h in the presence of PS20300, which necessitated measurements being made after about 2 h. Extended kinetic studies of PS-0.3DVB in the presence of PS17000 showed that the PCS and turbidity – wavelength data achieved constant values within 30 min of mixing.

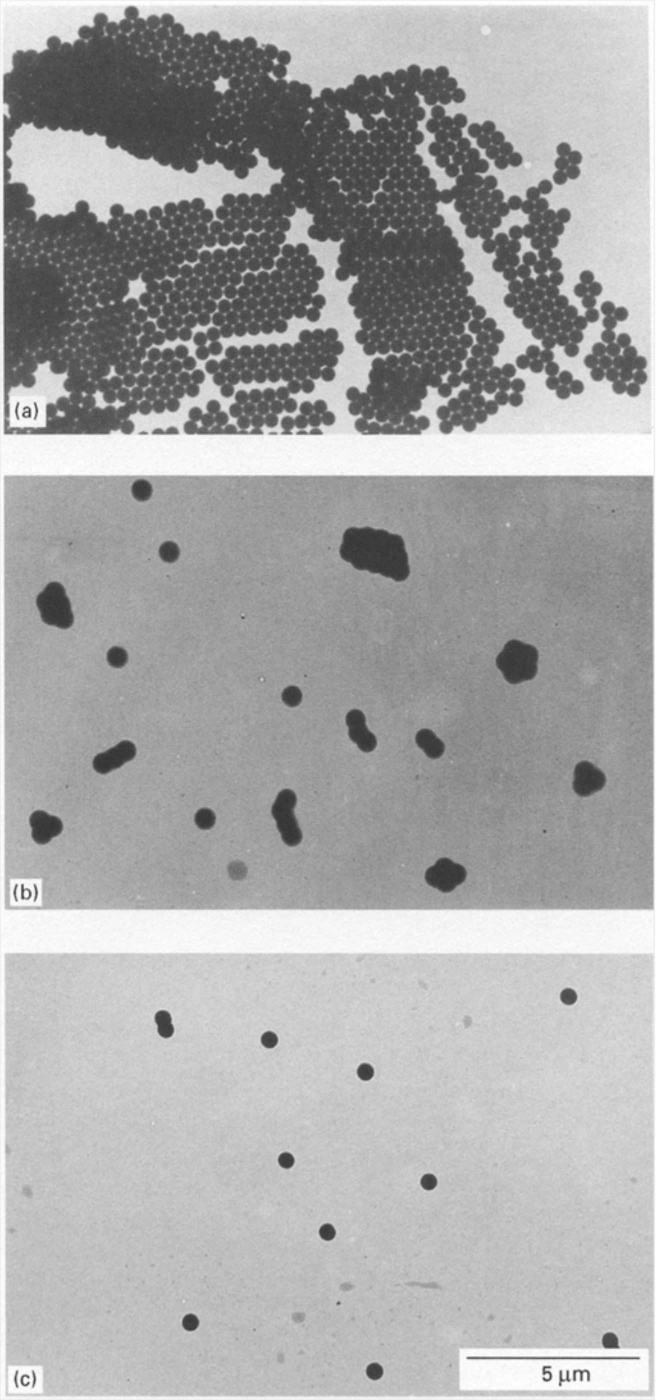

Fig. 1 Transmission electron micrographs of PS-0.3DVB deposited from water (a) and ethylbenzene (b), and also PS-1.4DVB deposited from ethylbenzene (c)

Results and discussion

Characterization of PS-0.3DVB and PS-1.4DVB by particle size measurements

Transmission electron micrographs of PS-0.3DVB and PS-1.4DVB particles deposited from water and ethylbenzene appear in Fig. 1. Particle size data derived from TEM appear in Table 2. The particles of PS-0.3DVB (Fig. 1a) and PS-1.4DVB (not shown) deposited from water are monodisperse and spherical, and have identical average diameters. The micrographs of the particles deposited from ethylbenzene (a good solvent) show evidence of

Table 2 Particle size data for PS-DVB microgels[a]

dispersion	"apparent" particle diameter (nm) TEM		particle diameter (nm) PCS	
	water	ethylbenzene	water	ethylbenzene
PS-0.3DVB	335 ± 14	540 ± 36	355 ± 3	660 ± 21
PS-1.4DVB	335 ± 15	415 ± 16	345 ± 7	570 ± 47

[a] The ± numbers represent one standard deviation.

coalescence (see Figs. 1b and c), and are similar to those reported by Hiltner for a related system [21].

