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ORIGINAL CONTRIBUTION

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Equilibrium and kinetic aspects of the pH-dependent swelling of poly(2-vinylpyridine-co-styrene) microgels

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Abstract Monodisperse, cationic microgels were synthesized by surfactant-free emulsion copolymerization of 2-vinylpyridine and styrene, using the cationic initiator 2,2′-azobis(2-amidinopropane) dihydrochloride. Low levels of divinylbenzene were employed as a cross-linking agent. The particle morphologies and diameters were characterized by a combination of TEM and photon correlation spectroscopy. At styrene contents less than 40% by weight, the particles were spherical with diameters of approximately 200 nm. The diameter decreased with increasing styrene content and the morphology changed from spherical to irregular. The pH-dependent swelling of the microgel particles was studied in constant ionic strength acetate buffers, as a function of styrene content and cross-link density. Particle diameters increased sharply below pH 4.6 due to ionization of the 2-vinylpyridine residues. At higher styrene levels, the transition pH is shifted to lower values and the extent of swelling is reduced. The pH at which swelling occurred was identical for the three cross-linker levels (0.25, 0.50 and 1.5 wt%), but the extent of swelling decreased in this order as expected. The rate of swelling of the particles was investigated by stopped-flow spectrophotometry; as microgels swell the turbidity of the dispersions decreases and this was followed as a function of time. Higher styrene contents not only reduce the extent of swelling, but also the rate at which maximum swelling is reached, whereas the level of cross-linker employed in this study has no effect on the rate of swelling.

Key words Poly(2-vinylpyridine) – microgels – pH-dependent swelling

Introduction

Slightly cross-linked copolymer gels formed from weakly inoizable monomers exhibit pH-dependent swelling. Such gels have been investigated for applications as diverse as drug delivery [1], rheology modification [2, 3], optoelectronic switches [4, 5], water purification [6] and as artificial muscle materials [7, 8]. Several studies have also focused purely on understanding the nature of the phase transition [9–14], and theories have been developed to describe the swelling [15, 16]. Important parameters include charge density [17], solvent dielectric constant [18] and ionic strength [12]. Tanaka has shown that the rate of swelling of a polymer gel is inversely proportional to the square of a linear dimension of the gel [19]. Therefore, for applications where the swelling transition is required to be rapid, gels with very small dimensions are required. A previous study also indicates that the swelling behavior can be varied by copolymerization with hydrophobic monomers [9], although these studies have been performed on macrogels.

We have investigated the use of microgel particles (dimensions in the colloidal range) for controlled uptake and release studies, where fine control over the swelling properties may aid in regulating the rate of uptake or release of a target compound. Towards this goal several papers have appeared on the swelling of microgels based on methacrylate monomers or N-isopropylacrylamide [14, 20–22].

Previous studies have shown that when 2-vinylpyridine is copolymerized with high levels of DVB by suspension polymerization, macroporous particles are produced which have ion-exchange properties [23]. However, particle swelling as a function of pH is not expected to be observed in this case due to the high cross-link densities of these particles.

It has been reported that surfactant-free emulsion polymerization of the weakly basic monomer 4-vinylpyridine results in macrogel formation and a polymeric emulsifier must be employed to obtain stable emulsions [24]. In the present study, we describe the synthesis of monodisperse microgel particles with diameters of approximately 200 nm achieved by surfactant-free emulsion copolymerization of 2-vinylpyridine with various amounts of styrene, and at various cross-link densities, employing DVB as the cross-linking monomer. Stable dispersions could be prepared with monomer weight fractions up to 1%, though higher levels produced significant amounts of coagulum. We present some equilibrium and kinetic aspects of the pH-driven swelling of these microgels and demonstrate how copolymerization with hydrophobic monomers can be utilized as a strategy to tailor their swelling characteristics.

Experimental

Materials

Ultra-pure water with a resistivity of 18.2 MΩ cm was provided by a Millipore Milli-Q system and was used throughout. 2-vinylpyridine (2VP, Aldrich, 99%) and styrene (ST, Aldrich, 99%) were distilled at a reduced pressure of approximately 2 mm Hg prior to use and stored at −10 °C for periods less than one month. Cross-linking monomer divinylbenzene (DVB, Aldrich, 55%) and 2,2′-azobis(2-amidinopropane) dihydrochloride (V50, Wako, 95%) were used as received. Constant ionic strength acetate buffer solutions were made from mixtures of sodium acetate (Aldrich, 99%), acetic acid (Aldrich, 99.8%) and potassium chloride (Aldrich, 99%).

Microgel synthesis

All microgel dispersions were prepared by surfactant-free emulsion polymerization at 70 °C ± 1 °C. To a one liter round-bottomed flask, fitted with a nitrogen gas inlet, water condensor and PTFE paddle stirrer, was added 787 g water. The water was deoxygenated by stirring at 300 rpm under a nitrogen gas flow for 30 min. After purging, 8.0 g of the monomer mixture was added (see Table 2 for recipes), followed 5 min later by V50 (0.32 g, 1.18 mmol) dissolved in 5 g water. In all cases the contents of the flask turned white within 10 min and the reactions were continued for 4 h. The product latices were dialyzed against ultra-pure water for a total of 21 days with two changes of water per day in order to remove unreacted materials and low molecular weight oligomers. The conversion of monomer to polymer was determined gravimetrically.

Physical measurements

Transmission electron micrographs were obtained using a Joel JEM-100 CX instrument. The particles were supported on carbon-coated copper grids. Particle diameters were determined from the micrographs using a "SeeScan" image analyzer with at least 500 particles being counted.

Hydrodynamic particle diameters were determined at 25 °C using a Brookhaven Instruments Zeta Plus dynamic light scattering apparatus fitted with a 635 nm He–Ne laser and a detector at 90°. Samples for these experiments were prepared by 250-fold dilution of the respective latex with constant ionic strength acetate buffer to give a final particle concentration of 0.004 wt%. The buffers were made by mixing appropriate volumes of 0.2 mol dm^{-3} sodium acetate, 0.2 mol dm^{-3} acetic acid and 0.1 mol dm^{-3} KCl followed by 100-fold volumetric dilution, giving a final ionic strength of 2×10^{-3} mol dm^{-3}. The amount of each component used to make up these buffers is given in Table 1, along with the corresponding pH values. Samples were then rotated end-over-end overnight before PCS measurements were made.

Optical density measurements on 0.004 wt% buffered dispersions were made at 400 nm using a Perkin-Elmer Lambda 5 spectrophotometer using matched quartz cells of 1 cm path length.

The stopped flow experiments were performed using a Hi-Tech Scientific stopped flow spectrophotometer instrument with a SF3C support unit and SF30C control unit. Equal volumes of 0.008 wt% dispersion and a buffer solution (which when diluted 1 : 1 by volume gave a pH of 3.8) were injected simultaneously via two separate syringes into the measurement chamber by an air piston. The

Table 1 Components and pH values of the 2×10^{-3} mol dm^{-3} acetate buffers

Volume of 0.2[M] acetic acid/ml	Volume of 0.2[M] sodium acetate/ml	Volume of 0.1[M]KCl/ml	pH
9.8	0.2	19.0	3.85
9.5	0.5	19.0	4.00
8.0	2.0	16.0	4.30
6.0	4.0	12.0	4.63
5.0	5.0	10.0	4.90
4.0	6.0	8.0	5.10
0.5	9.5	1.0	5.85

percentage transmission of light at 400 nm was recorded as a function of time.

Results and discussion

Microgel synthesis and TEM results

Figure 1 shows the conversion-time plots for the microgels containing 0, 10, 20 and 40 wt% styrene and 0.5 wt% DVB in the monomer feed. Although the polymerizations appear to be complete by 2 h, they were generally extended for a further 2 h in order to ensure maximum conversion of trace monomer. Longer reaction times caused yellowing of the dispersions in some cases, probably due to degradation of the 2VP units which can oxidize to 2-vinylpyrolidinone in the same way as the 4-isomer [25]. The kinetic data are broadly similar for the various styrene fraction latices. However, the particles made with 0% and 10% styrene show slower initial polymerization rates. This is probably due to the fact that styrene is less polar (and therefore, more hydrophobic) than 2VP, and therefore, particle nucleation in high-styrene-containing polymers will occur earlier in the polymerization, forming more particles and yielding higher reaction rates. For a fixed amount of monomer, an increased particle number concentration would also be accompanied by a reduction in the final particle diameter. TEM micrographs of latices containing 0–40 wt% of styrene are presented in Figs. 2a–d, respectively. Table 3 shows diameters from these TEM measurements compared with those from photon correlation spectroscopy. The diameters obtained by PCS are similar (within experimental error) to those determined from TEM micrographs, and follow the same trend. It is clear that increasing the styrene content yields smaller particles as is consistent with the above discussion on particle nucleation.

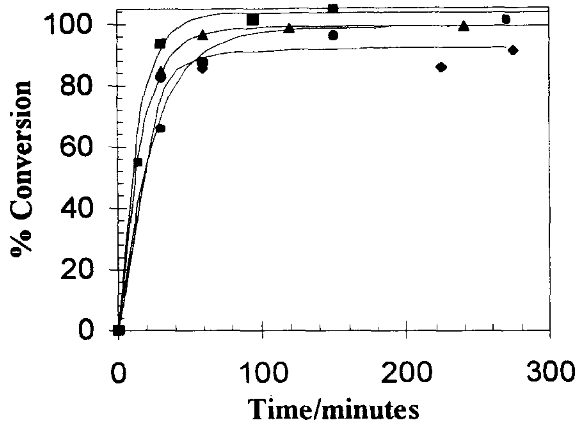


Fig. 1 % Conversion as a function of time for the styrene-containing microgels; (●) 0% styrene, (◆) 10% styrene, (■) 20% styrene, (▲) 40% styrene

Figure 2d shows the change in particle morphology from spherical to irregular when the styrene content is increased to 40%. This is a common feature of batch-produced emulsion copolymers and is caused by the phase separation of incompatible domains within the particle [26]. This can be reduced by adding the comonomers continuously over the polymerization period rather than as "one shot" at the beginning of the reaction. Figures 2e and f show the TEM micrographs for the 0% styrene-containing particles with 0.25% and 1.5% cross-linking monomer, which should be compared with Fig. 2a which has the same level of styrene, but 0.5% DVB. It is clear

Table 2 Microgel polymerization recipes

Reference	Composition 2VP:ST:DVB	Masses in grammes				
		2VP	ST	DVB	V-50	Water
L060396	99.75:0.0:0.25	7.96	0.0	0.04	0.32	792.0
L280596	99.50:0.0:0.5	7.92	0.0	0.08	0.32	792.0
L290596	98.50:0.0:1.5	7.88	0.0	0.12	0.32	792.0
L040496	89.50:10.0:0.5	7.13	0.79	0.08	0.32	792.0
L120496	79.50:20.0:0.5	6.34	1.58	0.08	0.32	792.0
L150496	59.50:40.0:0.5	4.73	3.16	0.08	0.32	792.0

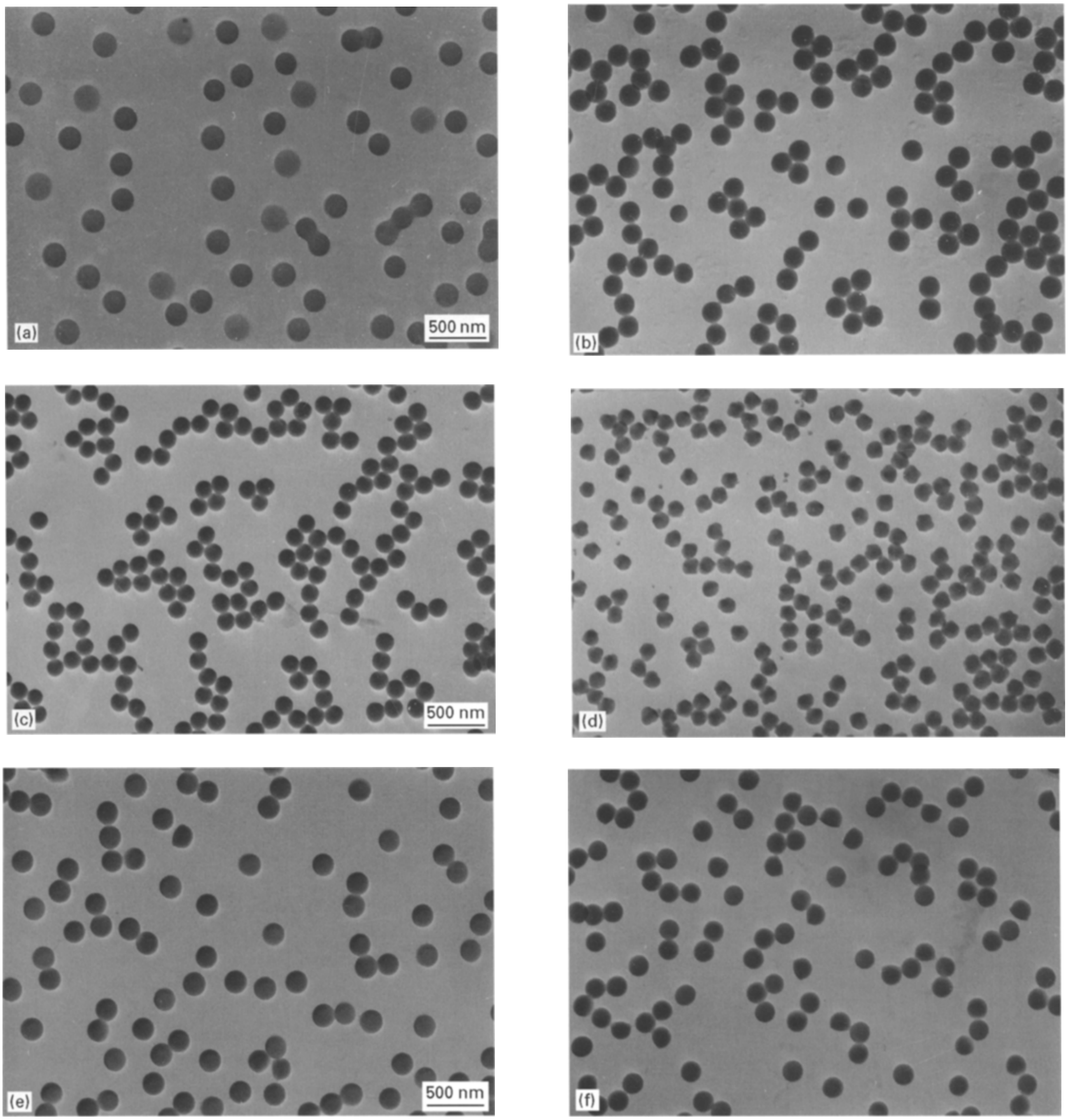


Fig. 2 Transmission electron micrographs of the microgel particles: a) 0.5% DVB; 0% styrene; b) 10% styrene; c) 0.5% DVB; 20% styrene; d) 0.5% DVB; 40% styrene; e) 0.25% DVB; styrene; f) 1.5% DVB; 0% styrene

that at these low levels of cross-linker, the particle morphology is spherical regardless of the DVB level, but the diameter decreases with increasing DVB content as would be expected for more highly cross-linked particles. The reduction in particle diameter with increasing DVB content is also supported by the PCS data in Table 3.

Microgel equilibrium swelling

Effect of styrene level

The hydrodynamic diameter obtained by PCS for the microgels containing 0, 10, 20 and 40 wt% styrene and

Table 3 TEM and PCS diameters of microgel particles in the shrunken state

% DVB	% Styrene	TEM diameter/nm	PCS diameter/nm [pH ~ 6.0]
0.25	0	205.0 ± 7.6	206.0 ± 10.0
0.50	0	199.0 ± 8.0	215.0 ± 10.0
1.50	0	175.0 ± 9.0	198.0 ± 10.0
0.5	0	199.0 ± 8.0	206.0 ± 10.0
0.5	10	195.0 ± 10.0	191.0 ± 10.0
0.5	20	160.0 ± 8.0	168.0 ± 10.0
0.5	40	156.0 ± 9.0	164.0 ± 10.0

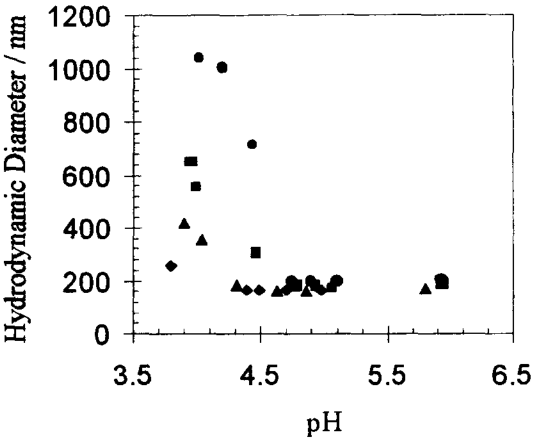


Fig. 3 Equilibrium swelling isotherms for the styrene-containing microgels: (●) 0% styrene; (■) 10% styrene; (▲) 20% styrene; (◆) 40% styrene

0.5 wt% DVB as a function of pH are presented in Fig. 3. Above pH 4.6 each set of particles exists in its unswollen state, whereas those equilibrated in buffers at lower pH values show significant swelling. Increasing the amount of styrene in the microgels has two effects. Firstly, a reduction in the extent of particle swelling is observed; for example the particles with no styrene increase in diameter by a factor of approximately 4.5, whereas those containing 20% styrene the factor is only 2.2. Secondly, the pH at which the swelling occurs is shifted to lower values. This was also noted by Batich et al. for poly 2VP macrogels [11], and by Siegel et al. [9] for poly(n-alkyl methacrylate) beads. Both effects can be attributed to the combination of increased hydrophobicity of the network with increasing styrene content, and reduction in the concentration of available ionizable groups as styrene replaces 2VP in the polymer chains at higher styrene contents.

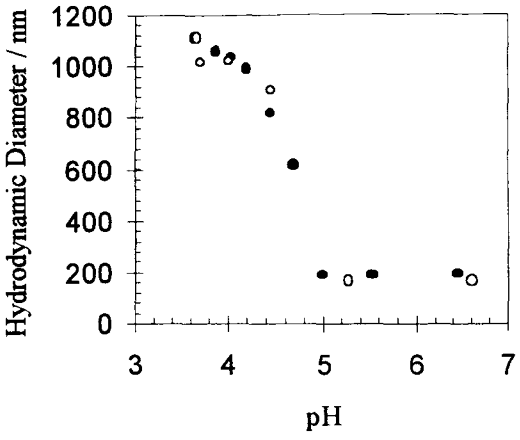


Fig. 4 Reversibility of swelling for the 0% styrene, 0.25% DVB-containing microgel: (●) addition of HCl (swelling); (○) addition of NaOH (deswelling)

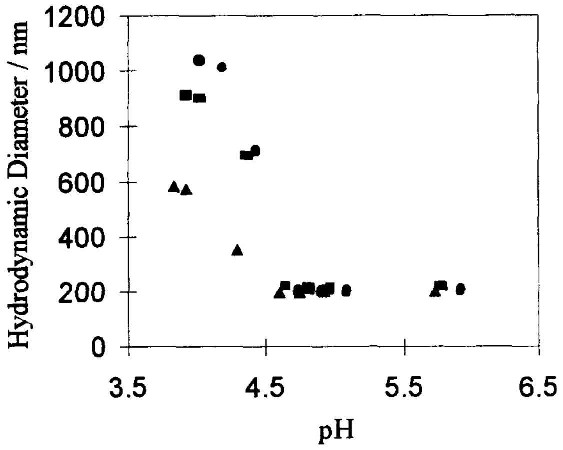


Fig. 5 Equilibrium swelling isotherms for the 2VP microgels at various DVB levels; (●) 0.25% DVB; (■) 0.5% DVB; (▲) 1.5% DVB

The reversibility of the pH-driven swelling is demonstrated in Fig. 4 where the hydrodynamic diameter of the pure 2VP microgel particles containing 0.25 wt% DVB is plotted as a function of pH. The closed circles show the effect of gradually reducing the pH with 0.2 M HCl, and the open circles show the deswelling which occurs on addition of 0.1 M NaOH to the same sample. In contrast to the same process investigated by Sawai [5] for poly(methylmethacrylate-co-acrylic acid) microgels, the lack of any hysteresis is clearly demonstrated. This cycle cannot be repeated indefinitely, however, as the concentration of salt formed by the repeated addition of HCl and NaOH eventually exceeds the critical coagulation concentration (CCC) for the collapsed microgels and then flocculation occurs. This aggregation occurred after two pH cycles in the present case, at a total ionic strength of approximately 1.25×10^{-3} mol dm^{-3}. Cationic poly(methylmethacrylate) microgels previously investigated by the authors exhibited a CCC of 1.5 mmol dm^{-3} in KCl in broad agreement with the above observation.

Effect of cross-linker level

The equilibrium hydrodynamic diameters of microgels containing 0.25, 0.5 and 1.5 wt% DVB are presented in Fig. 5. The pH at which the swelling transition occurs does not change with increasing DVB level since the hydrophobicity of the polymers is not significantly affected. However, the extent of swelling decreases with increasing DVB content as expected for more tightly cross-linked networks. This is because the increased elastic restoring force of the network balances the swelling force at lower degrees of swelling.

Optical density

Figure 6 shows the change in optical density (absorbance) at 400 nm as a function of pH for the 2VP microgel dispersions having 0.5 wt% DVB and various styrene levels. It is clear that on reducing the pH, thus swelling the particles, the optical density is reduced. Larger particles scatter more light than smaller particles, so it is reasonable to assume that the optical density of the present dispersions would increase as the particles swell, i.e. at lower pH values. A slight increase is indeed seen from pH 5.9 to pH 5.1 for all dispersions, but a steady decrease is then seen on further pH reduction. The reduction in optical density is due to the absorption of solvent into the particles during swelling, causing a decrease in the particle refractive index which offsets the effect of increase in particle size. Highly swollen, zero-styrene 2VP microgels appeared transparent. The general shape of the curves is the same for all microgel dispersions, but the difference in optical density between high and low pH is smaller, as expected, for the more hydrophobic, styrene-containing samples which exhibit less pronounced swelling.

Microgel swelling kinetics

Effect of cross-linker level

The change in transmission of light with particle swelling as discussed in the previous section was used to followed the rate of microgel swelling using the stopped flow apparatus. Figure 7 shows the transmission of light of wavelength 400 nm, as a function of time, for the three 2VP microgels with various cross-linker levels. The plateau region corresponding to equilibrium swelling is reached after about 30 s for all pure 2VP microgels, independent of cross-linker level.

On the basis of studying the kinetics of macrogels, Tanaka et al. proposed a kinetic equation for the swelling of gels that predicted poly(acrylamide) gels with diameters less than 1 μm should swell to their maximum size over millisecond time scales [19]. However, the present study indicates that the time scales are much longer for microgel particles. Tanaka's equation contains a term dependent on the diffusion coefficient of the gel, which is a measure of the rate of polymer chain diffusion through the solvent at the advancing gel–solvent interface. The difference in swelling time may be attributable to the difference in the chemical nature between the gels studied here and those studied by Tanaka, since chemical composition would be expected to have an effect on the diffusion coefficient. However, Saunders et al. [20] observed a 3 min lag in swelling times for poly(N-isopropylacrylamide) microgels which are quite similar to those used by Tanaka. It is possible that the theory does not hold at very small particle sizes. Nor does it take into account the time required for the diffusion of buffer molecules into the core of the microgels used in this study.

Fig. 6 Optical density as function of pH for the styrene-containing microgels: (●) 0% styrene; (■) 10% styrene; (▲) 20% styrene

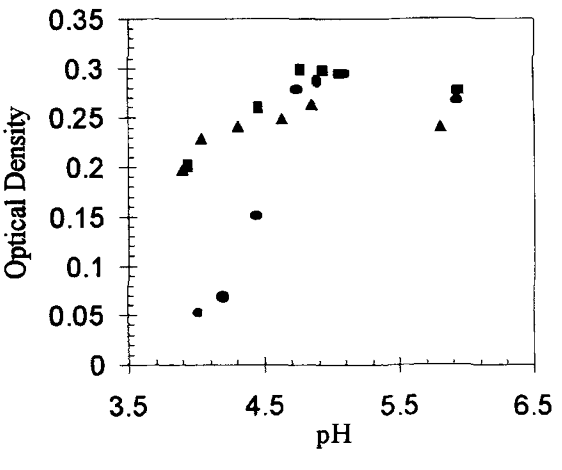
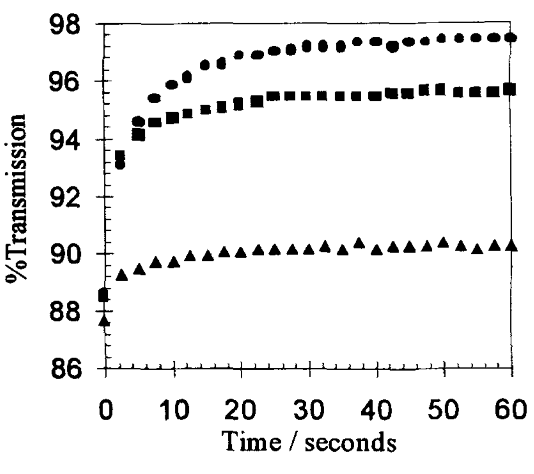


Fig. 7 % Transmission at 400 nm as a function of time for the 2VP microgels at various DVB levels: (●) 0.25% DVB; (■) 0.5% DVB; (▲) 1.5% DVB



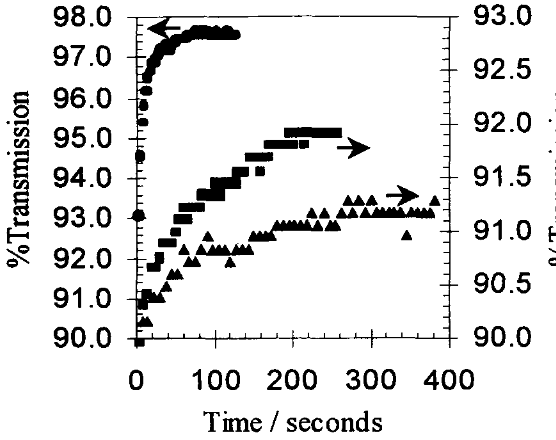


Fig. 8 % Transmission at 400 nm as a function of time for the styrene-containing microgels: (●) 0% styrene; (■) 10% styrene; (▲) 20% styrene

As already noted, the equilibrium swelling of particles is reduced with higher cross-linker levels, and this is reflected here in the reduction in the equilibrium value of the percentage light transmission.

Effect of styrene level

The transmission-time curves for the 10% and 20% styrene microgels with 0.5% DVB are presented in Fig. 8. The 10% styrene microgels reach equilibrium swelling in about 250 s whereas the 20% sample requires about 350 s; the fact that increased styrene content reduces the *rate* of swelling as well as the extent of equilibrium swelling is clearly demonstrated. The change in transmission for the 40% styrene microgels was comparable to the noise in the experiment and is, therefore, not shown.

Conclusions

Cationic poly(2-vinylpyridine) microgels can be readily prepared by emulsifier-free emulsion polymerization to yield monodisperse particles at concentrations up to 1 wt%.

Copolymerization with styrene reduces the particle diameter and when incorporated at 40 wt% causes the particle morphology to become irregular. The higher levels of styrene reduced the extent to which the particles swell when the pH was lowered, due to the increased hydrophobic nature of the particles and the reduction in charged groups. Increased cross-linker levels also reduced the degree of swelling due to an increase in the elastic restoring force of the microgels.

The fact that the dispersions become more transparent as the particles swell can be used to follow the kinetics of swelling. Increased styrene content reduced the rate at which the particles reached their equilibrium swelling, whereas increased cross-linker levels had no effect at the low levels used in this study.

It is clear that copolymerizing 2VP with hydrophobic and cross-linking monomers gives fine control over the extent and rate of particle swelling which may be exploited in applications such as controlled release of highly valuable materials from the particles.

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