

Morphology of Poly(isoprene-co-styrene-co-methacrylic acid) Latex Prepared by Two-Stage Seeded Emulsion Polymerization

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ABSTRACT: Heterogeneous latexes were prepared by a two-stage seeded emulsion polymerization process at 80°C using potassium persulfate as the initiator and sodium dodecyl sulfate as the emulsifier. Poly(styrene-co-methacrylic acid) latexes containing varying amounts of methacrylic acid (MAA) were used as seeds. The second-stage polymer was poly(isoprene-co-styrene-co-methacrylic acid). By using different methods for the addition of the MAA and by varying the amount of MAA, the hydrophilicity of the polymer phases could be controlled. The morphologies and size distributions of the latex particles were examined by transmission electron microscopy. The latexes were in all cases unimodal, and had narrow particle size distributions. The particles displayed different morphologies depending on the polymerization conditions and monomer composition. The hydrophilic properties of the two phases in combination with the internal particle viscosity and crosslinking of the second phase during polymerization were found to be the major factors influencing the particle morphology. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1543–1555, 1997

Key words: heterogeneous latexes; two-stage seeded emulsion polymerization; poly(isoprene-co-styrene-co-methacrylic acid); hydrophilicity; particle viscosity; crosslinking

INTRODUCTION

Large amounts of carboxylated styrene(S)–butadiene latex are used in the paper industry as binders in paper coatings. Although the binder is used in small amounts in the final coating, the film-forming ability as well as the physical and mechanical properties of the binder are of great importance to the performance of the coating. Desired binder properties are, for example, low film-forming temperatures and high modulus and stiffness at ambient temperatures. Such a combination of properties is difficult to obtain with conventional polymer latexes, e.g., S–butadiene copolymers. However, by using heterogeneous la-

texes as binders the desired properties of the paper coating would be attainable. In order to gain more knowledge about such binder systems we have initiated a study of paper coatings based on heterogeneous latex binders, with special emphasis on the relations between the properties of the coatings and the structure and morphology of the latex particles.

In the literature, numerous papers on heterogeneous latex particles prepared from different monomers have appeared. Many investigations have focused on the relations between polymerization conditions and latex morphology, as well as on other factors influencing the morphology development in heterogeneous latex particles.

The first report on a core–shell morphology was published in 1970 by Grancio and Williams,¹ who postulated that a monomer-rich shell surrounding a polymer core would be formed in a

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seeded S homopolymerization. By using a different monomer in the second stage than in the first stage in a seeded polymerization, a phase separation occurs and many different types of heterogeneous morphologies are formed.²⁻⁸

One factor influencing the particle morphology is the relative hydrophilicity of the different phases in the particle, which can be controlled by choosing monomers of different hydrophilicity.^{6,9-15} The polarity of the latex particle surface can also be influenced by the initiator end groups, which may affect the morphology of the heterogeneous latex particles, as reported by Cho and Lee.¹⁶ When hydrophilic monomers such as methacrylic or acrylic acid are used, as pointed out by these authors, the influence of terminal initiator end groups on the morphology can be neglected.

Another parameter of importance for the morphology development is the particle viscosity. Different factors influencing the internal particle viscosity have been studied, for example, polymerization temperatures, molecular weights, polymer phase ratios, and different polymerization techniques, such as starved and flooded polymerization.^{3,16-20} It was shown that the thermodynamically favored morphology was gained by a low internal particle viscosity.

A thermodynamic model²¹ describing the interfacial behavior of a three-phase liquid system was used to analyze²² the morphology of a system comprising a polymer encapsulating an oil droplet in the micrometer range. According to the model the thermodynamically favored morphology would be the one that corresponds to a minimum in the interfacial free energy of the system. The model has been further developed by several authors,^{18,23-26} and used to explain and predict the particle morphologies found in heterogeneous latexes, using both thermodynamic and kinetic considerations. Models describing conversion-dependent particle morphologies during a two-stage polymerization in two-^{27,28} and three-²⁹ component systems have also been proposed.

In the present article we report on the preparation of two-phase particles from isoprene (I) and S, and the relations between, on the one hand, the polymerization conditions and the monomer feed compositions, and on the other, the morphology of the final latex particles. The hydrophilicities of the two polymer phases were changed by adding varying amounts of methacrylic acid (MAA) as a comonomer in the two polymerization steps, and the effects of variations of the internal viscosity in the particles were studied by changing the phase

Table I Recipe for Seed Latex Preparation

Ingredients	Weight (g)
Water	1227
Styrene	325
Methacrylic acid	7.9
Na ₂ CO ₃	1.8
Na ₂ EDTA	0.6
SDS	2.4
Potassium persulfate	0.8
Σ	1566

ratios and using different monomer addition techniques, i.e., seeded batch and semicontinuous polymerizations. Osmium tetroxide (OsO₄) was used for staining of the latex particles and the particle morphologies were studied by transmission electron microscopy (TEM).

EXPERIMENTAL

Materials

S (Merck, pro analysi), I (Merck, pro analysi) and MAA (Merck, pro analysi) were purified by passing through a column filled with aluminium oxide (Merck, active base). The purified monomers were kept at 8°C before use. All other chemicals were of analytical grade and used as supplied. Distilled and deionized water was used.

Preparation of Seed Latexes

Seed latexes were prepared through batch copolymerization of S and varying amounts of MAA in a 2000-mL reactor using potassium persulfate as the initiator and sodium dodecyl sulfate as the emulsifier. A typical recipe is given in Table I.

The monomers and the other chemicals, except the initiator, were charged together with the water. The reactor was repeatedly degassed and purged with nitrogen before it was tempered at 80°C, and the initiator was added. The polymerization was performed at 80°C for 8 h. The temperature was then set at 50°C and the reactor content stirred gently overnight. The compositions of the seed latexes are given in Table II. Final conversions were determined gravimetrically. The seed latexes were used without further treatment in the second polymerization stage.

Table II Composition, Average Sizes, and T_g of Seed Particles Used

Seed	Composition (%)		Particle Size ^a (nm)	δ^b (MPa) ^{1/2}	T_g (°C) ^c
	Styrene	Methacrylic Acid			
A	98	2	76 (6)	19.1	105
B	80	20	55 (8)	19.7	^d
C	98	2	72 (4)	19.1	109
D	100	0	93 (14)	19.0	105

^a Diameters reported are number averages, D_n , obtained by TEM. Standard deviations shown in parentheses.

^b The solubility parameter, δ , of the seed polymer.³⁴

^c Obtained by DSC.

^d Wide glass transition interval.

Second-stage Polymerization

The second-stage polymerization was carried out in a 200-mL calorimetric reactor, which has been described in detail by Nilsson and colleagues.³⁰ The instantaneous heat of polymerization was measured and used for calculation of the polymerization rate and conversion. The monomers used were I, S, and MAA. The compositions, weight ratios, and polymerization techniques used are given in Table III.

The polymerization was performed either as a seeded batch process or as a seeded semicontinuous process with continuous addition of the second-stage monomers. The initiator concentration (given in Table III) varied within the range of $0.5\text{--}3 \times 10^{-3}$ mol/L, and was in most cases 1×10^{-3} mol/L. The initiator was charged together with the seed latex prior to the second-stage polymerization. No additional emulsifier was used.

In the batch experiments the reactor and the I monomer were repeatedly degassed and purged with nitrogen. The I was added to the reactor and after 1 h at room temperature with stirring, the polymerization was started by increasing the temperature to 80°C.

In the semicontinuous experiments the monomers and the reactor containing the seed and the initiator were repeatedly degassed and purged with nitrogen at room temperature, and the temperature was then raised to 80°C. I was charged into the reactor by isothermal distillation through a check valve. The driving force for the distillation was the consumption of monomer in the reactor. The design of the valve prevented leakage of initiator from the reactor into the I supply container. The check valve opened when the pressure difference between the supply container and the reactor exceeded $\frac{1}{3}$ psi, thus ensuring that the supply rate

always was rate-determining for the polymerization.

In the experiments where MAA was continuously added, a 20 wt % MAA aqueous solution, tempered at 80°C, was fed through a valve at the bottom of the reactor by means of a variable-speed motor-driven syringe.^{18,30} In some experiments all the MAA monomer was added at the end of the second-stage polymerization.

Differential Scanning Calorimetry (DSC)

Polymer films, prepared by applying latex onto clean glass plates and drying at room temperature, were analyzed with a Mettler DSC 30 instrument equipped with a low-temperature cell. The film samples were first heated to 130°C at 15°C/min. After 5 min at 130°C the samples were cooled to -150°C at a rate of 15°C/min, and finally reheated to 250°C at a rate of 10°C/min. The last run was used for detection of glass transition temperature (T_g).

Electron Microscopy

The morphologies of the latex samples were examined with a JEOL 100 U transmission electron microscope after staining of residual double bonds in the polyisoprene (PI) phase with OsO₄. Staining with OsO₄ is generally done in the vapor phase according to Kato,³¹ but in order to avoid distortion of the latex particles during drying, staining was done in the liquid phase.³² In the TEM micrographs the PI-containing phase appears as dark domains and the polystyrene (PS)-containing phase as bright domains. Calibration grids were used for determining the actual magnification. The average particle diameters were calculated

Table III Compositions and Properties of Heterogeneous Styrene–Isoprene Latexes

Latex	Seed	Phase Two Compositions								T_g (°C) ^f		
		Phase Ratio Step 2: Seed ^a	Method ^b	KPS ^c 10 ³ (mol/L)	Styrene (%)	Isoprene (%)	Methacrylic Acid (%)	Particle Size ^d (nm)	δ ^e (MPa) ^{1/2}	Dry Weight (%)	Soft Phase	Hard Phase
1	A	50 : 50	B A1 A2	1.0	0	92	8	96 (4)	15.5	31	−42	104
2	A	50 : 50	B A1 A2	1.0	29	67	4	99 (1)	16.3	32	−25	97
3	A	53 : 47	B A1 A2	1.0	40	56	4	101 (3)	16.7	33	−13	99
4	A	53 : 47	B A1 A2	1.0	58	37	4	94 (3)	17.4	34	26	99
5	A	53 : 47	B A1 A2	1.0	0	88	12	92 (4)	15.8	30	−39	104
6	A	72 : 28	B A1	1.0	0	100	0	109 (12)	15.1	44	−59	106
7	A	72 : 28	B A1 A2	0.5	0	96	4	112 (4)	15.3	27	−50	105
8	A	72 : 28	B A1 A2	0.5	0	92	8	119 (6)	15.8	26	−47	102
12	B	33 : 67	B A1	1.0	0	100	0	59 (5)	15.1	12		
14	D	52 : 48	B	1.0	0	100	0	108 (2)	15.1	26	−66	104
15	D	81 : 19	B	1.0	0	100	0	163 (2)	15.1	25	−59	106
16	D	52 : 48	B A2	1.5	0	90	10	120 (5)	15.6	27	−45	104
17	D	81 : 19	B A2	1.0	0	90	10	152 (2)	15.6	15	−30	102
18	D	55 : 45	SB	1.0	0	100	0	125 (5)	15.1	20	−59	101
23	C	57 : 43	SB A1 A2*	1.0	0	92	8	98 (5)	15.5	17	−58	105
24	D	55 : 45	SB A2*	1.0	0	91	9	126 (> 1)	15.6	18	−54	99
25	A	50 : 50	B A1	1.0	0	100	0	95 (2)	15.1	31	−56	103
26	A	50 : 50	B A1 A2	3.0	0	96	4	91 (5)	15.3	30	−51	103
27	C	46 : 54	SB A1	1.0	0	100	0	94 (4)	15.1	15	−60	103

^a Phase ratios are based on weight.

^b Polymerization method denotation: B, batch polymerization; SB, semibatch polymerization; A1, acid charged in seed; A2, acid batch charged in Step 2; A2*, acid continuously added in Step 2.

^c Initiator concentration is calculated as the sum of seed residual initiator and additional initiator in Stage 2.

^d The diameters reported are number averages, \bar{D}_n , obtained by TEM measurements using OsO₄-staining technique.³² Standard deviations appear in parentheses.

^e The calculated solubility parameter, δ , of the initial mixture of monomers.³⁴

^f Obtained by DSC.

from measurements on micrographs of OsO_4 -stained latex particles.³²

RESULTS AND DISCUSSION

Heterogeneous S-I latex particles were obtained by a two-stage emulsion polymerization, using PS seed particles prepared by batch copolymerization of S and various amounts of MAA. Seed particle size distributions were calculated from TEM micrographs and were found to be narrow and unimodal. The number average seed particle diameters, \bar{D}_n , are given in Table II. It can be noted that the average particle size decreased with increasing amounts of MAA in the monomer feed. This phenomenon, which has also been reported by Nishida,³³ may be explained by the formation of a large number of initial particles stabilized by carboxylic acid groups in the early stages of the polymerization.

The second-stage polymerization was performed either as a seeded batch or as a semicontinuous seeded process, as described in the Experimental section. Details are given in Table III. The final conversions were, with few exceptions, more than 90%. In latex nos. 5, 14, and 17 some coagulum was formed during the polymerizations, which in turn caused the particle sizes to be smaller than expected. The heterogeneous latex samples had unimodal particle-size distributions, which all were very narrow, except for latex no. 6. The standard deviations of the particle sizes, given in Table III, were similar to or smaller than the standard deviations of the corresponding seeds. This showed that no new particle formation had occurred and that the incorporation of monomers was done by competitive growth in the second polymerization step. The thermal properties of dried films of the latexes were studied by DSC. The results presented in Table III clearly show that the polymer particles have two different glass transitions, which indicates that two separate polymer phases are present. The glass transition observed at about 100°C can be ascribed to the PS seed phase. The second T_g , which varied from -66°C to 25°C depending on the polymer composition, can be attributed to the second-stage polymer.

The morphologies of the two-phase latex particles were studied by means of TEM after osmium staining of the I-containing phase.³² The morphologies clearly depended on the mode of addition of the second-stage monomers, as well as on the

relative hydrophilicities of the two polymer phases and on the weight ratios between the seed and the second-stage monomer. The significance of these parameters is discussed below.

Seeded Batch Polymerization

Because of a low T_g the I-containing second-stage polymer should have a high segmental mobility at the polymerization temperature. Consequently, the relative hydrophilicities of the two polymer phases should be key parameters for determining the particle morphologies, especially in a seeded batch polymerization. The hydrophilicities of the two polymer phases were controlled by adding different amounts of MAA as a comonomer in the polymerizations. In Table III the average solubility parameters, δ , of the initial mixtures of the monomers are shown. The solubility parameters were calculated from volume fractions using data from *Polymer Handbook*.³⁴ The hydrogen-bonding contribution from the carboxylic groups in MAA is not considered in the calculations, although there is a considerable hydrogen-bonding character in MAA as compared to I. However, the solubility parameters provide a rough estimate of the compatibility of the polymer phases, and also of the polymer phase in which the monomers tend to accumulate during the second step of polymerization. Solubility can be expected if $(\delta_1 - \delta_2)$ is less than about 4 MPa^{1/2}, provided there are no strong polar or hydrogen-bonding interactions either in the polymer or the monomer mixture, which of course makes the estimation of δ less practical when MAA is used.

Three sets of batch experiments were run using different seeds and different stage-2 monomer combinations, as seen in Table III. The weight ratio of stage 2 monomer/seed was kept at two levels in each set.

PS Seed

In the first set of experiments a homo-PS latex (Latex D, Table II) was used as the seed. I was copolymerized with varying amounts of MAA in the second stage (Table III, experiments no. 14-17). These polymerizations gave a large variety of particle morphologies depending on the amount of MAA used and the weight ratio between the seed and the stage-2 polymer.

The particle morphologies obtained are de-

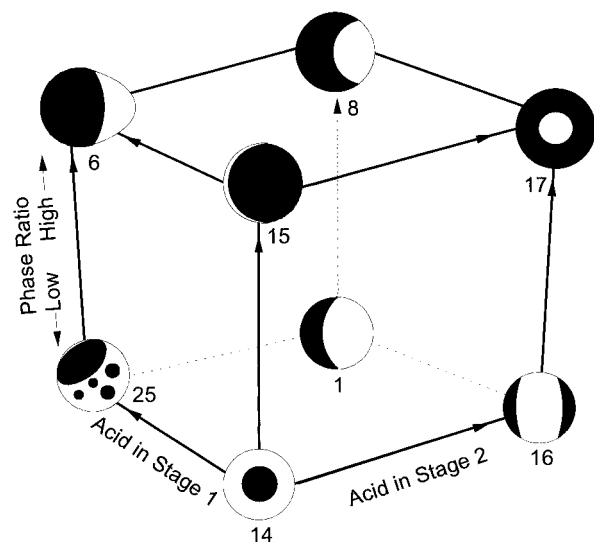


Figure 1 Schematically drawn particle morphologies representing latexes obtained from seeded batch polymerizations. Latex no. 14, containing no MAA in either stage, is placed in the origin. The x -direction represents the latexes containing MAA in the seed, and the y -direction latexes containing MAA in the second phase. The z -direction represents the weight ratio between the second phase and the seed. The numbers refer to the latex samples in Table III.

scribed by Figure 1. Each latex is represented in a three-dimensional coordinate system by a schematic drawing of the particle morphology. Adjacent to each drawing, the latex reference number from Table III is given. Latex no. 14, which contained no MAA in any of the polymer phases, is placed in the origin of the coordinate system. The y -direction represents the latexes containing MAA in the seed, and the x -direction latexes containing MAA in the second phase. The z -direction represents the weight ratio between the second phase and the seed.

In the preparation of latex no. 14, I was used in the second stage at a weight ratio to the seed phase of 52 : 48. The resulting latex particles exhibited an inverted core-shell morphology, as shown in Figures 1 and 2(a). The PS seed phase, being the most hydrophilic, was exposed to the aqueous environment. On increasing the weight ratio to 81 : 19 (latex no. 15), particles consisting of a very thin hemisphere of PS engulfing the PI phase were obtained, as schematically shown in Figure 1.

When 10 wt % MAA was copolymerized with I in order to increase the hydrophilicity of the second-stage polymer, the particle morphology changed drastically from an inverted core-shell

type to a sandwich, as shown for latex no. 16 in Figure 2(b) and schematically in Figure 1. The micrograph shows that the poly(isoprene-co-MAA) phase is located outside the original seed particles. The morphology inversion can be explained by changes in the interfacial energies of the different phases present, i.e., the aqueous phase and the two polymer phases, due to the introduction of carboxylic groups in the second-stage copolymer. By increasing the phase ratio from 52 : 48 to 81 : 19 (latex no. 17), the morphology inversion was even more pronounced. The resulting particles can be described as a mixture of sandwich, hemisphere, and core-shell structures, as shown in Figures 1 and 2(c). Although the hemisphere morphology represents a lower interfacial energy,^{18,27} sandwich and core-shell structures may be preserved due to crosslinking of the PI phase.

PS/MAA Seed

In the second set of experiments a series of latexes was prepared from seed A, which contained 2 wt % MAA (Table III, experiments no. 1, 5–8, 25, 26). In the second stage, a feed consisting of I and an increasing amount of MAA as a comonomer (0, 4, 8, and 12 wt %) was added. The rate of the second-stage polymerization was measured using a calorimetric reactor. In Figure 3, the rate of polymerization for latex no. 25, expressed as the heat generated per unit of time, is plotted as a function of time. Pure I was used as the monomer. It is evident from the figure that the polymerization was very rapid, showing an instantaneous peak in the polymerization rate. No constant rate period was noted, which indicated that all monomer charged in the second stage was swelled into the seed latex particles, or that any monomer droplets present at the start of the polymerization were consumed immediately. Experiments with swelling of PS latex by I³⁵ have shown that there probably will be a free monomer phase present at the start of the second polymerization step, at a second-stage monomer/seed weight ratio of 50 : 50. The peak in the polymerization rate curve for latex no. 25 appears at 24% conversion. This value is in accordance with the results from the swelling experiments, which showed that the free monomer phase should definitely be consumed before 35% conversion of the second polymerization step.

In the preparation of latex no. 25 no MAA was used as a comonomer in stage 2, i.e., the second-stage polymer should be less hydrophilic than the

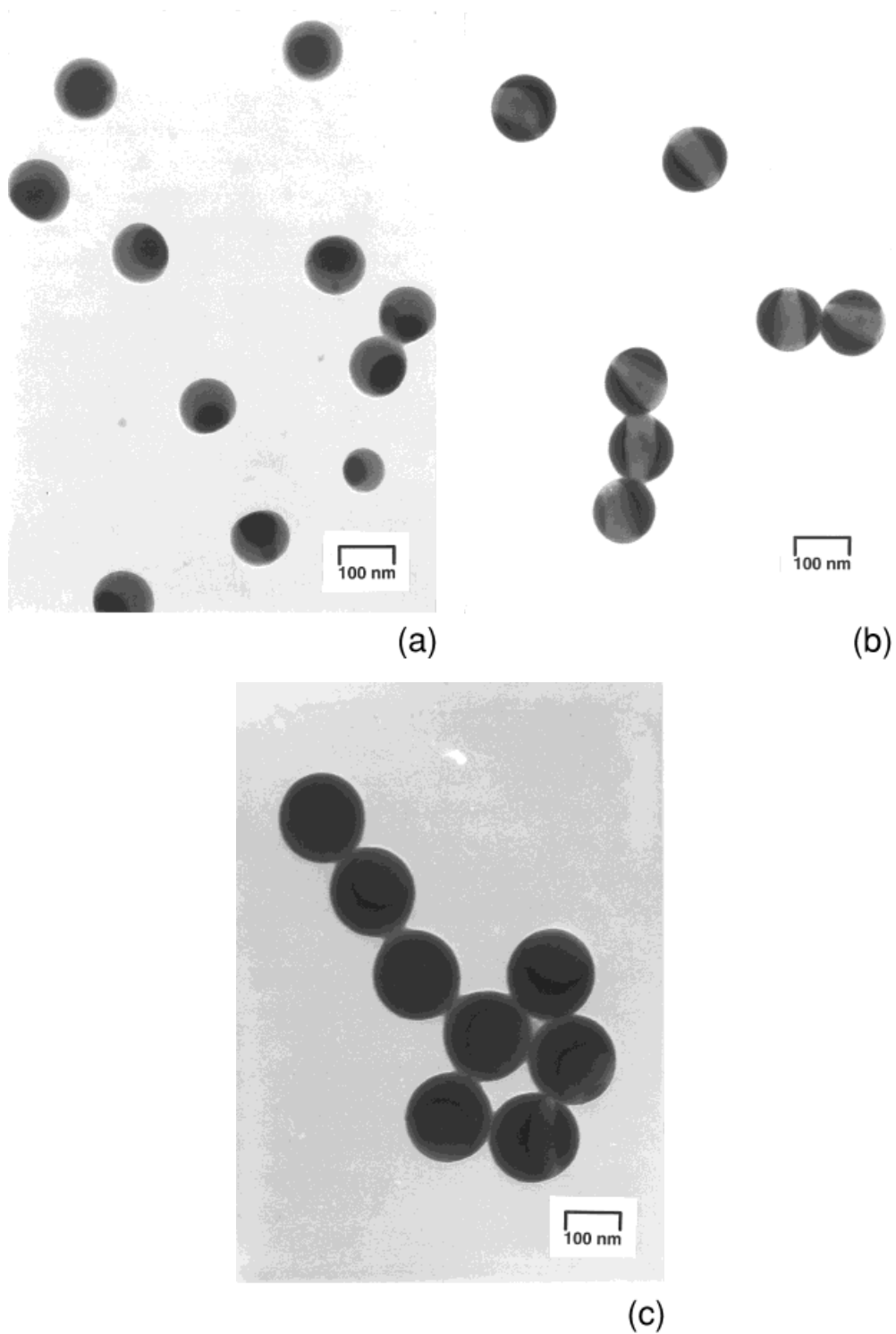


Figure 2 TEM micrographs showing the morphologies obtained from PS-seeded batch polymerizations (seed D). MAA content in the second-stage polymer and phase ratios are given in parentheses. (A) latex no. 14 (0 wt %, 52 : 48); (B) latex no. 16 (10 wt %, 52 : 48); (C) latex no. 17 (10 wt %, 81 : 19).

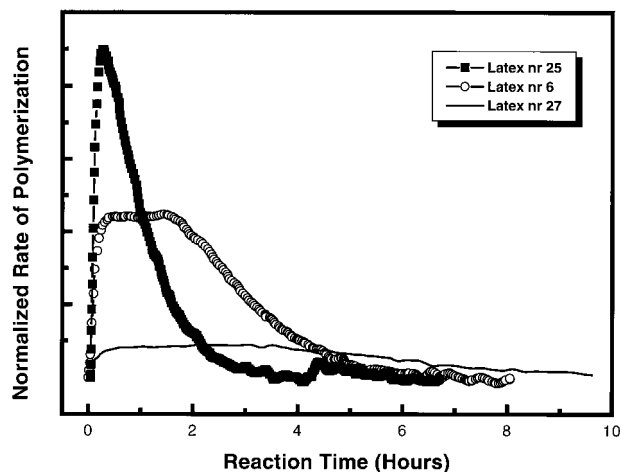


Figure 3 Normalized polymerization rate curves for latex nos. 25, 6, and 27.

seed. The latex particles had a morphology which can be described as an occluded simplified hemisphere.²⁸ The PI phase was divided into a large hemisphere partly engulfed by the PS phase, and several small occlusions completely surrounded by the PS phase [Fig. 4(a), Fig. 1]. With no MAA present in the second polymerization step the I monomer as well as the hydrophobic I-derived radicals should favor the hydrophobic interior of the seed particles, and the polymerization locus should be inside the particles. If monomer and polymer solubility parameters are considered (Table III), the I monomer would be expected primarily to swell the PI domains after the phase separation, and polymerize inside the PI phase. The small PI occlusions seen in the micrograph were probably locked into the PS matrix due to a high internal viscosity because of decreasing I concentration in combination with crosslinking of the PI domains because of chain transfer to polymer.

When the relative amount of the PI phase was increased from 50 to 70%, the small occlusions seen in latex 25 disappeared and a hemisphere-type morphology (eyeball) was obtained. This is illustrated for latex no. 6 in Figures 1 and 4(b). The rate curve for the second-stage polymerization is shown in Figure 3. In contrast to the corresponding curve for latex no. 25, a period of constant polymerization rate was observed, which indicates that the system was saturated with the stage-2 monomer and a free-monomer phase was present during most of the second-stage polymerization. Swelling of PS latex by I³⁵ showed that

at a second-stage monomer/seed ratio of 72 : 28 wt %, a free-monomer phase could be present at up to 75% conversion. Even though this value seems high compared with the 62% conversion recorded at the end of the constant rate period in the polymerization of latex no. 8 (Fig. 3), it strongly supports the idea that a free-monomer phase is present in the second-stage polymerization of latex no. 8. During this period the monomer-swelled particles should be in equilibrium with free monomer, and the internal particle viscosity should be lower than in the corresponding situation in the preparation of latex no. 25. The lower viscosity would allow the second-stage polymer to diffuse inside the particles to reach the thermodynamically more-favored hemisphere morphology.

An increase of the MAA content and thus the hydrophilicity of the second phase caused the morphology to change into a another hemisphere type (acorn), as schematically illustrated in Figure 5. The PI phase became increasingly exposed to the aqueous medium, engulfing the PS seed phase. At a level of 4 wt % MAA (latex no. 26, see Fig. 5) the small occlusions of PI had disappeared, and the PI phase formed a cap on the PS seed particle. An explanation for the disappearance of the occlusions at higher MAA contents may be that the oligo radicals produced in the aqueous phase would now be more hydrophilic and consequently likely to stay at the particle surface. The polymerization loci initially formed at the surface eventually coalesce and form the stage-2 polymer cap.^{36,37} The morphology is illustrated in Figure 4(c) by latex no. 5, which had the highest MAA content in the second phase (12 wt %). On increasing the weight ratio of stage-2 monomer/seed to approximately 70 : 30 at MAA levels of 4 and 8 wt %, respectively, in the second phase (Table III, no. 7 and 8), the resulting particle morphologies were similar to those obtained at lower weight ratios. The engulfing of the seed phase increases as the weight ratio of the more hydrophilic second phase/seed increases, and morphologies like that of latex no. 8 (see Fig. 1) will develop.

In the third set of experiments I was copolymerized with 4 wt % MAA and increasing amounts of S (0, 29, 40, and 58 wt %) in the second stage (Table III, no. 26, 2, 3, and 4). The initial solubility parameters of the monomer mixture approach the values of the seed polymer when the S content is increased. That implies an increased solubility of the second-stage polymer in the seed polymer, but the morphologies observed for these latexes

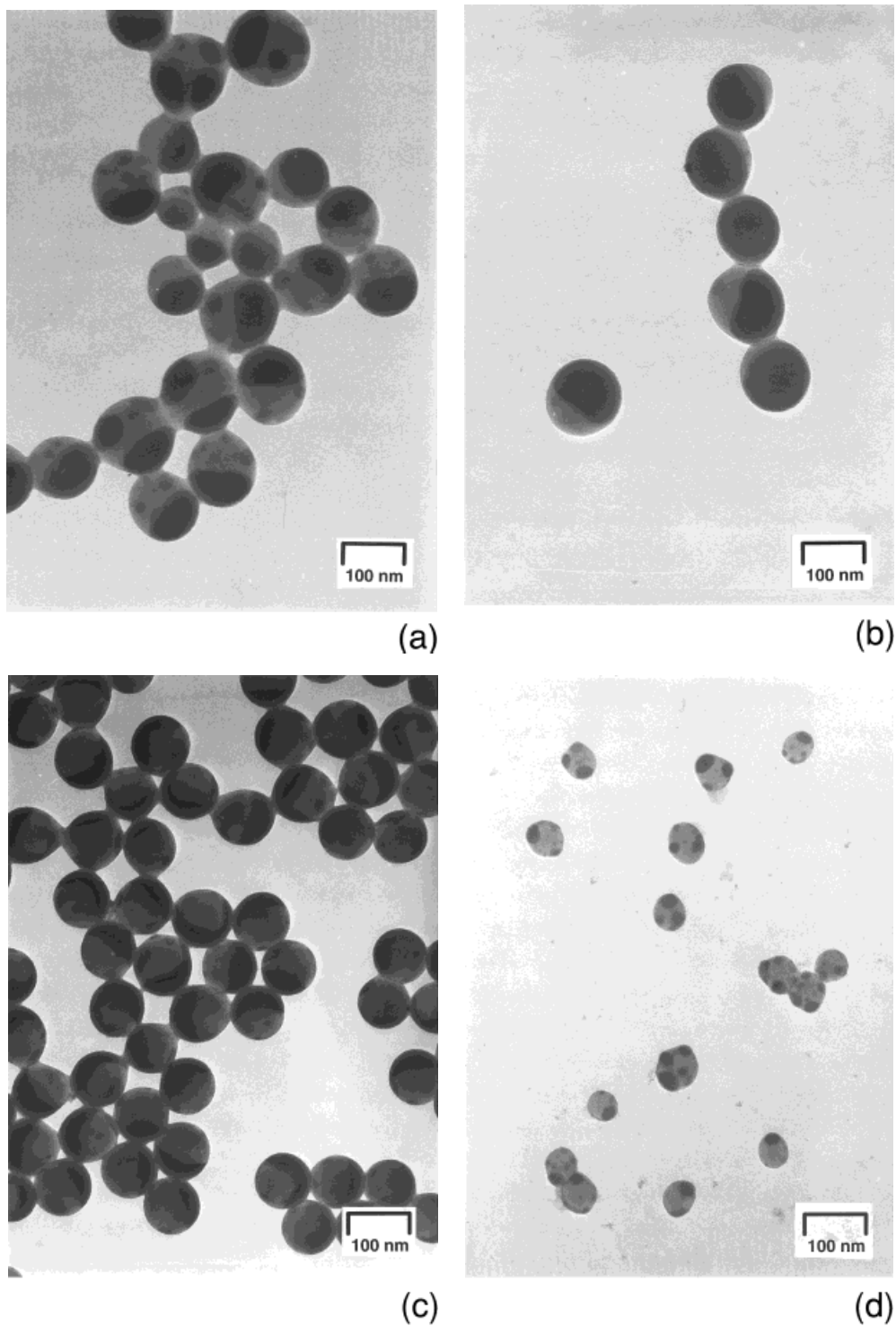


Figure 4 TEM micrographs showing the morphologies obtained from PS/MAA-seeded batch polymerizations (seed A, B). MAA content in the second-stage polymer and phase ratios are given in parentheses. (A) latex no. 25 (0 wt %, 50 : 50); (B) latex no. 6 (0 wt %, 72 : 28); (C) latex no. 5 (12 wt %, 53 : 47); (D) latex no. 12 (0 wt %, 33 : 67).

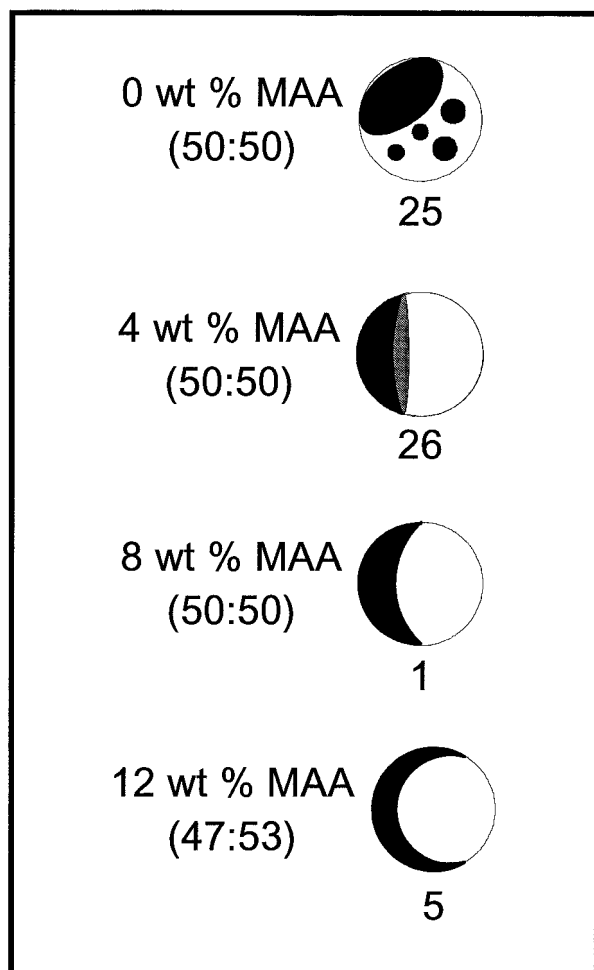


Figure 5 Schematically drawn particle morphologies representing the latexes obtained from seeded batch polymerizations (seed A) with increasing amounts of MAA copolymerized with I in stage 2.

were similar to that of latex no. 26 and consequently not visibly affected by the substitution of S for I in the second polymerization stage.

One experiment outside the scope of the investigation described above can be mentioned. Latex no. 12 was prepared from seed B, containing 20 wt % MAA, and I, at a weight ratio of stage-2 monomer/seed of 33 : 67. After the second polymerization step the particles were no longer spherical but showed a triangular-shaped cross-section with the occluded PI phase domains forming the corners of the triangle [Fig. 4(d)]. Because of the high acid content in the seed, phase separation should be highly favored. Furthermore, the low phase ratio will give a high internal

particle viscosity which will also contribute to an enhanced phase separation.²⁷

Semibatch Polymerization

PS Seed

In the preparation of latex no. 18, a seeded semibatch polymerization was carried out using a homo-PS seed (seed D, see Experimental section). The second phase was pure I at a weight ratio to the seed phase of 55 : 45. From Figure 6(a) it is evident that small PI domains are located inside the original PS seed particles. This is also schematically shown in Figure 7. It can be noted that in the corresponding batch experiment, i.e., no. 14, an inverted core-shell morphology with the PS seed phase in contact with the aqueous phase was formed. Seed D was also used for the preparation of latex no. 24, in which I-co-MAA was used in the second stage at a stage-2 monomer/seed weight ratio of 55 : 45. The particle morphology is shown in Figures 6(b) and 7. The second-stage polymer, now being hydrophilic relative to PS, was located at the particle surface. The PI domains were smaller than those seen in the corresponding batch polymerization (latex no. 16). The observed morphology difference between batch and semibatch polymerization should be a consequence of a restricted mobility of the PI phase due to the starved preparation conditions.

PS/MAA Seed

In experiment no. 27, I was polymerized onto a PS seed containing 2 wt % of MAA (seed C). The polymerization was performed similarly to the preparation of latex no. 18 described above, at a stage-2 monomer/seed ratio of 55/45. The polymerization rate given in Figure 3 was significantly lower than in the corresponding seeded batch polymerization (latex no. 25). This fact indicates that the polymerization was really performed under starved conditions. In the monomer feeding system used, charging of I is dependent on the reactor pressure, and because of the design of the feeding lines (see Experimental) the average reactor pressure will always be lower than the saturation pressure. Consequently, the internal particle viscosity should be significantly higher than in a corresponding batch polymerization. The PI formed initially will phase-separate from the PS seed as several small domains, and monomer as well as radicals diffusing from the aqueous phase will accumulate in the PI domains due to

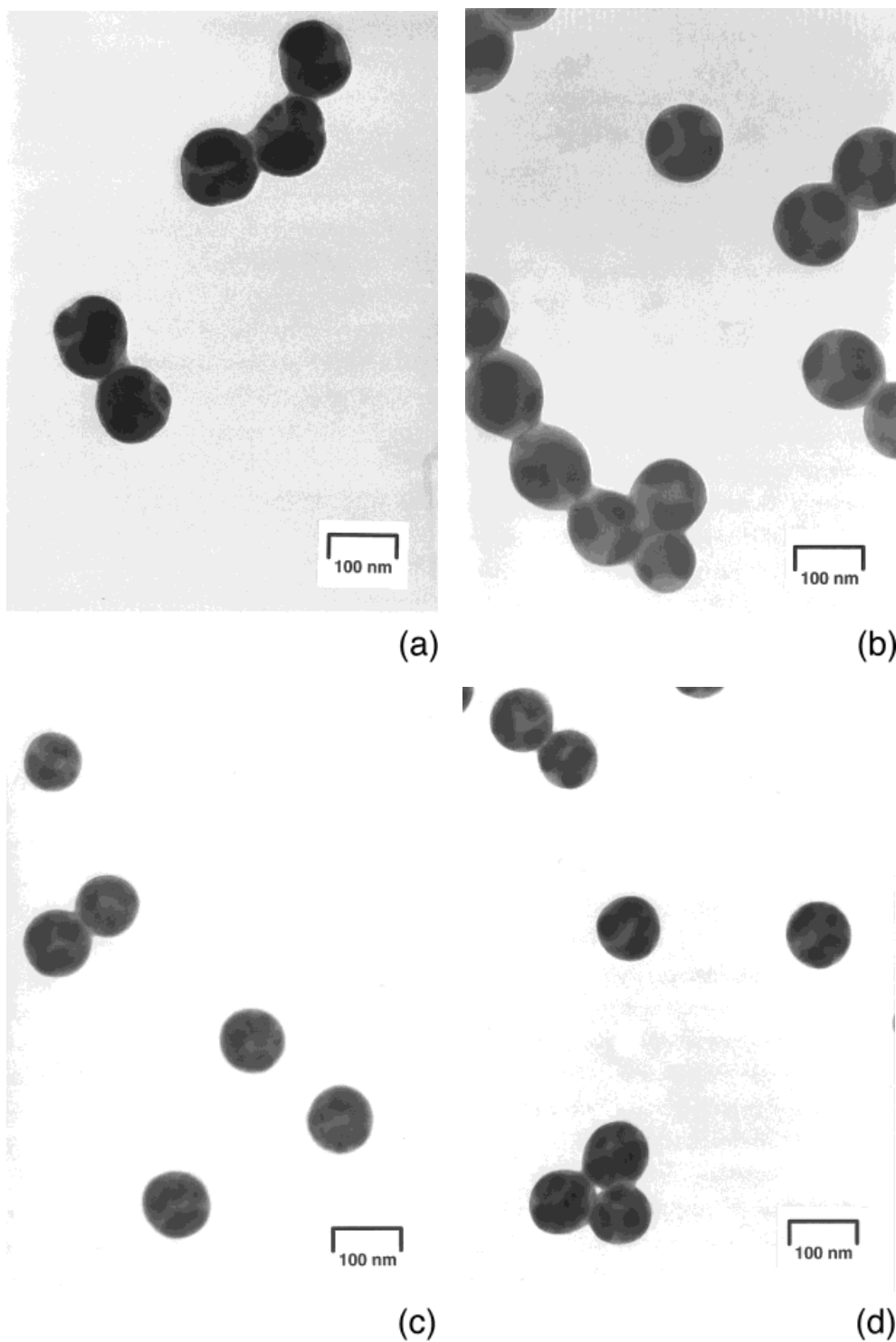


Figure 6 TEM micrographs showing the morphologies obtained from PS/MAA-seeded semibatch polymerizations (seed C, D). MAA content in the second-stage polymer and the phase ratios are given in parentheses. (A) latex no. 18 (0 wt %, 55 : 45); (B) latex no. 24 (9 wt %, 55 : 45); (C) latex no. 27 (0 wt %, 46 : 54); (D) latex no. 23 (8 wt %, 57 : 43).

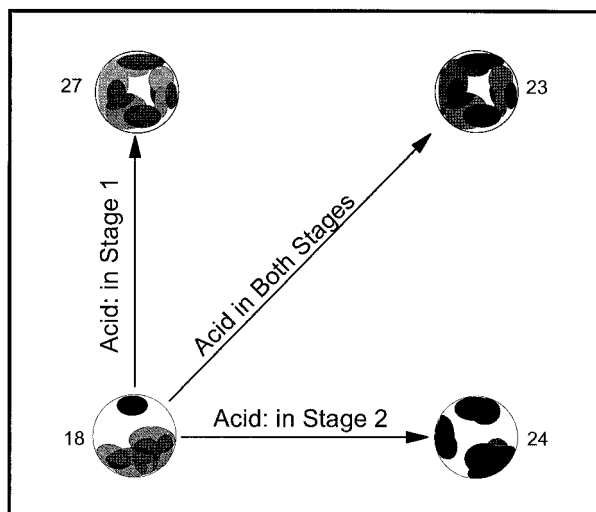


Figure 7 Schematically drawn particle morphologies representing the latexes obtained from seeded semi-batch polymerizations with varying MAA contents in the polymer phases.

solubility reasons. The initial morphology will be conserved because of the high viscosity and possible crosslinking of the PI phase, which inhibits coalescence of the domains. The resulting particle morphology is clearly shown in Figures 6(c) and 7. The small PI domains are evenly distributed but they seem to be slightly accumulated in the particle surface regions, although the more hydrophilic PS phase remains in contact with the aqueous phase.

The hydrophilicity of the PI phase was increased by addition of MAA in the second-stage polymerization (experiment no. 23). The I-MAA oligo radicals formed in the aqueous phase should be relatively hydrophilic and tend to grow larger in size than the corresponding homo-I oligo radicals before being captured by a particle. As a consequence, their ability to penetrate into the seed particles should be less than in the case of oligo-I radicals. The morphology obtained is illustrated in Figures 6(d) and 7. Small PI domains are collected in the surface regions of the particles. However, the morphological differences to latex no. 27, containing no MAA in the PI phase, were quite small.

CONCLUSIONS

In a seeded emulsion polymerization of S (seed) and I, many different particle morphologies may be obtained by varying the polymerization condi-

tions and the feed compositions in the two polymerization stages.

A low viscosity in the early stages of a seeded batch polymerization favors thermodynamic factors in the development of the particle morphologies. By increasing the phase ratio between the stage-2 monomer and the seed (from 50 : 50 to 80 : 20), i.e., decreasing the internal particle viscosity, no PI occlusions were observed in the PS phase in the final particles and all the PI was collected in one large domain with a smooth interfacial area. Changing the relative hydrophilicity of the two polymer phases by adding small amounts of MAA to the I monomer in the second-stage polymerization changed the latex particle morphology from an inverted core-shell structure (PI core/PS shell) to a sandwich or core-shell structure (PS core/hydrophilic PI shell). This morphology change is an indication of an initially sufficiently low viscosity, allowing the second-stage polymer to diffuse to form a more thermodynamically favored morphology. A shift in polymerization locus from the particle interior to the particle surface may also be anticipated because of the increased hydrophilicity of the propagating radicals.

In the later stages of a seeded batch polymerization and in a semicontinuous polymerization under starved conditions, the internal particle viscosity is high and kinetic factors will play a major role in the development of the latex particle morphology. The morphologies observed after semicontinuous addition of I in the second-stage polymerization showed several small domains of PI near or at the particle surfaces. Although a polymerization temperature of 80°C is sufficiently high for reducing the viscosity and allowing the second-stage polymer to flow, no formation of larger PI domains was observed. Crosslinking was probably the reason for the reduced molecular mobility in the PI phase, resulting in thermodynamically unfavorable particle morphologies.

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