The data shown in Table 2 reveal that the average diameters of the particles deposited from ethylbenzene are greater than those of similar particles deposited from water. Scanning electron micrographs of the particles appear in Fig. 2. Deposition of PS-0.3DVB particles from ethylbenzene resulted in extensive deformation of the particles to flattened oblate spheroids. Similar micrographs were obtained for poly(NIPAM) microgel particles deposited from water (a good solvent for poly(NIPAM)) [11]. The more highly cross-linked particles, PS-1.4DVB, are better able to maintain a spherical shape upon solvent removal. The inability of the particles to collapse to their preswollen dimensions (in water) upon removal of ethylbenzene by drying (as measured by TEM) is attributable to the conformational inflexibility of the polystyrene chains at room temperature.

Average hydrodynamic diameters measured for PS-0.3DVB and PS-1.4DVB dispersed in water and ethylbenzene appear in Table 2. The data show that the more highly cross-linked particles swell to a lesser extent in ethylbenzene, which is in agreement with the data of Clarke and Vincent [9].

Stability of PS-DVB microgel particles in the presence of free polystyrene

The establishment of the stability boundaries for the microgel particles in the presence of free polystyrene was a prerequisite for the PCS studies because accurate values for the de-swelling ratio can only be obtained for isolated particles. Long et al. [22] have shown that flocculation of polystyrene latexes may be detected by turbidity – wavelength measurements. Figure 3 shows a plot of log

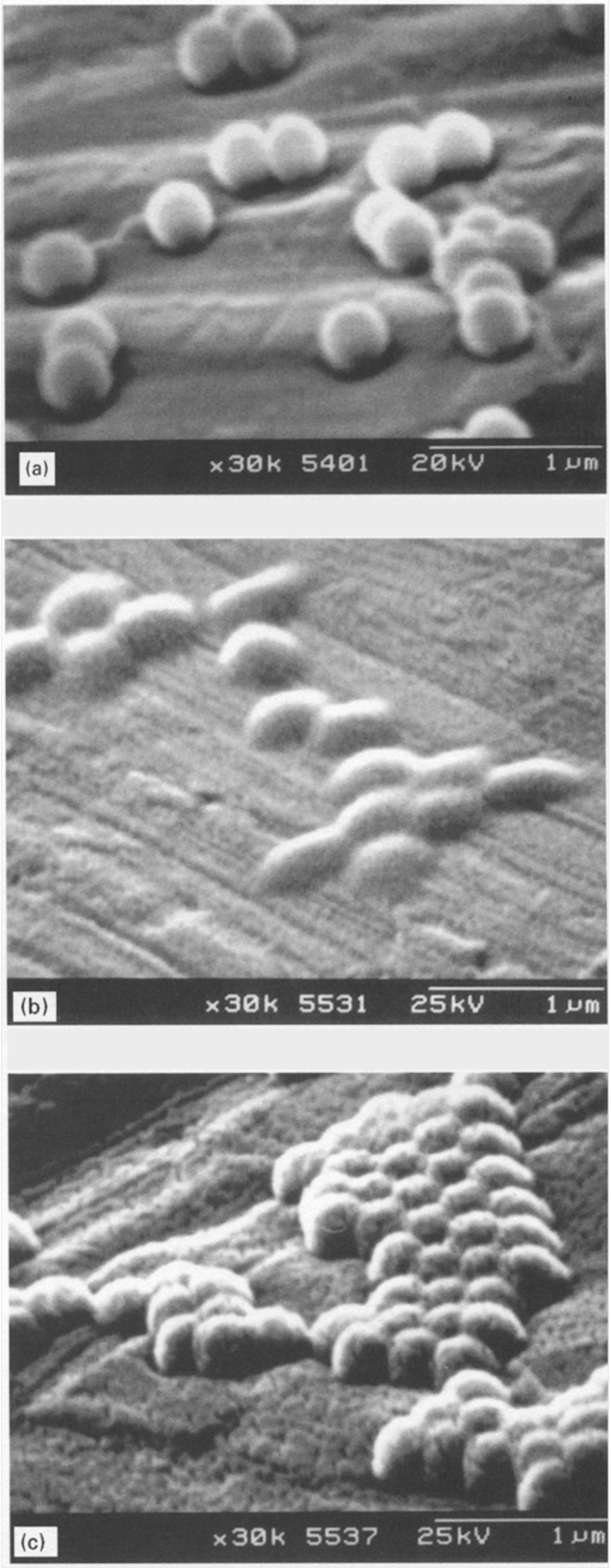

Fig. 2 Scanning electron micrographs of PS-0.3DVB deposited from water (a) and ethylbenzene (b), and also PS-1.4DVB deposited from ethylbenzene (c). The particles were viewed at an angle of 30° to the sample plane

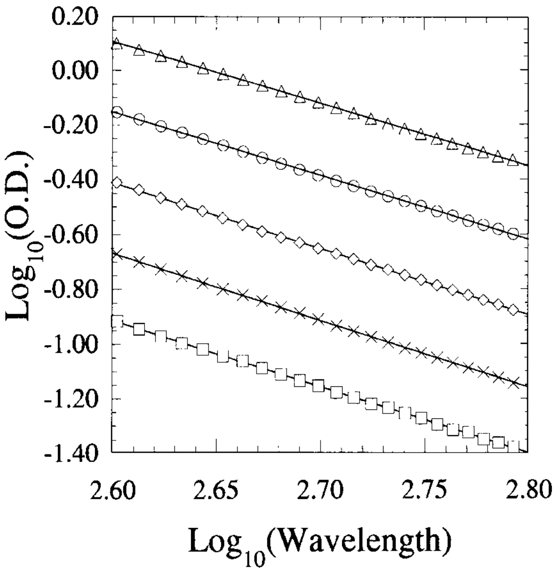

Fig. 3 Plots of $\log_{10}$(O.D.) vs. $\log_{10}(\lambda)$ for various PS-0.3DVB/ethylbenzene/PS12640 dispersions. The volume fractions of PS12640 are 0 (△), 0.048 (○), 0.095 (◇), 0.14 (×), and 0.19 (square)

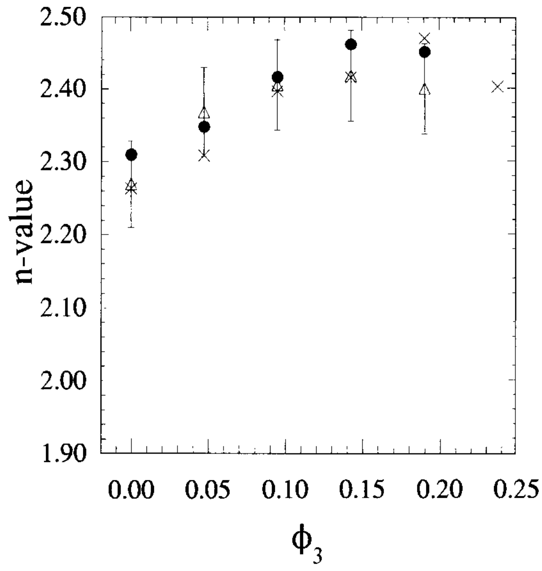

Fig. 4 Variation of the *n*-value of PS-0.3DVB with volume fraction of free polystyrene. The free polymers are PS5450 (△), PS8500 (×) and PS12640 (●). The error bars correspond to ± two standard deviations of *n*

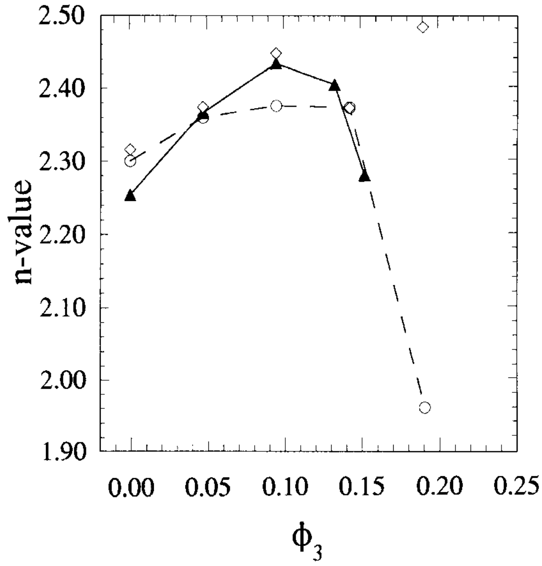

Fig. 5 Variation of the *n*-value of PS-0.3DVB with volume fraction of free polystyrene. The free polymers are PS17000 (◇), PS20300 (○) and PS42300 (▲)

optical density (O.D.) versus log wavelength (λ) measured for PS-0.3DVB in the presence of PS12640. It can be seen that the optical density decreases (at fixed wavelength) as the volume fraction of PS12640 increases. This effect is due to the increase of the refractive index of the free polymer solution with increasing free polymer volume fraction (ϕ_3). The refractive index difference between the microgel particles and continuous phase diminishes as ϕ_3 approaches ϕ_2.

From the gradient of the log(O.D.) versus log(λ) plots shown in Fig. 3, one may obtain n ($= -d\log(\mathrm{O.D.})/d\log(\lambda)$), a parameter which is very sensitive to changes in particle size. (The magnitude of n increases as particle size decreases for a given particle : medium refractive index ratio). An abrupt decrease in the magnitude of n is usually indicative of particle aggregation [22, 23]. Figures 4 and 5 show the variation of n for PS-0.3DVB in the presence of various free polystyrene polymers. The general increase of n with increasing volume fraction ϕ_3 is attributed to particle de-swelling and/or an increase of the refractive index of the free polystyrene solution. The data shown in Fig. 5 reveal that PS-0.3DVB particles flocculate when the volume fractions of PS20300 and PS42300 reach 0.19 and 0.15, respectively. These dispersions remain stable in the presence of the lower molecular weight PS samples, at least in the range of ϕ_2 values studied.

Adsorption of polystyrene chains (solvated by ethylbenzene) onto swollen polystyrene microgel particles is not thermodynamically favourable. Consequently, bridging flocculation is unlikely to be the cause of the flocculation observed in these experiments. Clarke and Vincent [9] reported that flocculation in their PS-DVB/ethylbenzene/free polystyrene dispersions was weak and reversible. Therefore, the flocculation observed in the present work may be attributed to depletion.

Similar experiments to those described above were performed using the PS-1.4DVB microgel in ethylbenzene.

