ORIGINAL CONTRIBUTION

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Preparation of composite latex particles by engulfment

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Abstract It can be predicted that, provided the interfacial energies are well chosen for two individual particles, then it is possible to engulf one particle into the other. This has now been achieved experimentally using poly-[butylmethacrylate] particles as the host material and poly-[styrene] particles for engulfment. Initially, anionic poly-[styrene] particles were heterocoagulated onto electrosterically stabilised cationic particles of poly-[butylmethacrylate]. Then on heating the heterocoagulated units above the glass transition temperature of the latter engulfment occurred.

Key words Engulfment – interfacial energy – heterocoagulation – Poly-[styrene] – Poly-[butylmethacrylate]

Introduction

The possibility of preparing polymer colloid particles with a well-defined morphology such as a core-shell with one polymer as the core and another as the shell is of considerable interest both from a fundamental point of view and from the standpoint of technological applications. Although considerable work has been reported on the preparation of particles using mixed monomers and with seeded polymerisations using a second monomer the outcome from these approaches has not always been predictable and many particle morphologies have been described [1–18]. However, recently a number of publications have appeared suggesting theories, based on the surface energies of the polymers, which enable the identification of the energetically favoured morphologies for composite particles [19–26]. These considerations suggested the possibility of preparing composite polymer particles by a process in which dissimilar preformed particles are induced to heterocoagulate. Then rearrangement of the composite, promoted by a reduction of the total interfacial energy, proceeds with one particle type spreading around or "engulfing" a particle of the other type when the temperature

is raised above the engulfing polymer glass transition [23, 25].

In one of the earlier experiments [24], random copolymer particles composed of poly-(methyl methacrylate), PMMA, and poly-(butyl acrylate), PBA, were used as the engulfing particles. These were prepared by emulsion polymerisation, using ammonium persulphate as the initiator and also using methoxy-polyethylene glycol methacrylate, to incorporate PEG chains of ca. 2000 molecular weight on to the surface to act as a steric stabiliser [24]; these had a number-average diameter of 670 nm. A latex of PBA with a number-average diameter of 95 nm was also produced by emulsion polymerisation using ammonium persulphate and constituted the smaller particles which were to be engulfed.

In order to prepare composite particles the PMMA/PBA copolymer particles were placed in a stirred container and the temperature raised to 65 °C. The smaller PBA particles and a 0.01 mol dm^{-3} solution of dodecyl trimethyl ammonium bromide were then added simultaneously but separately through different tubes over a period of 1.5 hours. The resultant particles, containing engulfed PBA, had a final diameter of 780 nm as determined by disc centrifuge photosedimentometry [24].

Several methods can be used to induce the necessary heterocoagulation. In the present work the dissimilar particles were prepared with opposite electrical charges at their surfaces. Cationic particles of poly-(butyl methacrylate), PBMA, prepared using a cationic initiator, were used as the host particles; these particles were, in addition, also sterically stabilised by the incorporation of MeOPEGMA chains onto the surface. The particles to be engulfed were poly-(styrene), PS, prepared by an emulsion polymerisation technique using ammonium persulphate. The engulfment process was carried out at 70 °C, which was 35 °C above the glass-transition temperature of PBMA..

Theory

The conditions for engulfment based on surface energy considerations have been discussed previously [23–26] but a short summary is given here to provide continuity. Initially, on the basis of two separated particles, as shown in Fig. 1, we can write that the total surface energy for one host particle of radius R_H and one core particle of radius R_C is given by:

$$E_{sep} = 4\pi R_H^2 \gamma_{HW} + 4\pi R_C^2 \gamma_{CW} ,$$

where γ_{HW} and γ_{CW} are respectively the surface energies of the host particles and the core particle in water. Alternatively, in terms of the volumes of the separated particles the equation can be written as,

$$E_{sep}/4\pi(3/4\pi)^{2/3} = V_H^{2/3}\gamma_{HW} + V_C^{2/3}\gamma_{CW} .$$

After engulfment has occurred (see Fig. 1) we can similarly write,

$$E_{eng} = 4\pi R_C^2 \gamma_{CH} + 4\pi R_T^2 \gamma_{HW}$$

and

$$E_{eng}/4\pi(3/4\pi)^{2/3} = V_C^{2/3}\gamma_{CH} + V_T^{2/3}\gamma_{HW} ,$$

where R_T = the radius of the final particle. It is also assumed that after engulfment the volume of the core particle has not changed. The energy involved is thus:

$$\Delta E = E_{eng} - E_{sep}$$

so that provided ΔE is negative the process is thermodynamically favourable. Alternatively, the condition for engulfment can be expressed as,

$$V_C^{2/3}\gamma_{CH} + V_T^{2/3}\gamma_{HW} < V_H^{2/3}\gamma_{HW} + V_C^{2/3}\gamma_{CW} . \tag{1}$$

Fractional volumes of the particles can also be expressed in the form,

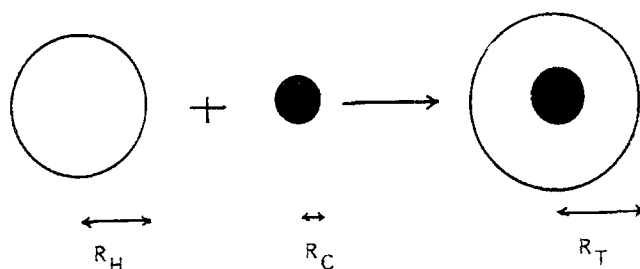$$\phi_C = V_C/V_T \quad \text{and} \quad \phi_H = V_H/V_T$$

Fig. 1 Schematic illustration showing the engulfment of a core particle of radius, R_C, into a host particle of radius, R_H, to form a composite particle of radius R_T

where,

$$\phi_C + \phi_H = 1 .$$

In terms of fractional volume it follows from the inequality (1) that,

$$\phi_H^{2/3}\gamma_{HW} + \phi_C^{2/3}\gamma_{CW} > \phi_C^{2/3}\gamma_{CH} + \gamma_{HW}$$

and

$$\frac{\gamma_{CW} - \gamma_{CH}}{\gamma_{HW}} > \frac{1 - \phi_H^{2/3}}{\phi_C^{2/3}} . \tag{2}$$

Figure 2 shows a plot of the right-hand side of the inequality (2) as a function of ϕ_C; this shows the region above the curve where the conditions for engulfment are fulfilled. The left-hand side of the expression (2) can also be written in terms of the contact angle, θ, in the form of Young's equation, namely,

$$(\gamma_{CW} - \gamma_{CH})/\gamma_{HW} = \cos \theta .$$

Thus complete spreading is acheived when $\cos \theta = 1.0$. However, it has been indicated [26–27] that the energy change, from separated to engulfed, can increase with increasing values for the interfacial energy expression to values greater than unity. The value increases with:

i) increasing γ_{CW}, that is with an increased hydrophobic nature of the core particle,

ii) decreasing γ_{HW}, that is with an increased hydrophilic tendency of the surface of the engulfing particles,

iii) decreasing γ_{CH}, which occurs if the interior of the engulfing particle becomes more like the surface of the core particle.

Kinetic factors have not been considered in this section, however, it is clear that internal re-arrangement of particle morphology towards the favoured structure may be completely inhibited or very slow in some systems, such as those in which the host polymer is cross-linked or is in the glassy state.
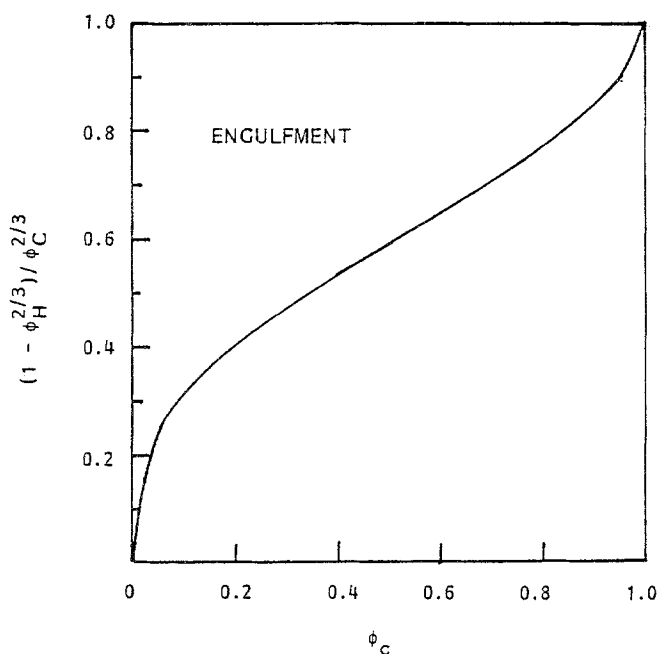
Fig. 2 A plot of $(1 - \phi_H^{2/3})/\phi_C^{2/3}$ against ϕ_C [see Eq. (1)] indicating the predicted region for engulfment

Experimental

Materials

The water used was doubly distilled from an all-Pyrex apparatus.

Styrene was BDH laboratory reagent grade material. Butyl methacrylate (BMA) was obtained from the Aldrich Chemical Company. Both monomers were purified by distillation under reduced pressure in an atmosphere of nitrogen. Purified monomers were stored in a refrigerator at 4 °C.

Ammonium persulphate was BDH AnalaR grade material and was recrystallised before use. 2.2′ azobis 2-amidinopropane dihydrochloride, ABA.2HCl, was obtained from the Wako Chemical Company under the trade name V50.

Methoxy PEG methacrylate, MeOPEGMA,

$$CH_2 = C \overset{\displaystyle CH_3}{\underset{\displaystyle \underset{O}{\overset{\|}{C}}-O-(CH_2-CH_2-O)_n CH_2-CH_2OCH_3}{}}$$
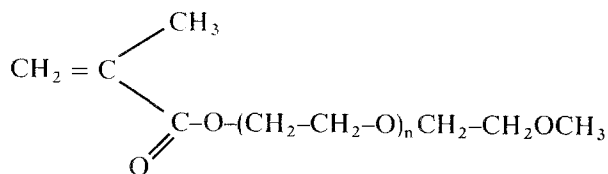
with n approximately equal to 45 units was prepared by the method previously described [28, 29].

Preparation of poly-(butylmethacrylate), PBMA, latices

The surfactant-free polymerisation of the PBMA latex was carried out in a five-necked flask equipped with a glass stirrer having a PTFE paddle, rotated at 350 rpm, under a constant flow of nitrogen gas. A water-cooled reflux condenser and a thermometer were inserted into two of the other inlets. The initial charge to the flask was 350 ml of water, 40 ml of butyl methacrylate and 0.24 g of sodium chloride. The flask was then immersed up to the neck in an oil bath which maintained the temperature of the contents at 70 °C. After allowing 20 min for the system to attain temperature equilibrium, 0.11 g of the cationic initiator, ABA. 2HCl, dissolved in 10 ml of water were added. The polymerisation reaction was then allowed to proceed for 24 h.

At this stage, following previous work [29], 5.87 g of a 60% w/w aqueous solution of MeOPEGMA was added to the flask followed by 20 ml of butyl methacrylate. After a short interval for the flask contents to return to 70 °C 0.2 g of ABA.2HCl were added and the reaction allowed to proceed for a further 24 h. The resultant latex, after cooling, was filtered through glass-wool into well-boiled Visking dialysis tubing and dialysed against distilled water, with daily changes of water, to remove oxidation products, salt, and residual initiator and monomer.

Preparation of polystyrene latices

This preparation was carried out using an emulsifier free formulation [30] with the equipment described above. The initial charge consisted of 0.9 ml of styrene, 779 ml of water and 0.47 g of sodium chloride dissolved in 10 ml of water. After attainment of temperature, 70 °C, 0.5 g of ammonium persulphate dissolved in 10 ml of water were added. The reaction was allowed to proceed for 24 h after which the latex was treated in the manner described above.

Preparation of composite particles

In order to produce composite particles from the two separate dispersions described above the following procedure was used. Small aliquots of the two latices were mixed in a small sample bottle of volume ca 20 ml and the bottle then vigorously shaken. Prior to the mixing process the volume fraction and number concentration of each latex was determined from the w/w concentration.

As the mixed particles were of opposite charge the mixing process resulted in heterocoagulation i.e., the formation of particle clusters with small PS particles adsorbing on to the surface of the larger PBMA particles.

The ratio of PS to PBMA particles in the cluster was controlled by adjusting the particle number concentrations of the two latices prior to mixing. The concentration of the PS latex was chosen arbitrarily to be that needed to cover one-quarter of the surface area of the PBMA particles assuming that complete adsorption occurred. In principle therefore each cluster had a ratio of 68 PS particles to one PBMA particle. During the addition process the electrolyte concentration was maintained at about 10^{-5} mol dm^{-3} sodium chloride. The mixture was allowed to stand for 24 h at room temperature after which it was ultra-sonicated for 30 min to break up any flocs formed as a consequence of particle–particle bridging flocculation.

In order to achieve particle engulfment the mixed dispersion in the sample bottle was placed in an oil bath at 70 °C for 24 h. This temperature was above the T_g of PBMA (35 °C) and hence allowed the PS particles to become ingested into the PBMA spheres to produce a currant-bun type morphology.

Characterisation of the latex particles

Electron microscopy

For electron microscopy examination dilute samples of the latices were placed on carbon coated copper grids. These were examined at low beam intensities using a JOEL JEM-100CX transmission electron microscope. From the micrographs obtained prints were made and used in conjunction with a Carl Zeiss TGZ 3 particle size analyser to obtain a number-average particle diameter. For each determination about 800 particles were counted.

The particle clusters obtained from the heterocoagulation process were also examined using the same transmission electron microscope, using carbon replicas of the composite particles.

In order to obtain information on the internal particle morphology of the PBMA particles, after engulfment had occurred, thin sections were prepared for examination. Initially, the aqueous composite particle mixture was converted to a dry powder by freeze-drying. The powder was then imbedded in a resin which was prepared from 10 ml of Araldite CY212, 10 ml of dodecylenyl succinic anhydride and 0.4 ml of benzyl dimethylamine; this mixture was left at room temperature for 2 weeks to harden. Thin sections were prepared from the hardened resin using a Sorvall MT-2 ultramicrotome with a freshly prepared glass knife. The thin sections were floated off on to a water reservoir and those of suitable thickness collected on copper grids; the latter were placed on a thin piloform film for support and protection of the sections. Then, the sections were stained with ruthenium tetroxide to highlight the PS relative to the PBMA during electron microscope examination. Finally, the sections were carbon coated to provide stability in the electron beam.

Disc centrifuge photosedimentometry

A Brookhaven spinning disc centrifuge, type DCP-1000 Particle-Sizer, was also used for the determination of particle size and to obtain an estimate of the size distribution. Water (15 cm^3) was used as the spin fluid and just prior to running 1 cm^3 of 50% of a methanol/water (v/v) mixture was added in order to set up a density gradient. 0.2 cm^3 of an aqueous latex at an appropriate concentration (ca 1%w/v) to give a peak was injected on to the surface of this in 50% methanol/water. Within the instrument a photodetector was located at a known distance from the centrifuge axis, R_d, in order to measure turbidity at this position as a function of time, t, from injection of the sample R_i. This time is directly related to the angular frequency of the disc, ω, the particle diameter, D, the difference between the density of the particle and the fluid, $\Delta\rho$, and the fluid viscosity, η, by:

$$t = 18\eta \ln [R_d/R_i]/\omega^2 D^2 \Delta\rho \ . \tag{3}$$

It is clear from this equation that the time taken for a particle to move to the measuring point is inversely proportional to the square of its diameter thus giving good resolution in size. The Brookhaven software provided with the instrument converted the photometric turbidity measurements into a particle size distribution (see later). The density difference parameter, $\Delta\rho$, is an important parameter in the equation and hence the densities of all particles and the spin fluids were determined using an Anton Paar density meter.

Electrophoresis

In order to determine the sign of the electric charge on the particles and the magnitude of the zeta-potential as a function of pH, electrophoretic measurements were made on the particles of each latex. The PS latex which contained small particles was examined using a Malvern Zeta-sizer II. The PBMA latex particles were examined using a moving boundary technique in the manner previously described (31). The compound particles were examined using a Pen Kem, system 3000, electrokinetic analyser. All the measurements were made in a salt concentration of 10^{-3} mol dm^{-3}.

Results

Electron microscopy

Figure 3 shows transmission electron micrographs of the particles of PBMA, which were used as the host particles, and particles of PS which were used for engulfment into the host particles to form core particles. As can be seen both sets of particles were fairly monodisperse; particle size data obtained from electron microscopy is given in Table 1.
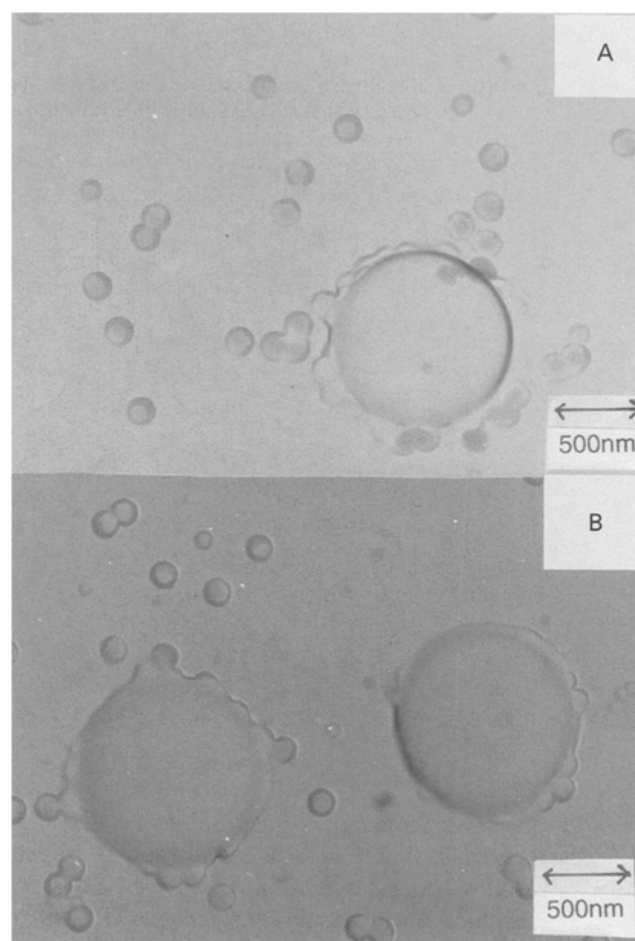
Some electron micrographs of carbon replicas of hetero-coagulated units formed by mixing the small PS particles with the large PBMA particles are shown in Fig. 4. The micrographs which were taken on samples following ultra-sonication but prior to heat treatment indicate that some partial engulfment already seems to have occurred.

Figure 5 shows electron micrographs of sections cut from particles which had been taken up to a temperature of 70°C, that is well above the T_g of PBMA. As can be seen engulfment has occurred and the PS particles are clearly visible in the PBMA host particles. It appears from the micrographs that some change in the PS particles has occurred during the engulfment and, as anticipated, that
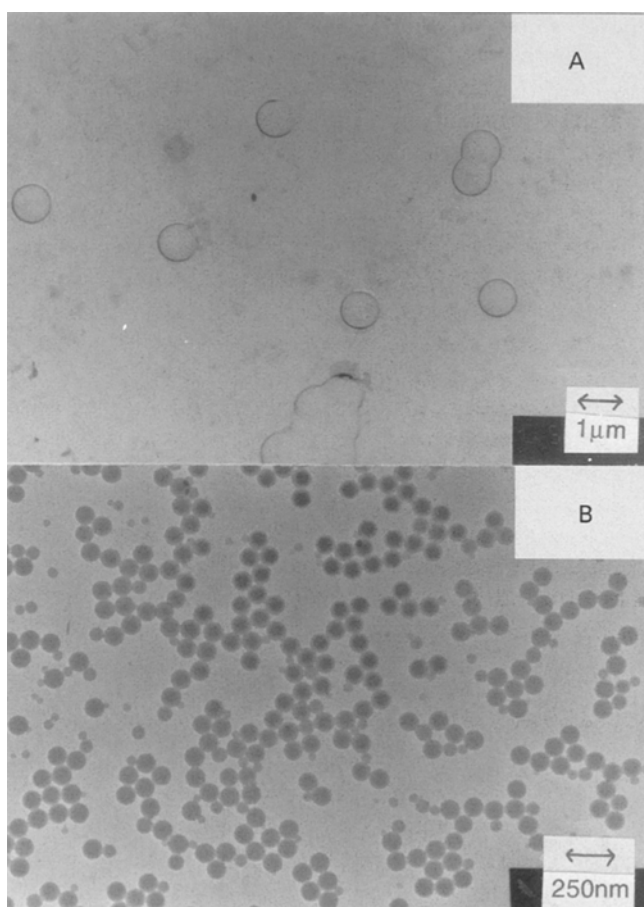
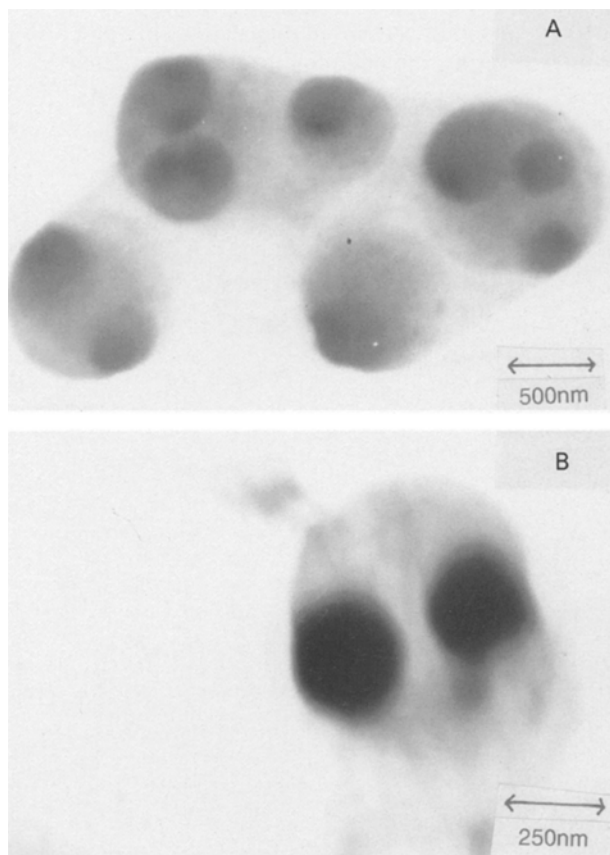Fig. 3 Electron micrographs of A PBMA particles and B PS particles

Fig. 4 Electron micrographs of carbon replicas of PS and PBMA particles following the heterocoagulation process

Table 1 Particle-particle engulfment

| Particle	Polymer	Radius/nm	Coef.Var.%	Tg/°C	Stabilisation mechanism
Host	PBMA	446[†]	2.9	35	Electrosteric/Cationic
Core	PS	45[†]	28.8	106	Electrostatic/Anionic

[†] Transmission electron microscopy, number average.

more than one PS particle per PBMA particle has been engulfed. Moreover, in places partial exposure of the PS surface appears to occur which suggests that for some particles the engulfment is incomplete; this feature is also illustrated in Fig. 6.
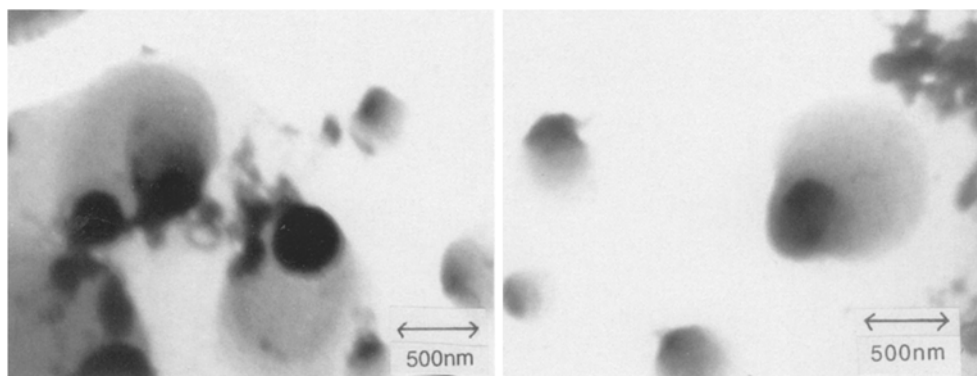
An additional feature of Fig. 5 is that the engulfed PS particles appear to be larger than the size of the original PS particles. One possibility is that the PS particles do not retain colloid stability within the host particle and hence flocculate. Thus if the PS particles join together this reduces the area exposed to the PBMA and hence reduces the interparticle interfacial energy which makes this a favourable process. It is also possible that some smearing of the PS particles could have occurred during microtome sectioning although this was carried out well below the T_g of PS.

Electrophoresis studies

Figure 7 shows the results of the electrophoretic examination of both PS and PBMA particles as well as an examination of the composite particles after engulfment had occurred. As anticipated the PS particles, which were prepared using a persulphate initiator, maintained a negative electrophoretic mobility over the whole of the pH range studied. The PBMA particles, which were prepared using an amidine initiator, had an isoelectric point at pH 4.2 ± 0.1. This value was lower than that found in previous work [32] but was confirmed by two experimental methods. Firstly, by microelectrophoresis, which uses a very low concentration of particles and can be susceptible to contamination by silicaceous anions from the glassware [33], and secondly by using a moving boundary apparatus at a much higher concentration of latex (10.0% w/v). However, the measurements were also made sometime after the preparation and as shown previously the cationic charge can decay slowly with time [32].

It should also be noted that in the present work the surface of the PBMA particle had chemically grafted MeOPEG chains on the surface which would influence the charge behaviour by displacing the surface of shear.

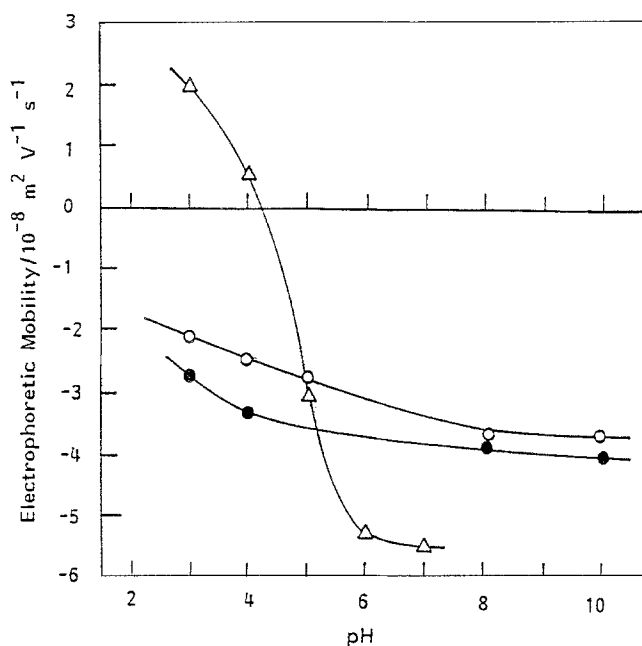The composite particles examined after engulfment had occurred also had a negative mobility over the pH

Fig. 5 Electron micrographs of sections cut from composite particles after the heterocoagulated particles had been raised 35 °C above to T_g of the PBMA particles

Fig. 6 Electron micrographs of sections cut from composite particles after the heterocoagulated particles had been raised 35 °C above the T_g of the PBMA particles to illustrate examples of particle engulfment

Fig. 8 Traces obtained by disc centrifuge photosedimentometry for **A** PBMA particles **B** composite particles after the engulfment process

range examined. This was unexpected since it was anticipated that engulfment of the PS particles would give the composite particles electrophoretic characteristics resembling those of the PBMA particles. In fact, the results resembled more closely those of the PS particles. This could be a consequence of the fact that not all the PS particles were completely engulfed and that some PS surface still remained exposed to the external aqueous phase. This view is to some extent supported by the electron micrographs of thin sections shown in Figs. 5 and 6.

Heterocoagulation

Since the electrophoresis studies indicated that the electrosterically stabilised PBMA particles were only positively charged below pH 4.2 mixing of the PS and PBMA particles was carried out below this value. As shown in the electron micrographs of Fig. 4 it is clear that heterocoagulation occurred under these conditions although, as anticipated, complete coverage of the surface of the PBMA particles did not occur.

Disc centrifuge experiments

Figures 8A and 8B show the traces obtained from the disc centrifuge experiments. The trace for the PBMA latex
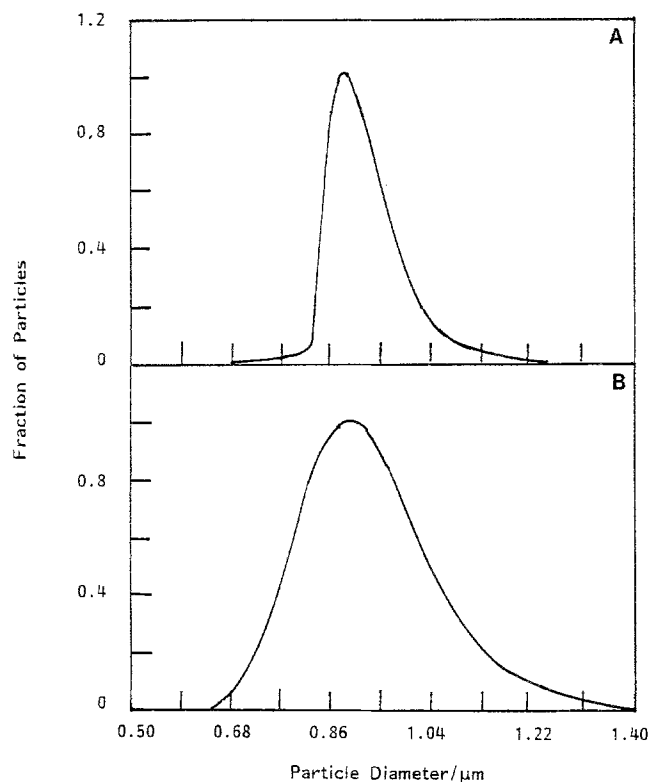
indicates a rather narrow size distribution with the mode of the curve at 885 nm; the weight average diameter was found to be 926 nm. The trace for the particles after the engulfment process was significantly broader and the mode of the curve had moved to 889 nm; the weight average diameter was found to be 938 nm. The shape of the traces suggests that a significant change has occurred in the size distribution of the PBMA particles after engulfment has occurred to form composite particles. In addition, a question arises as to whether a density distribution is generated within the composite particles as a consequence of the variation in the number of PS particles taken up by each PBMA particle. As mentioned earlier the density of the particles affects the $\Delta\rho$ term in Eq. (3) and thus the analysis of the results.

Discussion

Figure 9 illustrates schematically the basic objective of the present work which was to engulf one set of polymer colloid particles of high T_g into a host particle of lower T_g. The first stage of the process involved the synthesis of particles with appropriate size and bulk and surface
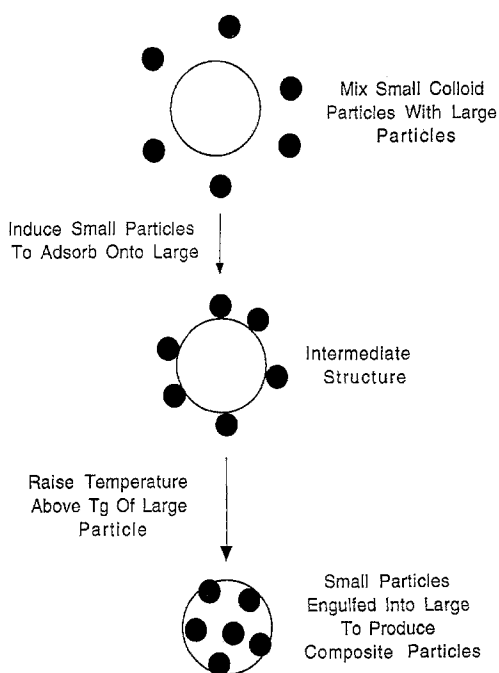
Fig. 9 Schematic flow chart of the process of particle engulfment

properties. PS particles of diameter 45 nm and a T_g of ca 106 °C were prepared using emulsifier-free polymerisation and a persulphate initiator. The host PBMA particles, diameter 446 nm and T_g 35 °C were prepared using emulsifier-free polymerisation and ABA.2HCl as initiator; towards the end of the polymerisation MeOPEGMMA was added to provide grafted MeOPEG chains on the surface and hence electrosterically stabilised particles.

The second stage involved mixing the cationic PBMA particles with the anionic PS particles under favourable conditions for heterocoagulation in order to obtain a coating of the small particles on the larger host particles.

Finally as the third stage the mixed system was heated to 70 °C for 24 h, a temperature 35 °C above the T_g of the PBMA.

As demonstrated in the previous section this scheme successfully produced composite particles of PS engulfed in PBMA. The final particles exhibited properties associated with electrosteric stabilisation, as for example exemplified by their good freeze-thaw properties, indicating that the MeOPEG chains remained on the surface of the composite particles following the engulfment process.

In the theoretical section of this presentation and in previous papers [23–26] a thermodynamic argument was proposed that if the surface energies of the host and core particles were correctly chosen then logically engulfment of the core by the host would occur, namely provided that

the magnitude of $(\gamma_{CW} - \gamma_{HW})/\gamma_{HW}$ was greater than one. Further theoretical development [27] indicated that a structure in which the core particles was only partially engulfed by the host would be favoured if $-1 < (\gamma_{CW} - \gamma_{CH})/\gamma_{HW} < 1$. The lower energy of the final state is a compelling reason for the thermodynamic transition and the success of the experiments carried out provide strong evidence in favour of the importance of the thermodynamic process. However, a complete test of the hypotheses involves a precise knowledge of the surface energies of the particles involved and at the present time data of sufficient precision is not available. Although a number of attempts have been made to obtain information for polymer surfaces [34, 35] the results have been qualitative rather than quantitative. In addition, neither the influence of surface charge nor the influence of MeOPEG chains has been assessed precisely. In principle, both of these should decrease the surface energy and these factors may well have facilitated engulfment by aiding the condition that $(\gamma_{CW} - \gamma_{CH})/\gamma_{HW}$ should be less than unity.

An additional question that must be considered is to what extent factors other than thermodynamic might influence the engulfment process. Although thermodynamic factors may supply the main motivation kinetic factors are also important since the process of a core particle passing into the host particle must, of necessity, involve hydrodynamic flow of the host polymer in order to allow passage of the incoming particle. Thus it is unlikely that this process could occur if the host particle was in the glassy state or cross-linked. For this reason PBMA was chosen as the polymer for the host particle since it has a low T_g and in order to achieve engulfment the temperature of the heterocoagulated units could be raised 35 °C above the T_g of PBMA. At this temperature engulfment was successful but using temperature as a variable was not examined in detail.

Although the present study has been confined to polymer colloid particles the principles should be more generally applicable. Other experiments have shown that a number of inorganic particles such as magnetite can be engulfed into a polymeric host particle by this process [36].

It is also of interest that some years ago surface energy arguments were used by Mudd et al. [37] to explain the process of phagocytosis, that is the engulfment of biologically alien particles by polymorphonuclear leucocytes.

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