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ORIGINAL CONTRIBUTION

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Nonionic latices in aqueous media

Part 4: Preparation and characterisation of electrosterically stabilised particles

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Abstract The rate of conversion of styrene into polystyrene by emulsion polymerisation has been investigated in the absence and in the presence of methoxy-polyethyleneglycol methacrylate, MeOPEGMA. The effect of adding MeOPEGMA at different stages of the polymerisation was also investigated. Additions at the beginning of the polymerisation and at the early stages gave a bimodal particle size distribution whereas late additions gave small particle size, monodisperse latices which were electrosterically stabilised. The latter materials were found to be colloidally stable to the addition of high concentrations of electrolyte and to freeze-thaw conditions.

Key words Polymer colloids – polystyrene – electrosteric stabilisation

Introduction

In order to generate stable polymer colloid dispersions in aqueous media, it is necessary to provide a repulsive interaction that outweighs the magnitude of the van der Waals attraction between the particles. For practical purposes, this can be achieved in several different ways. Firstly, by electrostatic stabilisation, in which the Coulombic repulsion between the charged colloidal particles is exploited. Secondly, by steric stabilisation, whereby stability is imparted by nonionic polymers or stabilisers adsorbed or grafted on to the non-charged colloidal particles. Lastly, by using a combination of electrostatic and steric stabilisation mechanisms, i.e. by electrosteric stabilisation. Although electrostatic stabilisation is widely used in aqueous colloidal dispersions, systems stabilised by this mechanism become unstable in high electrolyte concentrations, in various pH regions, in freeze-thaw cycling and at high rates of shear. Under these conditions sterically stabilised dispersions can frequently be used. However, the synthesis of purely sterically stabilised particles under aqueous conditions is not always straightforward. Consequently a combination of the two stabilisation mechanisms is recognised as a useful route to obtain aqueous polymer colloid dispersions with good stability behaviour.

In the preceding papers of this series, [1–3], the preparation, characterisation and the stability behaviour of an electrostatically stabilised polystyrene latex and a sterically stabilised latex in aqueous media were described. In addition, the combination of an electrostatic plus a steric mechanism was investigated by polymerising a charged polystyrene latex in the presence of a comonomer/stabiliser, namely, methoxy-polyethylene glycol methacrylate (MeOPEGMA). This polymerisation which was labelled PS*–PEG in paper 1 [1] provided some interesting results. As briefly discussed in this paper, the dispersion properties and the distribution of the PS*-PEG particles showed marked differences from that of the charged particles. Moreover, the particles prepared in the absence of MeOPEGMA by emulsion polymerisation (PS*) had a number average diameter of 190 nm, whereas the PS*–PEG particles had a number average diameter of

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600 nm when MeOPEGMA was added at the beginning of the preparation. It was suggested from this work that the difference in particle size was most probably due to the coagulation of the particles during the nucleation stage of the polymerisation. In an attempt to understand this effect further, an investigation of the formation of polystyrene latex particles in the presence of MeOPEGMA was undertaken. The time of addition of MeOPEGMA to the system during the polymerisation process was found to be an important feature. Accordingly, a series of polymerisations was carried out in which fixed amounts of MeOPEGMA were added at different time intervals during the polymerisation. The colloid stability of the latices produced in these experiments was then investigated.

Experimental

Materials

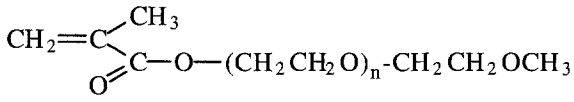
The distilled water used was doubly distilled from an all-Pyrex apparatus. Styrene was BDH laboratory reagent material. This was purified by distillation at 40° to 50 °C in an atmosphere of nitrogen. The purified styrene was stored in a refrigerator.

Potassium persulphate was BDH AnalaR grade material used without further purification. The anionic surface active agent Manoxal MA (sodium di(methyl-amyl) sulphosuccinate) was obtained as a 60% solution in a water/alcohol mixture from Manchem Limited. The critical micelle concentration (CMC) of Manoxal MA in water is quoted as 3.0×10^{-2} mol dm^{-3} at 25 °C [4].

The non-ionic surface active agent Levelan P208 (a nonyl phenol ethylene glycol condensate with 20 ethylene glycol units) was obtained as an 80% aqueous solution from Lankro Chemicals Limited. The CMC of Levelan was obtained from surface tension measurements as 2.82×10^{-4} mol dm^{-3} at 25 °C based on an average molecular weight for the monomeric material of 1100.

The non-ionic comonomer/stabiliser, methoxy-polyethylene glycol methacrylate (MeOPEGMA), was prepared by the method described previously [1, 3].

The chemical structure of MeOPEGMA where n is approximately equal to 45 units, is essentially,



Preparation of polystyrene latices

Charge-stabilised latex (PS)*

The polymerisation was carried out in a five-necked flask equipped with a glass stirrer with a PTFE paddle, under a constant flow of nitrogen gas. A water-cooled reflux condenser and a thermometer were inserted into two of the other outlets. The reaction flask was maintained at the required constant temperature using a thermostatted water bath. Manoxal MA and sodium bicarbonate were dissolved in 190 cm^3 of water and then transferred to the reaction vessel and heated to 75 °C. At this stage the styrene monomer was added and emulsified for 20 min by stirring. The stirrer speed was kept constant at 350 rpm throughout the polymerisation. The initiator, potassium persulphate, dissolved in 10 cm^3 water was then added to the system in the flask. The polymerisation was carried out at 80 °C for 18 h. The resulting latex was filtered through glass wool into well-boiled Visking dialysis tubing and then dialysed for 2 weeks against water to remove residual monomer, oxidation products, and salt. The ratio of dialysate volume to latex used was about 15:1. The dialysate was changed every 24 h.

PS*–PEG Latices

The basic preparative method was essentially that described above for the PS* latices and as used previously [1]. However, for the PS*–PEG latices, additions of MeOPEGMA were made at various time intervals into the preparation as listed in Table 1. An additional amount

Table 1. PS*–PEG Polymerisation Details

Latex code	% MeOPEGMA on monomer	Time of addition h	Final particle diameters–Number average mean small/nm	CV%	large/nm	CV%
PS*	None	—	219	9.6	—	—
*PEG 5–0	5.0	0	206	4.0	456	24.4
*PEG 5–0.40	5.0	0.40	231	18.0	433	8.8
*PEG 5–1.25	5.0	1.25	246	7.7	253	14.1
*PEG 5–2.0	5.0	2.00	186	6.1	—	—
*PEG 5–4.0	5.0	4.00	207	7.6	—	—

CV = coefficient of variation on the number average mean diameter

of initiator was added at the time of the MeOPEGMA addition.

PS*–DME Latex

This was prepared by a polymerisation procedure as described for the PS*-PEG latices except that polyethylene glycol dimethylether (DME) was added initially instead of MeOPEGMA; DME was the fully methylated ether derivative of PEG and had the same number of ethylene oxide units as MeOPEGMA. Following preparation the latex was dialysed against distilled water.

Experimental Techniques

Kinetics of monomer conversion, PS–PEG latices*

The rate of conversion of monomer to polymer was measured using a gravimetric technique. Samples were removed from the reaction vessel at regular time intervals and the solid polymer content of the latex sample was determined. On removal of the sample from the reaction mixture it was immediately cooled to arrest further reaction. The percentage of monomer converted to polymer at different reaction times was obtained from the respective solid contents.

Electron microscopy

Samples of dialysed latices were diluted with distilled water to give a concentration of about 0.05% polystyrene and drops of this dispersion were placed on either Formvar- or Colloidon-coated electron microscope grids. These were then examined in a Hitachi HS7 Electron Microscope. In order to obtain representative sampling for particle size analysis a number of grids were examined for each sample and photographs taken at intervals across the grid. The particle size determinations were made using a Carl Zeiss TGZ3 particle size analyser. For each sample approximately 500–1000 particles were measured.

Stability of latices

The stability of the latices to added electrolyte was examined by following the changes in absorbance, as a function of time, at various concentrations of added barium chloride. A Unicam SP600 spectrophotometer, with optical cells of path length 1 cm, was used for these measurements. All the experiments were carried out at room temperature using incident light of wavelength 546 nm. The dialysed latices were adjusted to give an absorbance of about 1.3 cm^{-1}, by diluting them with double distilled water to ca. 0.05% w/v. A 5 cm^3 aliquot of diluted latex was transferred to a clean tube and then 5 cm^3 of barium chloride solution of known concentration was added to this. After initial agitation, the mixture was allowed to stand for 2 h. The mixture was then lightly centrifuged using a bench centrifuge at 2000 rpm for 10 min. After centrifugation, the supernatant was carefully removed and its absorbance measured. This procedure was repeated over a range of barium chloride concentrations and a plot constructed of absorbance against electrolyte concentration. The critical coagulation concentration was then obtained by extrapolating the sharply decreasing portion of the absorbance curve to intersect the electrolyte concentration axis; this point was taken as the critical coagulation concentration [2].

Electrophoresis

The electrophoretic mobilities of the latex particles were measured using a Pen Kem 3000 electrokinetic analyser [2, 5]. All measurements were made at room temperature using an addition of 1 cm^3 of the diluted latex (0.05% w/v) to 20 cm^3 of barium chloride solution of known concentration.

Freeze-thaw stability

The freeze-thaw stability of the latices was estimated by a semi-quantitative method using absorbance measurements [3]. After freezing the diluted latex at $-18\,^{\circ}C$ for 3 days, it was allowed to thaw completely at room temperature. The samples were then lightly centrifuged and the absorbance of the supernatant was measured. As a control, the same measurement was made for a similarly diluted sample left at room temperature. The ratio of the absorbance of the supernatant after freeze-thaw conditions (A_{F-T}), to that of similarly diluted latex which had not been subjected to freeze-thaw conditions (A_O), was taken as the freeze-thaw stability ratio. Consequently, this ratio could vary from near zero for an unstable latex to approaching unity for a completely stable latex.

$$\text{Freeze-thaw stability ratio} = \frac{A_{F-T}}{A_O}.$$

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Results

Polymerisation kinetics

The kinetics of monomer conversion were measured in the absence of MeOPEGMA, and in the presence of it. The results are illustrated in Fig. 1. The full line in this figure shows the conversion curve for the polymerisation of styrene, in the absence of MeOPEGMA; this preparation was designated PS*, since the procedure used was the same as that used in the previous paper [1]. The dashed line shows the results obtained on the addition of MeOPEGMA at the beginning of the polymerisation; this preparation was designated as PEG 5–0, since MeOPEGMA was added at 5% based on monomer at zero time. Kinetically, polymerisation under these conditions started off at the same rate as in the absence of the macromonomer but then proceeded more slowly, 100% conversion taking 4 h rather than 2 h in the absence of MeOPEGMA. Also indicated in Fig. 1 are the points at which additions of MeOPEGMA were made to the basic PS* preparation. Table 1 summarises the conditions used for the various preparations.

Transmission electron micrographs of the latices examined at the end of the reactions, which are detailed in Table 1, are shown in Figs. 2a to f; all the micrographs are reproduced at the same magnification. The particle size distributions obtained from these experiments are shown in Figs. 3a to f. The latex PS* (Fig. 2a) which was prepared in the absence of MeOPEGMA had a number average diameter of 219 nm and a coefficient of variation on the mean of 9.6% (see also Fig. 3a). This preparation essentially reproduced the monodisperse latex PS* described in a previous paper [1] which had a number average diameter of 190 nm.

The addition of MeOPEGMA at the beginning of the polymerisation, latex *PEG 5–0 (Fig 2b), had a substantial effect on the particle size distribution of the final latex (Fig. 3b). The dominant population had a number average diameter of 456 nm. In addition there was a population of smaller particles present with a rather broad distribution and a mean diameter of 206 nm.

Figures 2c and d show the micrographs obtained on the latices *PEG 5–0.40 and *PEG 5–1.25; for these preparations the MeOPEGMA was added at times of 40 and 75 min into the polymerisation process. The micrograph of latex *PEG 5–0.40 (Fig. 2c) and the particle size distribution shown in Fig. 3c shows that the preparation was clearly bimodal with the two modes corresponding to particle sizes of 231 nm and 433 nm in approximately similar proportions by number. Preparation *PEG 5–1.25 was also bimodal as evident from microscopy (Fig. 2d) and the size distribution (Fig. 3d). In this case the distribution of the smaller particles, the largest population with a number average diameter of 246 nm, was quite uniform; the population of large particles had decreased considerably. An interesting change occurs between the distributions shown in Figs. 3b, 3c and d where the major population shifts from the larger to the smaller size.

The micrographs obtained from polymerisation with MeOPEGMA additions after 2 h (> 90% conversion) and 4 h respectively are shown in Figs. 2e and f. Both of these preparations gave particles with a narrow size distribution as illustrated in Figs. 3e and f. The particles of *PEG 2.0, however, are smaller than those of *PEG 4.0. The size of the particles in the latter preparation, 207 nm, is very close to that of *PS, suggesting, as anticipated, that the polymerisation was nearly complete at the time the MeOPEGMA was added. However, examination of the particle properties (see later) confirms that the MeOPEGMA was effectively grafted to the particle sur-

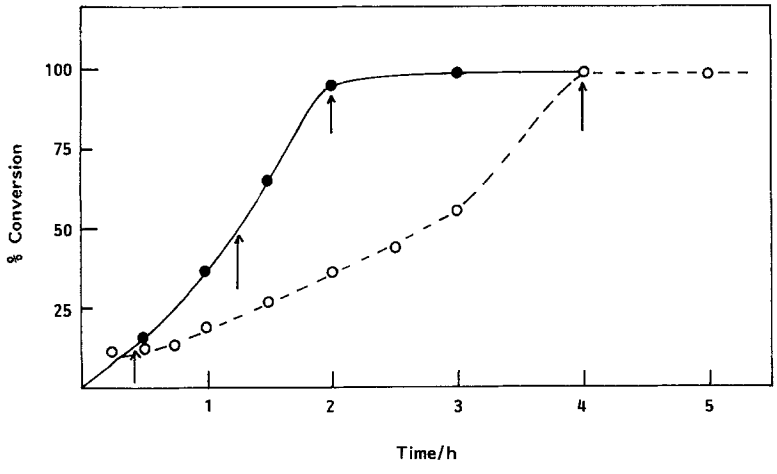

Fig. 1 Percentage conversion against time:- —●—, results in absence of MeOPEGMA, latex PS*; —○—, results with MeOPEGMA present, latex *PEG 5–0; ↑, times of addition of MeOPEGMA for latices *PEG 5–0.40, *PEG 5–1.25, *PEG 5–2.0, *PEG 5–4.0.

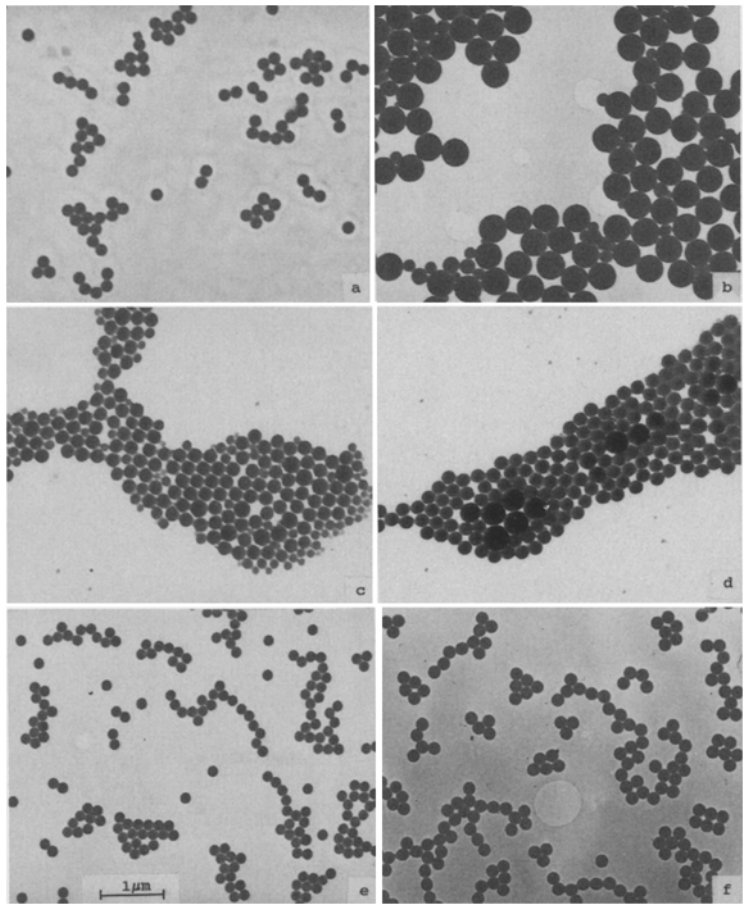

Fig. 2 Transmission electron micrographs of latices:- a) PS*, b) *PEG 5–0, c) *PEG 5–0.40, d) *PEG 5–1.25, e) *PEG 5–2.0, f) *PEG 5–4.0.

face suggesting that the surface of the particle at this stage was still monomer swollen and that there was still residual monomer in the aqueous phase. This is an important point as it indicates that sterically stabilised particles can be produced by a late addition of the stabilising monomer. This procedure also ensures that the stabiliser is domiciled at the surface to the maximum extent and minimises the possibility of burying in the particle. Moreover, combined with emulsifier-free polymerisations [6, 7] it suggests a method of obtaining monodisperse latices of various particle sizes and latices with a bimodal distribution.

Dispersion stability

The plot of optical density against log barium chloride concentration for the PS*-PEG latex series is shown in Fig. 4. Stability to barium chloride up to a concentration of 0.5 ml dm^{-3}, is seen for latices *PEG 5–2 and *PEG 5–4. This result indicates that the MeOPEGMA is either adsorbed or more likely chemically grafted [1, 2] on to the polystyrene particles. The other latices shown in Fig. 4 exhibit instability to barium chloride addition. The instability in the case of a *PS latex, where MeOPEGMA is absent, can be attributed to the compression of the electrical double layer around the particles, i.e. the behaviour is that expected for negatively charged particles in the presence of a 2:1 electrolyte [8, 9]. A reasonable explanation for the instability of *PEG 5–0 and *PEG 5–0.40, could be related to the formation of large particles during polymerisation (see Figs. 2 and 3), and the suggestion (see later) that complete coverage of the surface with MeOPEGMA had not occurred. The results would, however, suggest that some grafting of MeOPEGMA had occurred and that this had occurred to a greater extent with the *PEG 5–0.40 particles.

Electrophoretic mobility

A plot of electrophoretic mobility as a function of barium chloride concentration for the PS* and the *PEG series is

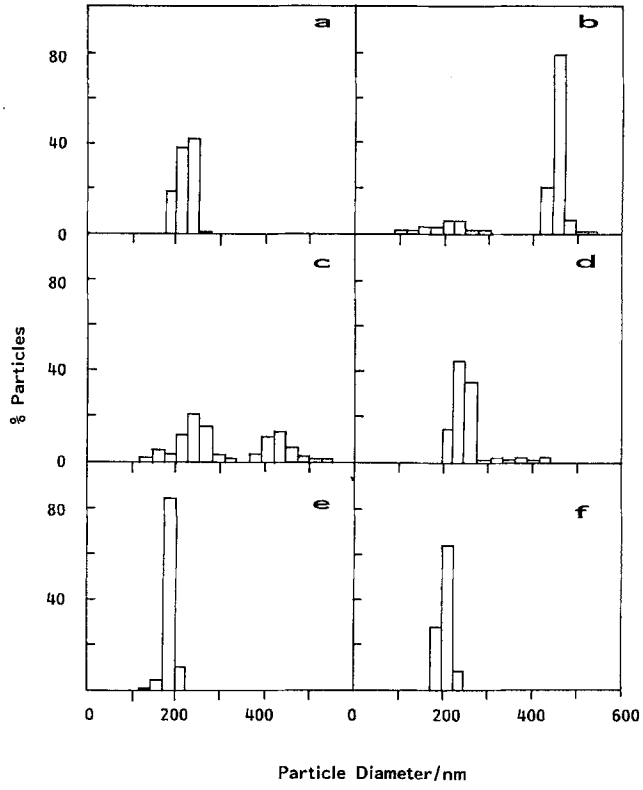

Fig. 3 Particle size distribution curves of latices:- a) PS*, b) *PEG 5–0, c) *PEG 5–0.40, d) *PEG 5–1.25, e) *PEG 5–2.0, f) *PEG 5–4.0.

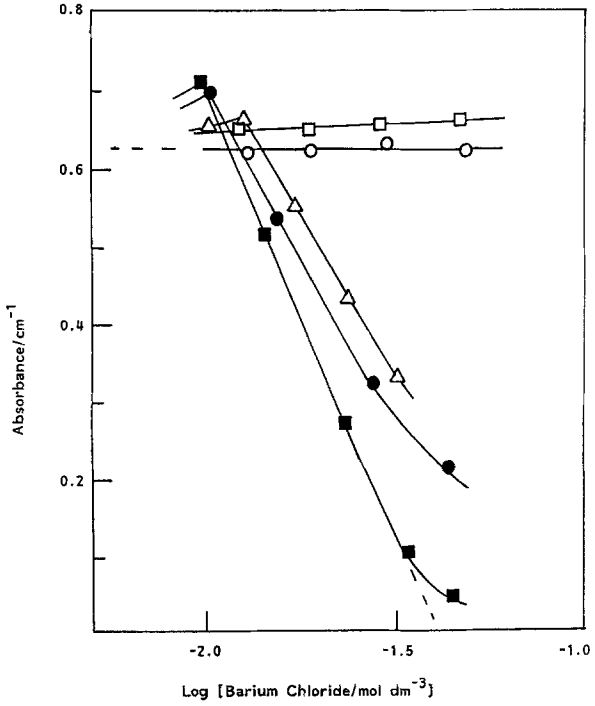

Fig. 4 Absorbance against Log (Barium chloride concentration/mol dm^{-3}) for latices: ■, PS*; ●, *PEG 5–0; △, *PEG 5–0.40; ○, *PEG 5–2.0; □, *PEG 5–4.0.

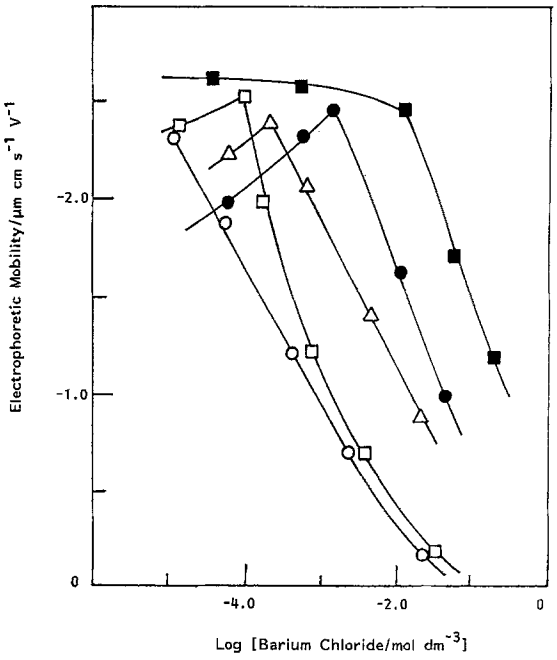

Fig. 5 Electrophoretic mobility against Log (Barium chloride concentraion/mol dm^{-3}) for latices: ■, PS*; ●, *PEG 5–0; △, *PEG 5–0.40; ○, *PEG 5–2.0; □, *PEG 5–4.0.

shown in Fig. 5. At a particular concentration of barium chloride, the *PEG 5–2 and *PEG 5–4 latices show relatively low mobility values, in comparison with the other latices. This probably reflects the displacement of the plane of shear away from the particle surface, due to the presence of polyethylene glycol chains of MeOPEGMA on the particle surface. The higher mobility values seen for the *PEG 5–0 and *PEG 5–0.40 latices, in comparison to PS*, suggests that effective coverage of the MeOPEGMA has not taken place due to the coagulation of the particles during the nucleation stage of the polymerisation. Consistent with the stability results the inference is that somewhat more grafting has occurred in the case of the *PEG 5–0.40 particles.

Freeze-thaw stability

The freeze-thaw stability ratios shown in Table 2 indicate that the latices prepared in the presence of MeOPEGMA, irrespective of the time of addition, exhibit a certain level of freeze-thaw stability.

The results confirm, as anticipated, that the charge stabilised latex PS* is coagulated by freezing and thawing. However, the latices prepared using MeOPEGMA show enhanced freeze-thaw stability, the best performance being obtained when the MeOPEGMA was added at the beginning of the preparation; a stability ratio of ca. 0.5 gives

Table 2. Freeze-thaw stability Ratios

Latex code	Freeze-thaw stability ratio
PS*	0.03
*PEG 5–0	0.57
*PEG 5–1.25	0.45
*PEG 5–2.0	0.45
*PEG 5–4.0	0.47
PS*–DME	0.12

a freeze-thaw stable system. The PS* DME latex gave a better result than PS* but was not as stable as the *PEG latices. This suggests that the DME, which does not have a polymerisable vinyl group desorbs from the surface under freeze-thaw conditions and provides additional evidence for grafting of the MeOPEGMA molecules to the latex surface.

Discussion

In previous work [1–3] it was shown that by using a polymerisable nonionic monomer, MeOPEGMA, and a nonionic initiating system composed of hydrogen peroxide and ascorbic acid, uncharged polymer colloid particles could be prepared which were colloidally stable to high electrolyte concentrations and to freeze-thaw conditions. In addition to preparing these sterically stabilised particles it was also shown by the use of ionic initiators that electrosterically stable particles could be prepared.

Previous work [2] also showed that the post addition of MeOPEGMA to charge stabilised latex particles (e.g., PS*) did not significantly enhance colloid stability. However, incorporating MeOPEGMA as a comonomer/stabiliser in the polymerisation was shown to have a considerable influence on both the colloid stability and the particle size distribution of the latex [1]. The present work was undertaken in order to examine the effects of adding MeOPEGMA at different stages during the emulsion polymerisation process. Consistent with previous work Fig. 2b shows for PEG 5–0, where MeOPEGMA was added at the beginning of the preparation, that a bimodal distribution was obtained, with one part of the distribution having a diameter of 456 nm, which is considerably larger than the particle size formed in the absence of MeOPEGMA, i.e. 219 nm. This trend was also observed when additions were made at 40 min and 75 min after commencement. With later additions, however, the population density of the larger particles diminished; in fact, these were not detected when additions were made at 2 h and 4 h.

In earlier work on the formation of polystyrene particles under emulsifier-free conditions [1–3], it was found that the addition of electrolyte had a considerable effect on the final particle size, in that the greater the electrolyte concentration present the larger was the size of the particles formed. In order to explain this effect a theory was advanced [11, 12] that a self-limiting coagulation process occurred in the early part of the reaction. The hypothesis was that the particulate units initially formed were composed of only a small number of chains; consequently, they had a low surface charge and were colloidally unstable. Hence, coagulation occurred until the particles so formed attained a surface charge density and radius sufficiently large to render them stable colloid particles. In the present context it seems likely that the population of larger particles was formed as a consequence of a coagulation process occurring at the early stages of the reaction. This suggestion, however, raises a question about the mechanism of the coagulation process. The salt concentration used was rather low and no effect was noticed in the absence of MeOPEGMA, namely in the preparation PS*, hence an electrolyte coagulation process seems unlikely.

The effect must therefore be attributed to the presence of the polymerisable monomer. However, the molecular weight of the latter would seem to be rather low for it to be considered as a bridging flocculant on its own. In view of the polymerisable group on the monomer it seems more than likely that some copolymerisation must occur to form polystyrene-MeOPEGMA molecules. With growth of the polystyrene chain this material would become insoluble or conceivably could form micelles. Another possibility is that these species remain as single entities which cause flocculation either by bridging or alternatively by combining with initially formed particles (nuclei) thus lowering their effective charge before they have colloidally stabilised. This process would involve a probability collision factor so that not all nuclear particles would necessarily capture a copolymer molecule; those that did not would form a charged particle of a smaller size. Hence, a bimodal distribution would ensue. In the experiments with MeOPEGMA addition at the later stages of polymerisation charge stabilisation would be important at the early stages leading to a small final particle size. Thus the dispersions at the late addition point would have a large number concentration and surface area and it seems possible that both MeOPEGMA and any polystyrene-MeOPEGMA moeities would be grafted to the surface of existing particles.

The stability, electrophoresis and freeze-thaw investigations showed that the PS* particles were effectively charge stabilised and that *PEG 5–2.0 and *PEG 5–4.0 particles were effectively sterically stabilised although the particles did have a charge. In the case of *PEG 5–0 and

*PEG 5–0.40 there were some indications of the slight electrosteric effect suggesting that some grafting of MeOPEGMA had occurred; moreover, their freeze-thaw stability was quite good. With these preparations it would seem possible that some of the MeOPEGMA molecules had become buried in the particles as a consequence of the coagulation mechanism. In the case of *PEG 5–2.0 and *PEG 5–4.0 effective surface grafting seems to have occurred.

The experiments described indicate that the addition of MeOPEGMA to an emulsion polymerisation reaction, initiated by sulphate free-radicals, leads to the formation of electrosterically stabilised polystyrene particles. The reaction is sensitive to the time at which the MeOPEGMA is added. Additions at the early stages of the reaction can produce bimodal particle size distributions whereas additions towards the end of the reaction can lead to dispersions with a narrow distribution of particle sizes.

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References

1. Ottewill RH, Satgurunathan R (1987) Colloid Polym Sci 265:845
2. Ottewill RH, Satgurunathan R (1988) Colloid Polym Sci 266:547
3. Ottewill RH, Satgurunathan R, Waite FA, Westby JM (1987) Br Polym J 19:435
4. Haffner FD, Piccione GA, Rosenblum C (1942) J Phys Chem 46:662
5. Pen Kem, Inc. Bedford Hills, NY 10507
6. Goodwin JW, Hearn J, Ho CC, Ottewill RH (1973) Br Polym J 5:347
7. Goodwin JW, Hearn J, Ho CC, Ottewill RH (1974) Colloid Polym Sci 252:464
8. Verwey EJW, Overbeek JThG (1948) Theory of the Stability of Lyophobic Colloids, Elsevier, Amsterdam
9. Ottewill RH (1990) In: Candau and Ottewill (eds) An Introduction to Polymer Colloids, Kluwer, Dordrecht
10. Dunn AS, Chong LC-H (1970) Br Polym J 2:49
11. Goodwin JW, Ottewill RH, Pelton R, vianello G, Yates DE (1978) Br Polym J 10:173
12. Ottewill RH (1982) In: Piirma (ed) Emulsion Polymerisation, Academic Press, New York