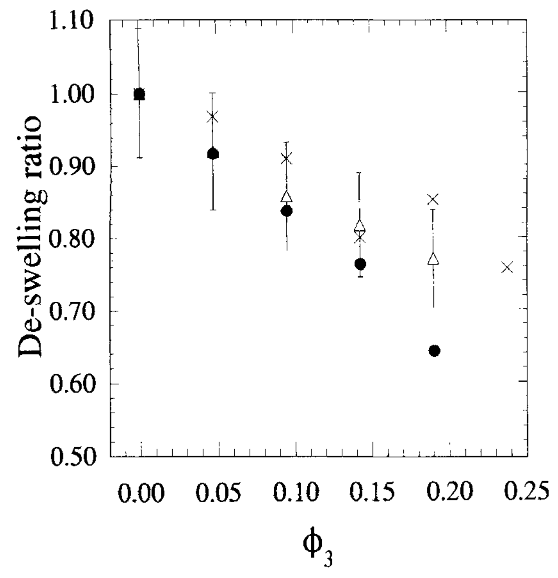

Fig. 6 Variation of the de-swelling ratio of PS-0.3DVB with volume fraction of free polystyrene. The free polymers are PS5450 (△), PS8500 (×) and PS12640 (●). The error bars correspond to ± two standard deviations of the de-swelling ratio

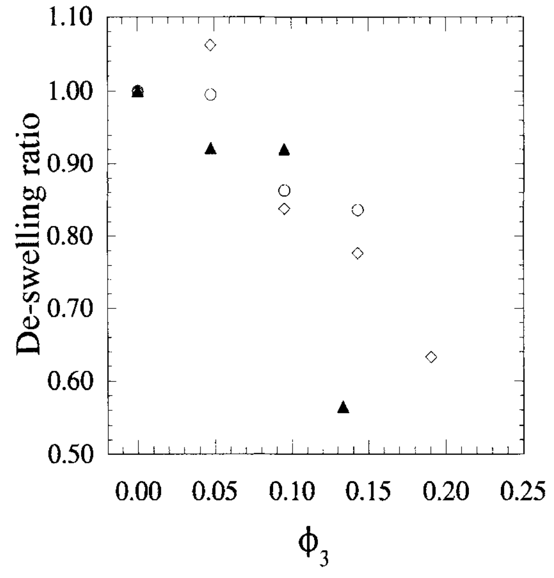

Fig. 7 Variation of the de-swelling ratio of PS-0.3DVB with volume fraction of free polystyrene. The free polymers are PS17000 (◇), PS20300 (○) and PS42300 (▲)

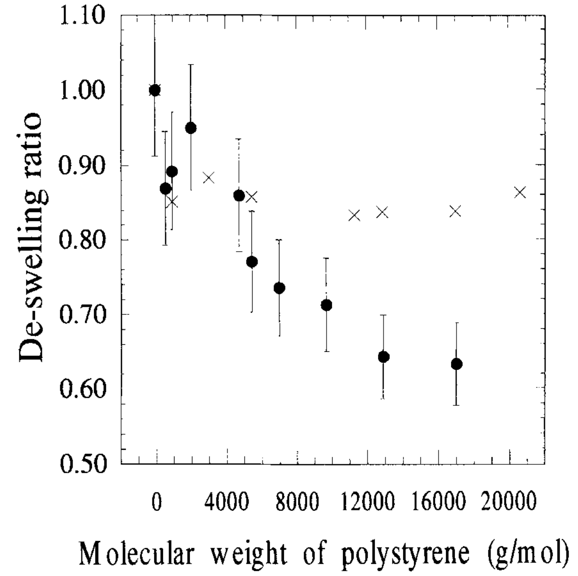

Fig. 8 Variation of the de-swelling ratio of PS-0.3DVB with molecular weight of free polystyrene. The volume fractions of free polystyrene are 0.095 (×) and 0.19 (●). The error bars correspond to ± two standard deviations of the de-swelling ratio

It was invariably the case that PS-1.4DVB particles flocculated at lower free polymer volume fraction (for a given free polymer molecular weight), than PS-0.3DVB. The PCS studies reported below were confined to the more stable PS-0.3DVB/ethylbenzene/free polystyrene systems identified above.

Osmotic de-swelling of PS-0.3DVB

The variation of the de-swelling ratio of PS-0.3DVB with volume fraction of a range of free polystyrene polymers is shown in Figs. 6 and 7. The de-swelling ratio generally decreases with increasing volume fraction of free polystyrene. This result is what is expected for osmotic de-swelling. The data shown in the figures generally are in agreement with those reported by Bastide et al. [18] for polystyrene *macrogel* in the presence of free polystyrene. In addition, a similar trend has been observed for poly(NIPAM) microgel particles in the presence of PEG/water solutions [11].

The ranges of de-swelling ratio values shown in Figs. 6 and 7 are much higher than that which would correspond to complete collapse of the PS-0.3DVB microgel particles (i.e., $\alpha = 0.13$). It might be possible to achieve this if the volume fraction of free polystyrene were increased to high enough values (ca. $\phi_3 > 0.5$). However, obtaining reliable PCS data for such systems would be difficult, if not impossible, due to the combined problems of refractive index matching, high solution viscosity, and depletion flocculation. The microgel particles in the poly(NIPAM)/water/PEG system exhibited superior osmotic de-swelling and almost completely collapsed in the presence of PEG ($\phi_3 = 0.15 - 0.2$) [11].

Figure 8 shows the variation of the de-swelling ratio of PS-0.3DVB microgel particles with molecular weight of free polystyrene for two values of ϕ_3 (0.095 and 0.19). It is interesting that at the lower ϕ_3 value, α appears to be more-or-less independent of the molecular weight of free polystyrene (M_3). However a strong dependence is apparent at the higher ϕ_3 value (with α decreasing in turn possibly to some limiting value, with increasing M_3). Broadly similar trends were found with the poly(NIPAM)/water/PEG systems investigated previously [11].

Comparison of experiment with theory

The extent of swelling of the microgel particles is expressed in terms of ϕ_2 in the discussion that follows. In order to apply the thermodynamic model presented earlier to the experimental data the mole fraction of cross-linker incorporated into the microgel particles x_A, must be determined. Using equations (1) and (3), the swelling data shown in Table 2, and $\chi_{12} = 0.45$ [24], values of x_A of 7.0×10^{-4} and 1.4×10^{-3} were calculated for PS-0.3DVB and PS-1.4DVB, respectively. These values correspond to effective DVB incorporation efficiencies of 53 and 24%, respectively, for PS-0.3DVB and PS-1.4DVB based on the mole fractions of pure DVB used during synthesis. Funke et al. [5] reported crosslinking efficiencies of DVB in the range 10–60% for PS-DVB microgel particles. In the present work intramolecular ring formation, inhomogeneous cross-linking, and unreacted pendant vinyl groups would contribute to the low calculated efficiencies of DVB incorporation.

The thermodynamic model presented earlier (Eqs. (8) and (9)) was applied to the swelling data for PS-0.3DVB in the presence of free polystyrene (see Figs. 9 and 10). The scaling model proposed by Bastide et al. [18] namely

$$\left(\frac{\phi_2}{\phi_2^0}\right)^{2.25} - \left(\frac{\phi_2}{\phi_2^0}\right)^{0.5} = \left(\frac{\phi_3}{\phi_2^0}\right)^{2.25} \tag{10}$$

was also tested, ϕ_2^0 is the volume fraction of the network in the absence of free polymer. However, the disadvantage of such scaling models is that they offer little physical insight into the swelling process. The data shown in Fig. 9 show the variation of ϕ_2 with ϕ_3 for a fixed value of M_3 (17000). The scaling theory of Bastide et al. (Eq. (10)) shows reasonably good agreement with these experimental data. The thermodynamic model on the other hand clearly overestimates the value of ϕ_2 for all values of ϕ_3.

In applying the thermodynamic model it has been assumed [24] that $\chi_{12} = \chi_{13} = 0.45$. Noda et al. [25] measured the volume fraction dependence of the interaction parameter for polystyrene/benzene solutions and fitted their data to a linear dependence of χ on ϕ_3. However, the agreement between theory and experiment in the present work is not significantly improved if the values of χ_{12} and χ_{13} are allowed to vary with ϕ_3 in the manner reported by Noda et al.

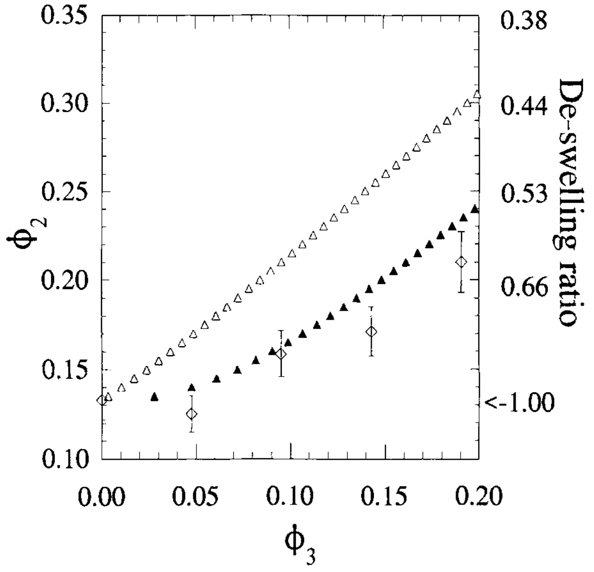

Fig. 9 Experimental (◇) and theoretical data for the variation of ϕ_2 with ϕ_3 for the PS-0.3DVB/ethylbenzene/PS17000 system. The theoretical data were obtained using the thermodynamic model (△, Eq. (8)) and scaling theory, (▲, Eq. (10)). The error bars in the experimental data correspond to ± two standard deviations of ϕ_2

An alternative explanation, which could account for the much lower values of ϕ_2 observed experimentally in Fig. 9, compared to the predictions of the simple thermodynamic model, has to do with the fact that this model assumes reversible (elastic) swelling/deswelling of the microgel particles. However, evidence from the electron microscopy studies (Table 2) suggests that only partial de-swelling occurs on drying. It is quite likely therefore that addition of free polymers also only leads to limited, rather than equilibrium, de-swelling, i.e., ϕ_2 values are much smaller than predicted.

The breakdown of the simple thermodynamic model is worse when we examine the M_3 dependence of ϕ_2, and hence α. The comparison is shown (for a fixed value of $\phi_3 \sim 0.19$) in Fig. 10. The thermodynamic model implies that ϕ_2 should increase as M_3 is reduced.* This is in direct opposition to the trend observed experimentally. One possible explanation is penetration of the microgel particles by free polymer chains, which would tend to be more pronounced the lower M_3. The thermodynamic model assumes complete exclusion of polymer

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* The same trend would hold, and indeed be stronger, if the Flory–Krighann theory of dilute polymer solutions were used instead of the Flory–Huggins theory for concentrated polymer solutions [19], in modelling the free polymer solution.

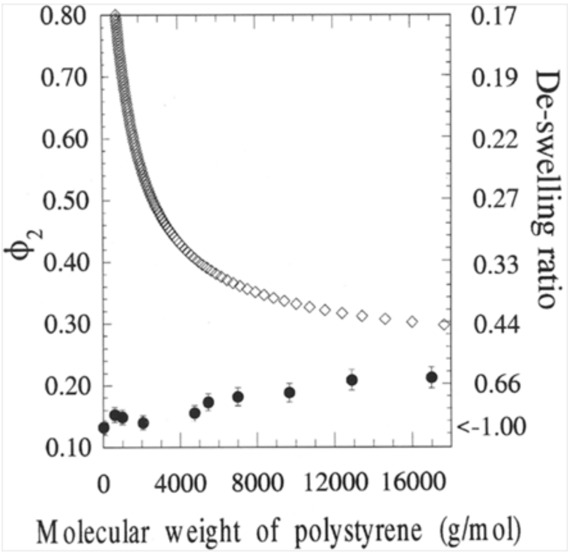

Fig. 10 Experimental (●) and theoretical data (◇, Eq. (9)) for the variation of ϕ_2 of PS-0.3DVB with molecular weight of free polystyrene ($\phi_3 = 0.19$). The error bars in the experimental data correspond to ± two standard deviations of ϕ_2

chains. The lower M_3 the greater the ease (and extent) of penetration. De-swelling would then be more suppressed, the lower M_3, but would become pronounced as M_3 increases, as free chains find it more difficult to enter the microgel particles. Thus, ϕ_2 would increase (i.e. α decreases) as M_3 increases, for a given value of ϕ_3, in line with the experimental findings presented in Fig. 10. Eventually at a high experimental value of M_3, penetration would cease.

The radial distribution of the pore sizes within the microgel particle will also influence the nature of osmotic deswelling. The pore size distribution of PS-DVB microgel particles has not been reported to our knowledge. It may be that the average pore size increases with increasing distance from the particle centre. The diameter of the particle interior free of linear polystyrene would therefore increase with M_3.

Conclusion

Cross-linked polystyrene particles dispersed in ethylbenzene do not collapse to their original unswollen dimensions upon solvent removal, i.e., the swelling/de-swelling process is only partially reversible. It is believed that this is the main reason why the osmotic de-swelling of the polystyrene microgel particles is significantly less than predicted by the simple Flory thermodynamic models, on adding free polymer (at a relatively high molecular weight). The fact that the de-swelling is less, the lower the molecular weight of the added polystyrene, in complete contrast to theoretical predictions, is most likely due to (partial) penetration of the microgel particles by the free polymer. Such penetration would be more pronounced, the lower molecular weight of the added polymer. In this respect it would be of interest to determine "absorption" isotherms for the free polymer into the microgel particle, as a function of free polymer molecular weight and concentration. However, such experiments are not straightforward.

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References

1. Pelton RH, Chibante P (1986) Coll and Surf 20:247
2. Snowden MJ, Marston NJ, Vincent B (1994) Coll Polym Sci 272:1273
3. Pelton RH, Pelton HM, Morphesis A, Rowell RL (1989) Langmuir 5:816
4. Murray MJ, Snowden MJ (1995) Adv Coll Interf Sci 54:73
5. Funke VW, Beer W, Seitz U (1975) Progr Coll Polym Sci 57:48
6. Shashou VE, Beaman RG (1958) J Polym Sci 33:101
7. Sieglaff CL (1963) Polymer 4:281
8. Sieglaff CL (1959) J Polym Sci 41:319
9. Clarke J, Vincent B (1981) J Chem Soc, Faraday Trans I 77:1831
10. Raquois C, Tassin JF, Rezaiguia S, Gindre AV (1995) Progr Org Coat 26:239
11. Saunders BR, Vincent B (1996) J Chem Soc, Faraday Trans 92:3385
12. Boyer RF (1945) J Chem Phys 13:363
13. Rijke AM, Prins W (1962) J Polym Sci 59:171
14. Vasilevskaya VV, Khokhlov AR (1992) Macromolecules 25:384
15. Momii T, Nose T (1989) Macromolecules 22:1384
16. Inomata H, Nagahama K, Saito S (1994) Macromolecules 27:6459
17. Ishidao T, Akagi M, Sugimoto H, Iwai Y, Arai Y (1993) Macromolecules 26:7361
18. Bastide J, Candau S, Leibler L (1981) Macromolecules 14:719
19. Flory PJ (1953) Principles of polymer chemistry, Cornell University Press, London
20. Jenkins PD (1994) PhD Thesis, University of Bristol
21. Hiltner PA, Papir YS, Krieger IM (1971) J Phys Chem 12:1881
22. Long JA, Osmond DWJ, Vincent B (1973) J Coll Int Sci 42:545
23. Smith NJ, Williams PA (1995) J Chem Soc, Faraday Trans 91:1483
24. Price GJ, Smith PF (1992) Polymer 33:2224
25. Noda I, Higo Y, Ueno N, Fujimoto T (1984) Macromolecules 17:1055