Synthesis of Model Latices for the Study of Coalescence Mechanisms

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SYNOPSIS

This work describes the synthesis of model latices devoted to the study of the influence of particle–water and particle–air interfacial energies on coalescence mechanisms. Core–shell particles with the same diameter ($\simeq$ 2600 Å) and narrow size distributions were prepared. The core is a poly(styrene-co-butyl acrylate) (60/40 wt %) copolymer; it represents 90% of the volume of the particle. The shell is a poly(St–BuA–methacrylic acid) terpolymer with 10, 15, or 25 wt % MAA. The St–BuA weight ratio in the shell is also 60/40. The amount of MAA in the shell determines the particle–water or air interfacial energies. In order to limit the use of an emulsifier and to ensure a homogeneous particle surface layer, an inverted core–shell synthesis was performed. The hydrophilic shell was prepared first and used as a seed for the synthesis of the hydrophobic core. For all three core–shell latices, about 45% of the introduced MAA was found at the surface of the particles, which indicates that the core–shell inversion was successful. The synthesis of the latices with 10 or 15 wt % MAA was relatively easy, whereas the particle size was difficult to control in the 25 wt % MAA latex synthesis.

INTRODUCTION

The understanding of coalescence mechanisms of polymer colloids is of major practical importance and fundamental interest. Several authors have tackled the problem in the past.[1-5] Recently, Dobler et al.[6] reviewed the literature on this subject. It appeared that more work was needed in order to reach a satisfactory level of knowledge of the phenomenon. This study describes the synthesis of model latices devoted to further studies of coalescence mechanisms.

The following are the most important parameters that influence the coalescence mechanisms: the particle diameter, the water–air, particle–water, and particle–air interfacial energies, the colloidal stability at small interparticular distances, and the viscoelastic properties of the polymers. The temperature and relative humidity conditions are also of great importance in the phenomenon. We were mainly interested in the study of the influence of interfacial energies on the coalescence process. It is necessary to vary one parameter without affecting the others. Thus, we had to synthesize monodispersed latices with the same particle diameter, the same viscoelastic properties but different particle–water and air interfacial energies. The monomers we used were styrene (St), butyl acrylate (BuA) and methacrylic acid (MAA). Different particle–water and air interfacial energies were achieved by varying the amount of MAA in the outermost surface layer of the particles. The higher the MAA content at the surface, the lower the interfacial energy with water. Homogeneous particles with different amounts of MAA would have different viscoelastic properties especially in water, which acts as a plasticizer in MAA-containing polymers. It was then necessary to produce core–shell particles. In our case the core represents 90% of the total volume of the particle and is composed of a styrene–butyl acrylate copolymer (60/40 wt %). Being by far the major part of the particle, it determines its viscoelastic properties. The St–BuA ratio was chosen in such a way that the T_g of the copolymer was around 40°C.[7] This is convenient in the coalescence mechanism study.[8] The shell (10% volume fraction) is a meth-

acrylic acid–styrene–butyl acrylate terpolymer containing 10, 15, or 25 wt % of MAA. The St–BuA ratio in the shell is also 60/40. The interfacial energy depending on short distance forces is determined by a surface layer around 30 Å thick.[9] Our shell thickness had to be in this range, which means that the total particle diameter had to be at least 1700 Å. Of course, the shell has also to form a homogeneous surface layer. If the core emerged at some parts of the surface, the interfacial energy would be ill defined.

It appeared that an "inverted core–shell synthesis" had a better chance of producing such particles. In a direct core–shell synthesis the core is synthesized first and then the shell. This procedure has the following drawbacks. It is likely that the hydrophilic terpolymer (MAA–St–BuA) will form a new particle population by homogeneous nucleation giving a bipopulated latex.[10] These new particles can also flocculate on the hydrophobic St–BuA seed to give particles with heterogeneous surface structure. Furthermore, the St–BuA seed latex would require a certain amount of emulsifier to be stabilized. In an inverted core–shell synthesis, the hydrophilic shell is polymerized first; the hydrophobic monomers are then added, swelling these seed particles and polymerizing inside them, thus producing the core. The St–BuA chains should remain in the core because of their hydrophobicity. However, the possibility exists that some St–BuA chains come to the surface due to the polarity of the initiator residues at their ends.[11] This inverted core–shell synthesis has the other advantage of avoiding the use of an emulsifier to stabilize the latex, which is also important in a coalescence mechanism study.

We used this inverted core–shell procedure. The synthesis of the latices containing 10 and 15 wt % MAA in the shell was relatively easy, whereas the 25 wt % MAA latex was more difficult to perform. This will be discussed in the following text.

EXPERIMENTAL

Reagents (Merck, Darmstadt)

Distilled water was used throughout. Monomers—styrene, butyl acrylate, and methacrylic acid—were purified by vacuum distillation. Sodium dodecyl sulfate (SDS) (purity over 99%) was used without further purification. The initiator was either $(NH_4)_2S_2O_8$ (purity 99%) or the couple $(NH_4)_2$-S_2O_8–$Na_2S_2O_5$ (purity 98%). It was used directly from the bottle.

Reactor

The syntheses were performed in a double-wall Sovirel 1.5 L glass reactor. Reaction temperature was controlled through water circulation in the jacket and measured with a platinum thermistor. Nitrogen was passed over the reactants during all syntheses. The agitator was rotated at 250 rpm. Monomer mixtures and, if necessary, aqueous solutions of initiator, surfactant or sodium hydroxide were added continuously using Dosapro Milton-Roy pumps. The addition rate could be varied from 12 to 120 mL/h.

Latex Purification

Latices (solids content between 10 and 15%) were purified by serum replacement using a Millipore membrane.[12] The excess pressure in the cell was 0.2–0.5 bar. Latices were continuously stirred during all the purification process, which was carried out until the conductivity of the collected water was less than 3 μS/cm.

Latex Characterization

Particle Size Distribution

The mean particle diameter was determined in a salt solution (NaCl $0.01M$) by dynamic light scattering using an Autosizer C apparatus. Salt was added in order to reduce the thickness of the particle–water interphase (bounded water). The size distribution was checked by either scanning or transmission electron microscopy (TEM). When the pictures showed narrow size distributions, we used the mean particle diameter obtained by light scattering as it is quite accurate in this case.

Methacrylic Acid Distribution

There are four possible locations of MAA in the latex. It is very important to determine its distribution among them:

1. At the surface of the particles.
2. In a subsurface layer.
3. Buried inside the particles.
4. In the aqueous phase.

Before all MAA distribution studies, the latices were purified. The MAA percentage in the aqueous phase was determined by conductometric titration of the collected serum.

The total percentage in the particles was measured by titration in an organic medium. Five mil-

liliters of purified latex (solids content: 10%) were dried in a vacuum oven at 60°C for 24 h. The dry polymer was dissolved in 100 mL DMF. The MAA content was titrated with sodium methanolate in the presence of phenolphthalein. The difference between the MAA in the particles and the total amount introduced corresponds to the acid in the liquid phase. The previous result (conductometric titration of the serum) could be cross-checked.

The distribution of MAA in the particles was determined by recording the variation with time of the conductivity of a purified latex (0.5% solid content) in the presence of excess sodium hydroxide.[13] Once the conductivity stabilized (after 24 h), a back titration with HCl gave the total number of neutralized carboxylic acid functions. The percentage of neutralized MAA at time t, $\tau(t)$, is given by

$$\tau(t) = \frac{[\rho(t_i) - \rho(t)] \, N(\infty)}{[\rho(t_i) - \rho(\infty)] \, N_I}$$

where $\rho(t_i)$ is the conductivity at $t = 0$. The dilution effect of the added latex is taken into account:

$$\rho(t_i) = \frac{V_i}{V_i + V_l} \rho_i$$

ρ_i = conductivity of the NaOH solution
V_i = volume of NaOH solution
V_l = volume of added latex
$\rho(t)$ = conductivity at time t
$\rho(\infty)$ = constant conductivity reached after 24 h
$N(\infty)$ = total number of neutralized carboxylic acid functions (HCl back titration)
N_I = total number of moles of MAA in the latex (quantity introduced)

The initial conductivity drop (between $t = 0$ and $t = 30$ s) was extremely sharp. At the end of this 30-s period (which was reproducible), the conductivity drop became less sharp. The initial drop was attributed to the neutralization of the MAA at the surface of the particles. The drop between $t = 30$ s and $t = 24$ h corresponded to the MAA in the subsurface layer. By difference, the buried MAA, out of contact with NaOH, was determined.

All experiments were performed under nitrogen flow to avoid carbonazation.

Synthesis: General Conditions

As mentioned in the introduction, an inverted core-shell polymerization process was used: the hydro-philic terpolymer, poly(St–BuA–MAA), was synthesized first and used as a seed for the polymerization of the St–BuA monomer mixture, which forms the core. In order to obtain final core–shell particles with the same diameters (but different surface composition), all seed latices must also have the same diameters. In order to improve the control of seed particle diameter, the seed latex itself was synthesized in a seeded process. Therefore, the actual polymerization was a three-step procedure: preseed, seed, and final core–shell latex syntheses. The preseed had the same composition as the corresponding seed. The preseed latices are noted: P10, P15, and P25 when they contain 10, 15, and 25 wt % MAA, respectively. The seed and final core–shell latices are noted: S10, S15, S25 and CS10, CS15, CS25, respectively.

The preseed latices were prepared via a batch process at 50°C. The solids content was around 7%. A small amount of sodium dodecyl sulfate (0.2 g/ L) shortened the particle nucleation step and allowed a narrower size distribution to be reached. This was shown by Sakota and Okaya[14] in the case of the copolymerization of acrylic acid and styrene.

The seed latices were synthesized by semicontinuous addition of styrene, butyl acrylate, and methacrylic acid to the corresponding preseed. The reaction temperature was 50°C and the solids content 20%. The monomer addition rate was less than the polymerization rate. These starved conditions avoided a copolymer composition drift and ensured a good copolymerization of MAA with St and BuA. The semicontinuous process maintained the amount of MAA in the water phase to a low level, avoiding synthesis of large quantities of water-soluble polymer and nucleation of new particles.

The initiator, in the preseed and seed synthesis, was the $(NH_4)_2S_2O_8/NaHSO_3$ redox system in order to ensure a high enough rate of radical production at 50°C. $NaHSO_3$ was formed by dissolution of $Na_2S_2O_5$ in water. The initiator decomposition reaction can be written as follows:

$$S_2O_8^{2-} + HSO_3^- \rightarrow SO_4^{-\cdot} + HSO_3^{\cdot} + SO_4^{2-}$$
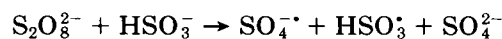
This initiator gives rise to a pH decrease due to the formation of strong acids: H_2SO_4 and H_2SO_3 by reaction of $SO_4^{-\cdot}$ and $HSO_3^{\cdot}$ with water molecules. The pH of the medium had to be maintained at values between 4 and 5. The growing particles were stabilized by the MAA introduced. At a pH lower than 4, carboxylic acid functions are only weakly dissociated. The charge density on the particles is too low to stabilize efficiently the latex. On the other

hand, at a pH higher than 6, MAA tends to homopolymerize in the aqueous phase as shown by Guillaume et al.[15] These hydrosoluble polymers may cause some particle flocculation. Therefore, the pH had to be kept in the right range (4 to 5). This was achieved by addition of proper amounts of sodium hydroxide during polymerization.

The final core–shell latices were produced either by a batch polymerization or by a semicontinuous process. In the first case some coagulum was formed, but the rate of polymerization could be determined. The solid content was 30% and the reaction temperature 70°C. This temperature was higher than the T_g of the copolymers. It is important to give them enough molecular mobility to allow the core–shell inversion. The initiator was $(NH_4)_2S_2O_8$. Its concentration was low to avoid the presence at the surface of $p(St/BuA)$ chain ends. Sodium hydroxide was also used in small quantities to ensure the electrostatic stabilization of the latex.

After the end of the semicontinuous addition of monomers, for the core–shell and for the seed synthesis, polymerization was completed during 3 h at the same temperature.

Control of the Number of Particles

To obtain a narrow particle size distribution, nucleation of new particles or limited flocculation in step 2 (seed latex synthesis) and 3 (core–shell latex synthesis) should be strictly avoided. The mean diameter of the particles was measured at each step. The ratio R_i is defined as

$$R_i = \frac{D_i / D_{i-1}}{(m_i / m_{i-1})^{1/3}}$$

with D_i = mean diameter after step i
   D_{i-1} = mean diameter after step $i - 1$
   m_i = mass of the particles after step i
   m_{i-1} = mass of the particles after step $i- 1$,
       $m_i - m_{i-1}$ = mass of added monomers
       in step i

As the diameter of a particle is proportional to the cubic root of its mass, $(m_i / m_{i-1})^{1/3}$ represents the ratio of the diameter of the particles obtained after step i-1 and i if the number of particles remains constant. And R_i should always be equal to 1. If $R_i > 1$, the particle number has decreased and limited flocculation has occurred. If $R_i < 1$, new stable particles have been nucleated in step i.

By dynamic light scattering, the hydrodynamic diameter is measured, i.e., the real diameter plus twice the thickness (α) of the bounded water layer; α is independent of the real diameter. If these hydrodynamic diameters are used, R_i becomes

$$R_i = \frac{(D_i + 2\alpha)/(D_{i-1} + 2\alpha)}{(m_i / m_{i-1})^{1/3}}$$

R_i is then slightly less than 1 even if the particle number remains constant. For example, if $\alpha = 30$ Å, for $i = 3$ (final latex synthesis), $D_3 = 2700$ Å, $D_2 = 1250$ Å and $(m_i / m_{i-1}) = 10$, R_i becomes 0.975.

RESULTS

Synthesis

Preseed

Table I shows the conditions of the preseed latex batch synthesis, the pH at the end of the polymerization, and the mean particle diameters as measured by light scattering. The reaction temperature was 50°C during 6 h and 70°C during 1.5 h. The three mean diameters are relatively close.

S10 and S15 Seed Latices

The S10 and S15 latices were prepared following the recipe in Table II. Monomers and an aqueous solution containing sodium hydroxide and more initiator were added during a period of 6 h at 50°C. At the end of the monomer addition, conversion reached 87%, and polymerization was continued for 3 h at 50°C. The $p(St–BuA–MAA)$ copolymer synthesized in this step represents about 85% of the

Table I   Batch Synthesis Conditions of the Preseed Latices Containing 10, 15, or 25 wt % MAA[a]

Preseed Latex	P10	P15	P25
MAA (%)	10	15	25
St (g)	37.7	35.6	31.2
BuA (g)	25.1	23.7	20.8
MAA (g)	7.0	10.5	17.3
SDS (g)	0.2	0.2	0.2
$Na_2S_2O_5$ (g)	0.19	0.19	0.19
H_2O (g)	929.5	929.5	930.3
$(NH_4)_2S_2O_8$ (g)[b]	0.30	0.30	0.30
pH	3.4	3.3	3.4
D_1 diameter	660Å	630Å	560Å

[a] Reactor content degased under nitrogen flow for 30 min and then heated to 50°C.

[b] Added once reaction temperature was reached.

Table II   Synthesis Conditions of the Seed Latices Containing 10 or 15 wt % MAA[a]

Seed Latex	S10	S15
Initial charge		
Preseed particles (g)	30.91	24.7
$Na_2S_2O_5$ (g)	0.42	0.41
NaOH (mol)	$1.53.10^{-3}$	$1.53.10^{-3}$
H_2O (g)	694.3	683.5
$(NH_4)_2S_2O_8$ (g)[b]	0.077	0.075
Semicontinuous addition (6 h)		
St (g)	94.27	88.24
BuA (g)	62.84	58.83
MAA (g)	17.46	25.95
Aqueous solution S–C addition (6 h)		
$(NH_4)_2S_2O_8$ (g)	0.642	0.658
NaOH (mol)	$13.2.10^{-3}$	$13.5.10^{-3}$
H_2O (g)	113.6	117.0
Conversion at end of add.	0.88	0.87
pH	4.9	4.7

[a] Initial charge degased under nitrogen flow for 30 min and heated to 50°C.
[b] Added once reaction temperature was reached.

Table IV   Recipe for the CS10 and CS15 Latex Synthesis

Core–Shell Latex	CS10	CS15
Initial charge[a]		
Seed particles (g)	30.58	29.74
St (g)	17.76	18.03
BuA (g)	11.84	12.02
H_2O (g)	677.2	684.8
$(NH_4)_2S_2O_8$ (g)[b]	0.40	0.40
Semicontinuous add. (3 h)		
St (g)	147.3	142.78
BuA (g)	98.21	95.19
Aqueous solution S–C addit. (1 h)		
SDS (g)	0.072	0.082
NaOH (mol)	$6.6.10^{-4}$	$6.7.10^{-4}$
H_2O (g)	16.6	16.9
Conversion at end of add.	0.35	0.34
pH	3.00	3.25

[a] Initial charge degased under nitrogen flow during 1 h and heated to 70°C.
[b] Added at 50°C.

total weight of the seed particles, the remaining 15% corresponding to the preseed particles. Table III presents the mean diameters of the S10 and S15 latices together with the R_2 parameters. The values of R_2 close to 1 indicate that the number of particles has been maintained. These latices were suitable for the following step.

CS10 and CS15 Final Core–Shell Latices

The final latices were synthesized by semicontinuous addition of styrene and butyl acrylate to the seed (Table IV). The addition rate was 3 g/h g of seed polymer. The rate was chosen (with the help of a batch experiment) in such a way that the particles were swollen by the monomers to ensure a low viscosity (this facilitated the core–shell inversion) but did not allow the particules to be too swollen, thereby avoiding coagulation. If the particles are too soft,

they tend to partially coagulate under the influence of agitation. One-tenth of the total monomer charge was added to the seed one hour before the start of the polymerization in order to lower the viscosity inside the particles before the reaction was initiated. Conversion at the end of monomer addition was 35%. Particle swelling remained important, and core–shell inversion was facilitated. Table V shows the mean particle diameters and the R_3 parameters. The particle number was maintained in the final step. Scanning electron microscopy pictures indicate that the particle size distribution is narrow (see the case of CS10 in Fig. 1). When purified or more concentrated, these latices are clearly irridescent, further evidence of a narrow size distribution. The latices are perfectly stable thanks to the presence of MAA at the surface. At a pH close to 3, stabilization is probably of steric nature due to hydrated p(St–BuA–MAA) chains extending in water.

Table III   Mean Diameters and R_2 Parameters for Seed Latices Containing 10 or 15 wt % MAA

MAA (%)	10	15
D_2	1210 Å	1220 Å
R_2	0.98	0.97

Table V   Mean Diameters and R_3 Parameters for CS10 and CS15 Latices

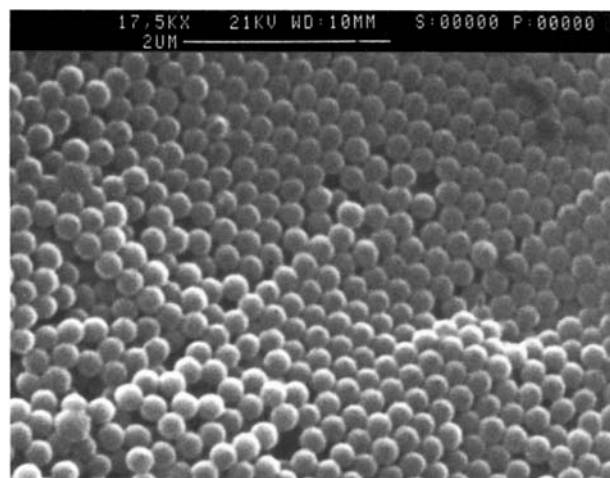| Latex	CS10	CS15
D_3 (Å)	2500	2550
R_3	0.96	0.97

Figure 1 Scanning electron microscopy picture of the CS10 latex. The bar represents 2 μm.

S25 Seed Latex

The S25 latex was less easy to synthesize than the S10 and S15 latices because of limited flocculation. Table VI, synthesis A, shows that if the conditions of S10 and S15 synthesis are used for S25, limited flocculation occurs as indicated by the R_2 values superior to 1 (R_2 = 1.55). If 1 g of SDS is added with the monomers (Table VI, B), flocculation is less important (R_2 = 1.13) but still occurs. Figure 2 shows the variation of R_2 as a function of reaction time under various conditions. The increase of R_2 starts during the monomer addition period and continues until the end of the reaction. If the initiation rate is decreased by decreasing the initiator concentra-

tion (Table VI, synthesis C, D, and E) by a factor of 2.2, flocculation tends to disappear. It can be completely eliminated by addition of increasing amounts of SDS. With no SDS (Table VI, E), R_2 = 1.11; with 0.46 g of SDS (Table VI, D), R_2 = 1.03; and with 0.98 g of SDS (Table VI, C), R_2 = 0.97. These last conditions were used to produce the seed latex for the synthesis of the CS25 latex, the final core–shell latex containing 25 wt % MAA in the shell.

CS25 Core–Shell Latex

The same procedure as for CS10 and CS15 latices was used (see Table IV): 30 g S25 seed, 30 g St–BuA (60/40), and 0.38 g $(NH_4)_2S_2O_8$ were put in the reactor. Then 240 g St–BuA (60/40) were added semicontinuously in 3 h and $1.75.10^{-3}$ mol NaOH in water in 1 h (for 1000 g latex with 30% solids content). The final diameter was 1700 Å instead of the expected value of 2500 Å; the R_3 was 0.66: new particles were nucleated (Table VII, C1).

It appeared that the conditions of both seed and core–shell latex synthesis had an influence on this nucleation phenomenon. Table VII shows different seed synthesis conditions, the corresponding D_2 and R_2 values, and the D_3 and R_3 values of the core–shell latices prepared with these seed latices. If the NaHSO$_3$ amount is divided by a factor of 5 (synthesis C2), D_3 becomes 2000 Å; nucleation is only partially reduced. But, if the addition time of the monomers in the seed synthesis is reduced from 6 to 4.5 h, the D_3 values become correct. This parameter seems to determine the nucleation of new par-

Table VI Various Synthesis Conditions of S25 Latices and Corresponding Mean Diameters and R_2 Parameters

Synthesis	A	B	C	D	E
Na$_2$S$_2$O$_5$ (a)[a]	0.42	0.42	0.19	0.19	0.20
$(NH_4)_2S_2O_8$ (a)[a]	0.064	0.064	0.030	0.030	0.030
NaOH (a)[a]	0.042	0.035	0.015	0.015	0.015
$(NH_4)_2S_2O_8$ (b)[a]	0.64	0.64	0.29	0.29	0.29
NaOH (b)[a]	0.42	0.55	0.55	0.57	0.57
SDS (b)[a]	0.00	0.99	0.98	0.46	0.00
pH[b]	4.33		4.42		4.43
Diameter	1820Å	1360Å	1180Å	1260Å	1350Å
R$_2$[c]	1.45	1.06	0.95	0.97	1.05
R$_2$[b]	1.55	1.13	0.97	1.03	1.11

[a] (a) and (b) = gram. T = 50°C; mass of latex = 1000 g; solids content = 20%. Initial charge: preseed particles (20.4 g) + reactants (a). Semicontinuous addition (6 h): reactants (b) in aqueous solution plus St, 81 g; BuA, 54 g; MAA, 45 g.
[b] Determined at end of synthesis.
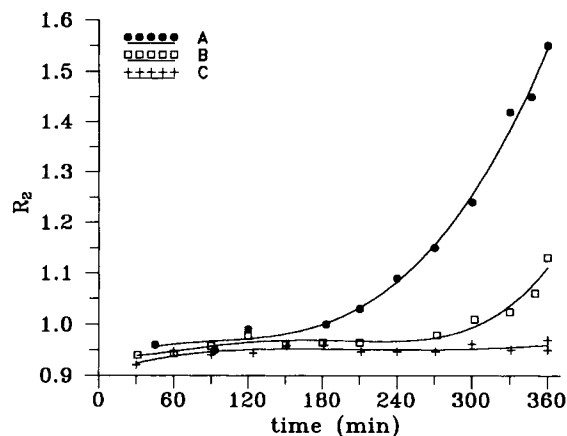[c] Determined at end of monomer addition.

Figure 2 Variation of R_2 as a function of reaction time (S25 synthesis) under various conditions (A, B, C) shown in Table VI.

ticles. Figure 3 shows the variation of $R_f(t)$ during the core–shell latex synthesis:

$$R_f(t) = D_{cs}(t)/D_s$$

where $D_{cs}(t)$ is the mean diameter of the core–shell latex at time t and D_s is the seed mean diameter. The R_f values are far from the expected ones for the C1, C2, and C3 synthesis but become correct for the C4 and C5 synthesis. On the other hand, if, using the seed C3, the St–BuA monomer mixture is added in 7.5 h instead of 3 h, $D_3 = 2310$ Å and $R_3 = 0.86$.

Again, the addition time plays an important role. In this last case the conversion after the end of the monomer addition is 92%; the swelling ratio of the particles is low.

Figure 4 shows the transmission electron microscopy pictures of the C1 and C4 seed latices. The particle size distribution is narrow; no small particles can be detected.

Table VIII recapitulates the conditions of the synthesis of the S25 and CS25 latices, which were finally used. An R_3 value close to 1 indicates that no new particles were nucleated. Figure 5 confirms that the particle size distribution of the CS25 latex is narrow.

MAA Distribution

The percentages of MAA in the various possible loci in the latices (serum, surface, subsurface, and inside particles) are indicated in Table IX for the final core–shell latices. The two methods of determining the MAA percentage in the aqueous phase give rather different results, especially at low MAA content. The direct conductometric titration of the serum probably overestimates the MAA concentration in water because, in this case, the experimental errors are important. For all three latices the percentage of MAA at the surface is similar and high: about 45%. This is good evidence of the success of the core–shell inversion procedure. Methacrylic acid,

Table VII Influence of the S25 Seed Synthesis Conditions on the Mean Diameters of the Final CS25 Core–Shell Latices

Synthesis	C1	C2	C3	C4	C5
Conditions of S25 seed synthesis					
$Na_2S_2O_5$ (a)[a]	0.19	0.042	0.20	0.20	0.20
$(NH_4)_2S_2O_8$ (b)[a]	0.23	0.23	0.23	0.15	0.15
SDS (b)[a]	0.99	0.69	0.69	0.69	0.00
t_A (c)[a]	6 h	6 h	8 h	4.5 h	4.5 h
R_2	0.98	0.98	1.04	0.95	1.02
Conversion (d)[a]	0.80	0.80	0.85	0.81	0.77
D_{seed}	1200 Å	1250 Å	1340 Å	1220 Å	1320 Å
After polymerization of the St–BuA mixture on the seed latices					
D_3	1700 Å	2000 Å	1850 Å	2430 Å	2700 Å
R_3	0.66	0.74	0.64	0.93	0.96

[a] (a) and (b) = gram. Seed latex synthesis: S–C addition: (b) added in aqueous solution, (c) t_A: monomer mixture addition duration, (d) conversion at end of monomer addition. Core–shell latex synthesis (for 1000 g; solids content 30%). Initial charge: 30 g seed latex; 30 g St–BuA (60/40); 0.38 g $(NH_4)_2S_2O_8$. S–C addition: 240 g St–BuA (60/40) (3 h); $1.75.10^{-3}$ mol NaOH in aqueous solution (1 h).
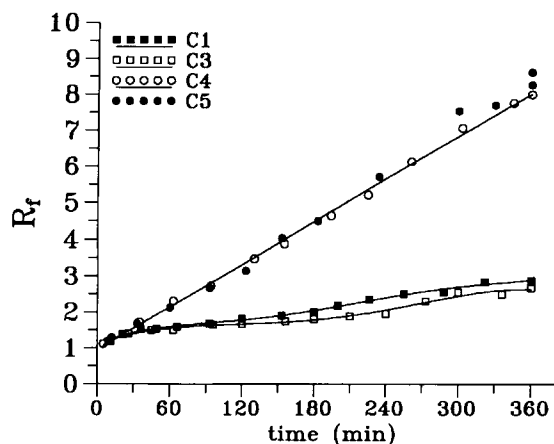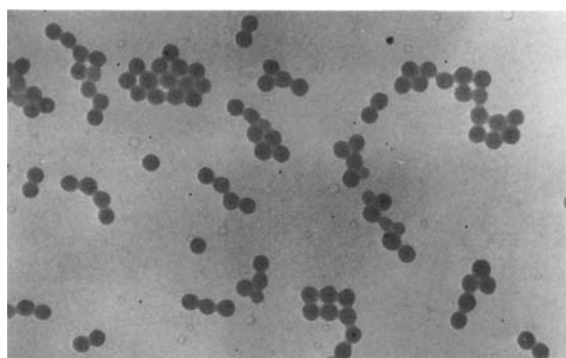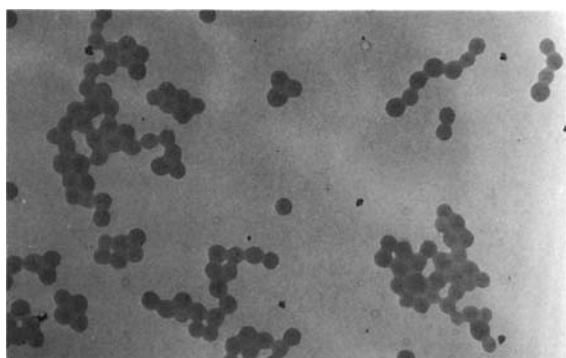
Figure 3 Variation of R_f as a function of time of CS25 latices. $R_f(t) = D_{cs}(t)/D_s$ where $D_{cs}(t)$ is the mean diameter at time t and D_s is the seed mean diameter. C1, C3, C4, and C5 refer to S25 synthesis conditions shown in Table VII.

C1

C4

Figure 4 Transmission electron microscopy pictures of the C1 and C4 S25 seed latices (see Table VII). