Morphology of Two-Phase Polystyrene/Poly(methyl methacrylate) Latex Particles Prepared under Different Polymerization Conditions

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ABSTRACT: Two-phase latex particles were prepared by polymerizing, at 60 °C, methyl methacrylate (MMA) in the presence of monodisperse polystyrene (PS) seed particles. Polymerization was induced by thermal decomposition of lauroyl peroxide present in the seed particles. The morphology of the particles was studied by transmission electron microscopy on thin unstained sections. The monomer, MMA, was added either batchwise or continuously. In the batch experiments, the monomer was allowed to diffuse completely into the seed particles at ambient temperature, prior to the initiation of the polymerization. The batch experiments resulted in particles with large PMMA domains in a continuous PS matrix. Continuous addition of MMA (polymerization under starvation conditions) produced particles with very small PMMA domains that were uniformly distributed over the entire particle volume. The domain size could be increased by decreasing the rate of polymerization and by lowering the glass transition temperature of the seed particles. The results imply that the formation of a core–shell structure requires inhibition of radical transport within the particles. Intermittent swelling of the two-phase particles, by addition and the subsequent removal of methylene chloride from the latex, produced composite particles containing one PS domain, partly engulfing a seemingly spherical PMMA domain (double-ball structure). Calculations of the interfacial energy indicated that this double-ball structure represents a thermodynamically favored, metastable situation for PS/PMMA composite particles in water.

Introduction

The production of two-phase latex particles with defined morphology is a problem of great technical interest. Presently, the practical use of two-phase latex particles is seriously hampered by the incomplete understanding of the relation between the polymerization conditions and particle morphology.

Previous work in this field suggests that particle morphology is controlled by many factors, including the hydrophilicity of the monomers and polymers,[1-3] particle viscosity,[4] the molecular weight of the polymers,[5] the degree of grafting between the polymers,[6-8] and the rate of transport of monomers, radicals, and oligomers.[9] Latex particle morphology has been studied by indirect methods[2,3,10] as well as by electron microscopy.[1,4,8,11]

This study involves the preparation of two-phase latex particles under strictly defined conditions and their subsequent morphological characterization by electron microscopy on unstained thin sections. The composite particles were prepared by polymerizing methyl methacrylate (MMA) in the presence of monodisperse PS seed particles. To facilitate electron microscopy on sectioned samples, relatively large seed particles (about 600 and 725 nm) were used. Polymerization was induced by thermal decomposition of lauroyl peroxide which was homogeneously distributed in the seed particles. The different process conditions studied included batch and continuous addition of monomer, rate of polymerization, and particle viscosity. The observed morphologies are discussed in relation to the expected equilibrium structure of two-phase PS/PMMA latex particles.

Methods

Chemicals. Styrene (Merck) and methyl methacrylate (Merck) were purified by passing the monomers through a column filled with aluminum oxide (Merck, active basic). The purified monomers were kept at 8 °C before use. Lauroyl peroxide (BDH) was used as supplied. The water used was distilled and deionized. All other chemicals were of analytical grade and used as supplied.

Table I
Particle Size Data of the Seed Latexes

	TSC,[a] %	
	4.80 PS1	6.90 PS2
D_n, nm	725	585
D_w, nm	728	593
D_v, nm	726	589
PDI	1.004	1.013

[a] Total solids content.

Preparation of Seed Latexes. The PS seed latexes were prepared by soap-free emulsion polymerization using potassium persulfate as initiator.[12] The unreacted initiator was removed from the seed latexes with a Dowex 2X8 OH^- ion-exchange column. Particle size data for the seed latexes are given in Table I.

Before the seed latexes were used in the MMA polymerization step, an oil-soluble initiator, lauroyl peroxide (LPO), was introduced in the particles by adding 7 mL of an acetone solution of the initiator to 100 g of seed latex. The mixture was stirred overnight at ambient temperature. The acetone was then removed by vacuum distillation.

Polymerization of MMA. The second polymerization step was carried out at 60 °C in a 200-mL calorimetric reactor that has been described in detail by Nilsson et al.[13] The reactor was repeatedly degassed and purged with nitrogen through a needle valve. The monomer was degassed and purged with nitrogen before being added to the reactor. In batch experiments, the monomer was allowed to diffuse completely into the seed particles at ambient temperature before starting the polymerization. In experiments requiring continuous addition of MMA, the monomer was fed by a motor-driven syringe connected to a valve in the bottom of the reactor via stainless steel tubing immersed in the water bath. In this way the monomer was preheated to the polymerization temperature before entering the reactor. During polymerization the reactor was submerged in a carefully temperature-controlled water bath. The polymerizations were

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Table II
Recipies Used in the MMA Polymerization Experiments

	A	B	C	D	E	F
addition of MMA	batch	cont	cont	cont	batch	cont
seed latex PS1, g	100.00	100.00	100.00	100.00		
seed latex PS2, g					100.00	100.00
lauroyl peroxide, mg/g[a]	3.70	3.70	3.70	3.70	0.42	3.70
cyclohexane, mL						10.00
MMA, mL	7.13	7.13	7.14	7.14	10.18	10.15
feed rate of MMA, mL/h		1.20	3.00	6.00		3.00

[a] Weight of initiator per weight of PS (mg/g).

followed by measuring the temperature difference between the water bath and the content of the reactor. By measuring this signal, we could evaluate the rate of polymerization using heat-flow data determined by calibration as previously described.[13]

In the experiments described here, the total amount of MMA used was calculated to give composite particles containing equal volumes of PS and PMMA. Sodium dodecyl sulfate (SDS) was added (48 mg/g of PS) in order to improve the stability of the latex. The antioxidant, ascorbic acid (0.15 g), was used to eliminate inhibition by oxygen. In one experiment cyclohexane was used as a plasticizing solvent. In this case the cyclohexane was allowed to swell the seed particles at ambient temperature before initiation of polymerization. The recipes used in the individual experiments are given in Table II.

Solvent Treatment of Composite Particles. In attempts to study the equilibrium morphology of the composite particles, the latexes were treated with methylene chloride ($MeCl_2$), a common solvent for both PS and PMMA. The solvent treatment was carried out by adding 15 mL of methylene chloride to a reactor containing 15 mL of latex and 60 mL of water. The reactor was submerged in a water bath and kept at 60 °C for 4.5 h under gentle stirring. The solvent was then removed by vacuum distillation at 60 °C.

Electron Microscopy. Latex samples were dried in an oven at 50 °C. The dried samples were embedded in epoxy resin and cured overnight at 60 °C. The embedded samples were sectioned with an LKB Ultratome V equipped with a Sapphatome knife. The sections (thickness of ca. 60 nm) were examined in a JEOL 100U transmission electron microscope. As PMMA decomposes in the electron beam, contrast between the polymer phases was obtained without staining.[14] In the micrographs, PS appeared as dark domains and PMMA as bright domains against a grayish background, corresponding to the epoxy resin.

Results and Discussion

Polymerization of MMA in the Presence of PS Seed Particles. Emulsion seed polymerization can be carried out either batchwise or under starvation conditions, i.e., conditions where the monomer is continuously fed to the reactor at a rate that is sufficiently low to avoid creating a pool of liquid monomer in the reactor. In terms of reaction rate, starvation conditions mean that one is operating on the descending side of the reaction rate versus time curve.

The rates of polymerization during one experiment with batchwise addition of MMA (A) and three experiments in which the monomer was continuously fed to the reactor at different feed rates (B–D) are shown in Figure 1 (for details see Table II). The total amounts of PS seed particles and of MMA added were the same. The batch polymerization exhibited a pronounced gel effect. In the continuous-feed experiments B and C the polymerization rates were constant during most of the feeding times. At the high feed rate experiment D, the total time for feeding the monomer seems to have been somewhat too short to give a period of constant polymerization rate. It is clear from Figure 2 that polymerizations B–D were all carried out under so-called starvation conditions. In Figure 2 the steady-state polymerization rates from experiments B and C and the maximum rate of polymerization in experiment

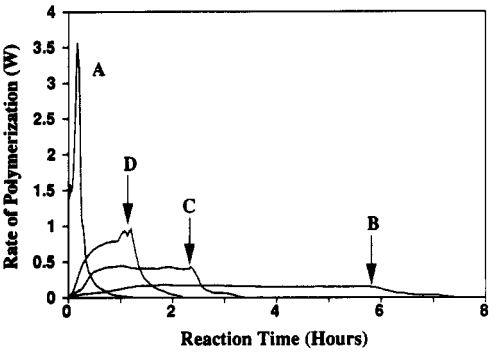

Figure 1. Polymerization rate curves for polymerization experiments A–D (cf. Table II). The arrows indicate the times at which the monomer feed was completed in runs B–D.

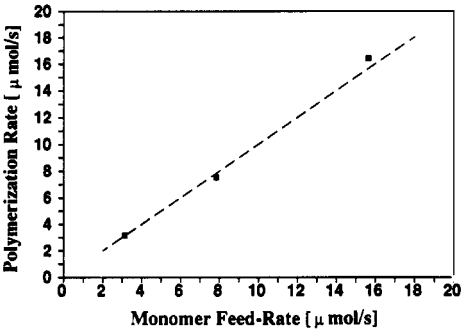

Figure 2. Constant polymerization rate vs monomer feed rate for the polymerization experiments carried out with continuous addition of monomer. The dashed line represents instantaneous polymerization; i.e., the monomer feed rate is equal to the rate of polymerization.

D are plotted against the corresponding monomer feed rates. The polymerization rates were calculated from the experimentally determined power of polymerization (Figure 1) using the value 57 kJ/mol for the heat of polymerization.[15] The dashed line has unity slope and corresponds to an instantaneous polymerization of added MMA. These conditions prevailed during the plateau periods in experiments B and C, whereas a steady-state condition was not fully reached in experiment D (Figure 2). From the dry-matter content of the latexes the residual monomer concentration in the final particles was estimated to be 0.3 mol/L. The additional amount of monomer in the particles during the continuous-feed runs could be estimated by comparing the rates plotted in Figure 2 with the conversion reached at the corresponding rates in the batch experiment. According to these estimates, the total monomer concentration in the particles during steady-state conditions (or for experiment D at the maximum rate) was 0.6 (B), 0.9 (C), and 1.1 mol/L (D).

Particle Morphologies by Electron Microscopy. Batch and Continuous Monomer Feed Polymerizations. When thin sections of the original PS seed particles, taken from samples embedded in the epoxy resin, were investigated in the electron microscope, the PS

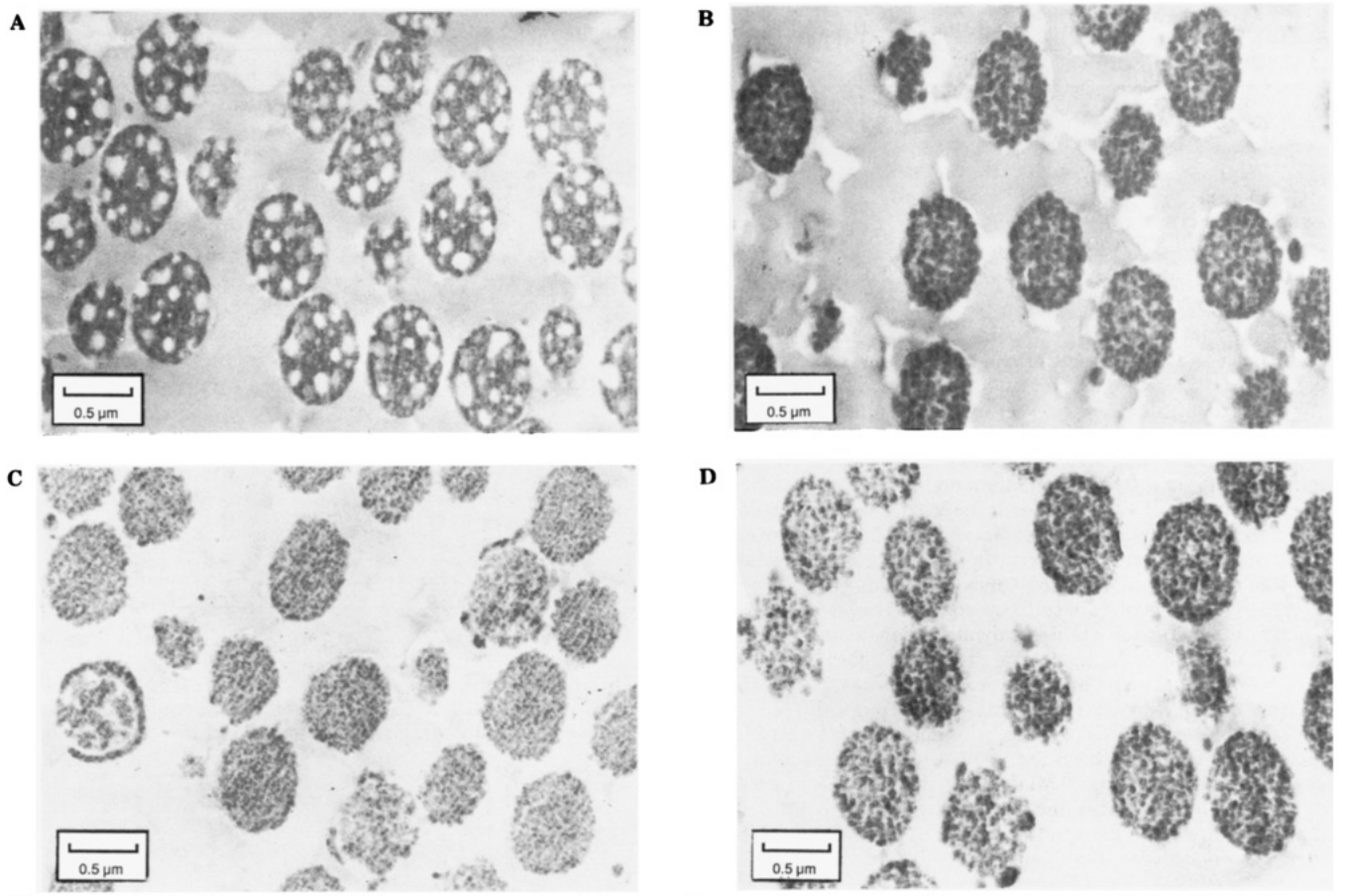

Figure 3. TEM micrographs of the internal structure of the two-phase particles, prepared in experiments A–D (see Table II).

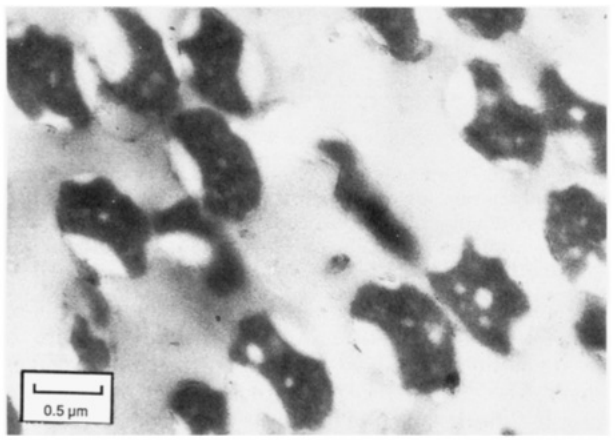

Figure 4. Particle morphology from polymerizing MMA with batchwise addition of MMA and at a lower rate of initiation (experiment E) than in the corresponding batch experiment in Figure 3A.

particles appeared as structureless, dark areas. The fact that no structural heterogeneity was evident in the PS particles shows that the embedding technique used in the present work did not introduce artifacts.

The micrographs in Figure 3 show that the particles obtained in experiments A–D contained two polymer phases. They also show that particle morphology strongly depends on the polymerization conditions used. In the micrographs, the particles appear as elliptical rather than circular. This is an artifact introduced by the microtome, which compresses the sections. The cutting direction is perpendicular to the long axis of the apparently elliptical particles. The electron beam intensity was gradually increased to the level required for obtaining micrographs with good contrast and short exposure time. The increase in intensity produced no noticeable changes in the apparent morphology of the particles due to radiation damage. As seen from Figure 3, the batch polymerization experiment resulted in particles with large PMMA domains in a continuous PS phase. In contrast, particles prepared under starvation conditions (continuous addition of MMA) contained very small polymer domains, uniformly distributed over the entire particle volume. The micrographs of the particles from experiments B–D (Figure 3) indicate that the PMMA phase might be the continuous phase. It should be borne in mind, however, that the two phases have different mechanical properties and that this may introduce small variations in the thickness of the sections cut by the microtome. Although PMMA might well be the continuous phase in the particles from experiments B–D, a definite conclusion is presently not possible.

The fact that experiments B–D resulted in particles with the same type of structure throughout and showed no signs of a core–shell structure proves that the transport rate of monomer was sufficiently high to maintain a uniform monomer concentration within the particles. This is in agreement with predictions made by Chern and Poehlein,[9] Napper,[16] and Gardon[17] but is at variance with conclusions drawn by Williams et al.[18,19] This strongly supports the notion that the generation of core–shell structures by emulsion seed polymerization requires the use of a strategy that prevents the transport of radicals toward the interior of the particle. This subject will be discussed in more detail in a forthcoming paper.

Influence of the Rate of Polymerization. The structure of a two-phase polymer particle from a batch polymerization experiment in which a low rate of initiation

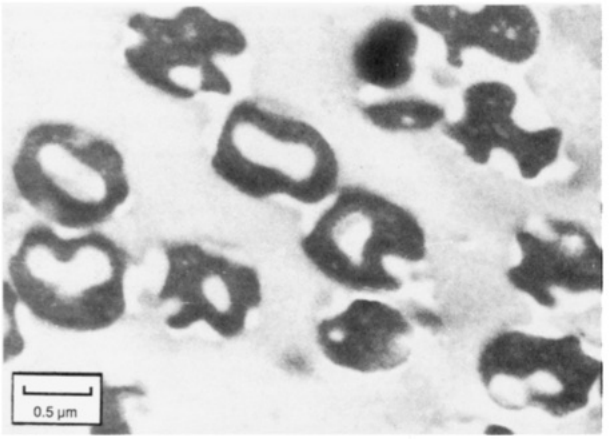

Figure 5. TEM micrograph of sectioned particles prepared from plasticized seed particles (cyclohexane) using continuous addition of MMA.

was used is shown in Figure 4. In this case the polymerization time was 10 h as compared to 1.3 h in the experiment described in Figure 3A. A comparison of Figures 4 and 3A shows that a decrease in the rate of polymerization results in an increase in the size of the PMMA domains. This comparison illustrates that particle morphology is strongly dependent on the "within-particle" transport rates of various species and the tendency toward decreasing the interfacial area between the polymer phases.

Effect of Particle Viscosity. The polymerization temperature in the present work, 60 °C, was much lower than the glass transition temperatures of the polymers (ca. 95 °C for PS and ca 110 °C for PMMA). This means that the polymerizations were carried out at high particle viscosity, particularly so in the experiments carried out under starvation conditions. In commercial polymerization processes, the polymerization temperature is often higher than the glass transition temperature of the polymer. It would be of interest, therefore, to elucidate the effect of particle viscosity on morphology. This was done by performing a continuous monomer feed experiment using PS seed particles swollen with cyclohexane (1.5 v/v cyclohexane/PS, experiment F in Table II). The morphology of the resulting particles is shown in Figure 5. As can be seen, the PMMA domains are much larger than in the particles of Figure 3C, which were prepared under similar conditions but with unplasticized seed particles. The glass transition temperature of a mixture of equal volumes of PS and cyclohexane was found to be below 0 °C, as determined by DSC. The glass transition temperature of the PS seed particles used in experiment F was far below the polymerization temperature.

Equilibrium Morphology by Postpolymerization Swelling. The morphology of particles from experiments A and C shown in Figure 6 was obtained from latexes subjected to a postpolymerization treatment with methylene chloride. The particles seem to have the same morphology irrespective of the morphology of the original particles.

Methylene chloride treatment involved adding about ten volumes of methylene chloride per volume of polymer particles. Separate experiments showed that one part of a 50/50 mixture of emulsion-polymerized PS (having sulfate end groups) and PMMA (polymerized by lauroyl peroxide) in 10 parts of methylene chloride formed a clear homogeneous solution in the temperature range of interest (20–60 °C). Thus, the morphology of the particles in Figure 6 should be due to phase separation from homogeneous polymer solution droplets, induced by solvent evaporation.

The results in Figure 6 show sections of different types. This might indicate the coexistence of particles with different morphologies. However, a more likely explanation is that the particles have the type of morphology shown in Figure 7, here referred to as a double-ball structure. Sectioning of such particles clearly may produce sections of the three different kinds found in Figure 6. In view of the fact that the particles were formed by phase separation from homogeneous mixtures of the two polymers, it is likely that the double-ball structure represents a thermodynamically stable or metastable morphology of PS/PMMA composite particles.

Latex samples from experiments A and C have also been subjected to heat treatment. In this case the latexes were heated in steel tubes for 6 h at 140 °C. Transmission electron microscopy of sectioned particles showed that no changes in morphology were produced by this treatment. A temperature increase to ca. 40 °C above the glass transition temperature thus does not seem to be sufficient to induce domain transport and coalescence.

Model Interfacial Free Energy Calculations. The observed morphology changes induced by the treatment with methylene chloride was analyzed by simple model interfacial free energy calculations. Such calculations have been previously shown to be useful in understanding the morphology of two-phase particles containing an oil phase and a polymer phase.[20]

The present model calculations assume a core–shell particle, consisting of a shell of polymer 1 and a core of polymer 2 in an aqueous phase, 3. The particle is assumed to undergo an inversion (cf. Figure 8) in which the core is successively squeezed out from the composite particle, forming first a double-ball structure and then two separate particles. The process proceeds until the former core polymer ends up as the shell of an inverted core–shell particle. Figure 8A shows the variation in the interfacial areas accompanying this inversion process. The parameter used to describe the structure is H/D, where H is the height of the cap of the partly engulfed polymer phase that protrudes out into the water phase and D is the diameter of the former core. Figure 8A was calculated by assuming (a) that there are equal volumes of polymers 1 and 2 and (b) that, at each instant, the individual interfaces had constant curvatures. The interfacial areas in Figure 8A are normalized by putting the surface area of the original core as unity.

The total interfacial free energy is defined as

$$\Delta G = \sum \gamma_{ij} \Delta A_{ij}$$

where γ_{ij} is the interfacial tension at the interface between phases i and j and A_{ij} is the corresponding interfacial area. Calculations of the total free energy for the process depicted in Figure 8A are shown in Figure 8B for four sets (1–4) of interfacial tension data. The numerical data in Figure 8B refer to an original core–shell particle having a core diameter of 720 nm. For curve 1, the interfacial energy is largest for the original core–shell particle and smallest for the inverted core–shell structure. In this case, there is a local minimum corresponding to a double-ball structure in which almost all of polymer 2 faces the water. Curve 2 has a similar shape, but the local minimum for the double-ball particle occurs at a lower value of H/D (about $H/D = 0.6$). Curve 3, which represents a case where γ_{12} and γ_{23} have equal values, possesses shallow minima for double-ball structures on each side of $H/D = 1$. Curve 4, which represents a physically highly improbable situation, has a minimum corresponding to two separate particles. These simple calculations indicate that double-

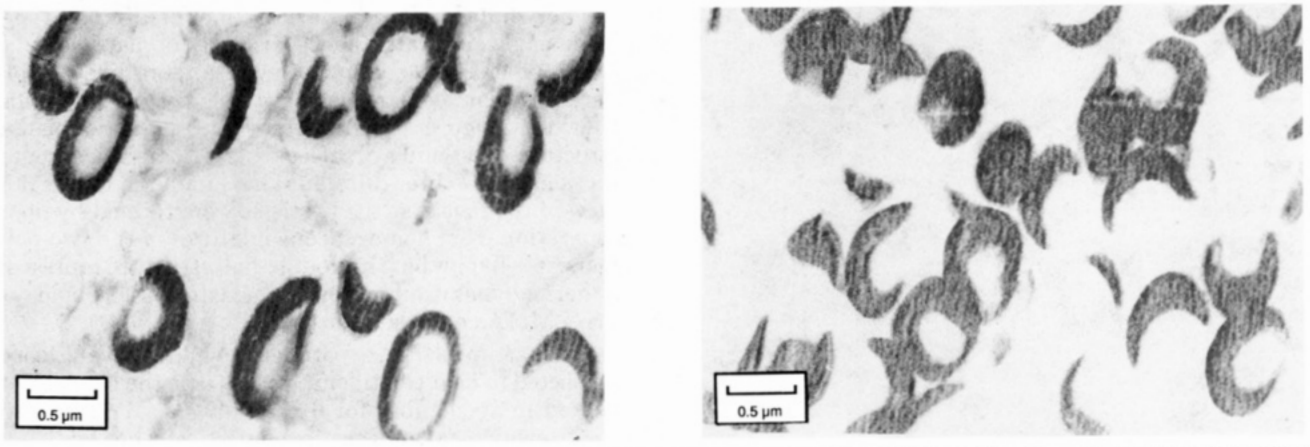

Figure 6. TEM micrographs showing the internal structure of the composite particles from experiment A (left) and experiment C (right) after treatment with solvent (methylene chloride). The morphology of the same particles before treatment with solvent is shown in Figure 4.

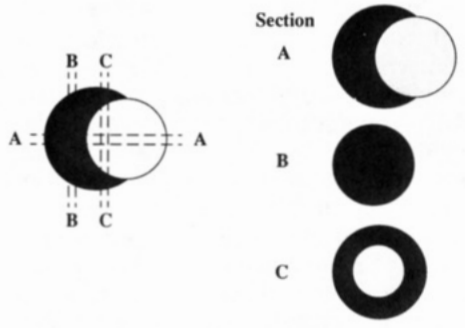

Figure 7. Schematic representation of the proposed double-ball morphology indicating three different types of sections (A–C) containing PS.

ball structures may represent thermodynamically stable (curve 3) or metastable (curves 1 and 2) situations. According to the literature, the interfacial tension data applicable to our present system is $\gamma_{PS/water}$ = 32.7 mN/m, $\gamma_{PMMA/water}$ = 26.0 mN/m,[21] and $\gamma_{PS/PMMA}$ = 3.2 mN/m.[22] Thus, the composite particles discussed in this work should be well represented by curve 2 of Figure 8B. This curve indicates that the double-ball morphology observed for the composite particles formed by postpolymerization treatment with methylene chloride would represent a thermodynamically metastable situation. However, it should be borne in mind that the real situation might involve complications not accounted for in the model calculations. Thus, the fact that polymers having mobile surface active groups (sulfate end groups on PS and lauroyl end groups on PMMA) may expose surfaces of different compositions toward different environments was not taken into account. Such an effect would shift the present system toward a behavior similar to that seen in curve 3 of Figure 8B. This would suggest that the observed structures might in fact represent true equilibrium morphologies.

Concluding Remarks

The present work has shown that the morphology of PS/PMMA particles prepared by seed emulsion polymerization is strongly affected by the process conditions used in the final polymerization step. Composite particles with small domain sizes were obtained by polymerizing under starvation conditions. Batch monomer addition gave particles with large domains. A reduction of particle viscosity or the rate of initiation leads to structures with increased domain sizes. The morphology can be brought

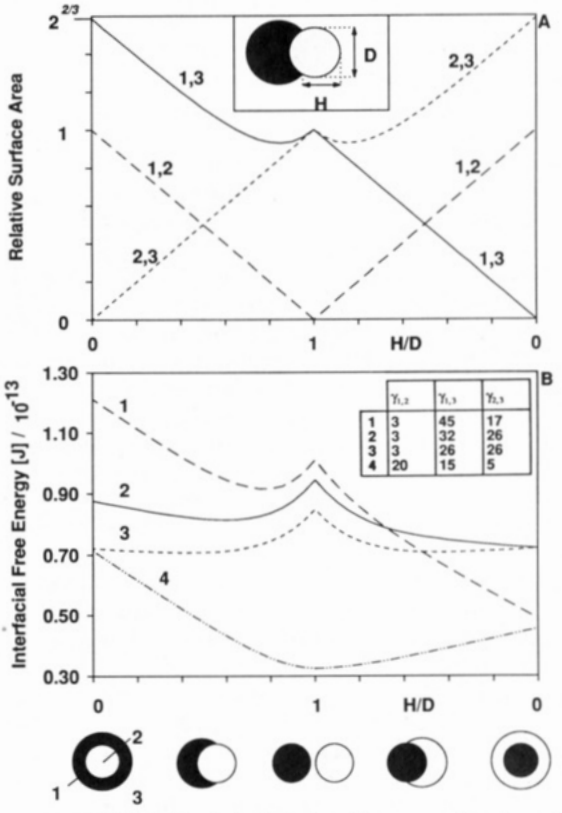

Figure 8. (A) Relative interfacial surface areas for two-phase particles in water. The interfacial surface areas were normalized by setting the surface area of the original core as 1. (B) Interfacial free energy for two-phase particles in water. The curves refer to the four sets of interfacial tension data given in the diagram.

toward an equilibrium situation by a postpolymerization treatment with solvents. The morphology produced by such a treatment is in good agreement with results from model calculation of the interfacial free energy of composite polymer particles.

The detailed processes occurring when a second monomer is polymerized in a polymer seed particle are rather complicated as are the processes that lead to morphological changes during storage. The morphological changes observed in this work can be qualitatively explained. A fuller understanding requires a more detailed knowledge of the importance of several factors, such as the transport rates of primary radicals and oligomers, phase separation as a function of molecular weight and monomer

concentration, and the distribution of the monomer between the polymer phases.

The fact that the PS/PMMA particles prepared under starvation conditions from large, "initiator-loaded" PS seed particles showed no evidence of a core–shell differentiation (Figure 3B–D) proves that the monomer concentration gradient in the particles was too small to exert an effect on particle morphology. This principle can be extended to include most situations of practical interest, since these normally involve smaller particles and in most cases polymerization temperatures above rather than below the glass transition temperature of the polymer. Hence, the successful preparation of core–shell particles must utilize a mechanism for reducing the rate of radical transport within the particles. This principle will be demonstrated and discussed in a forthcoming paper.

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Registry No. PMMA, 9011-14-7; PS, 9003-53-6; $MeCl_2$, 75-09-2; lauryl peroxide, 2895-03-6.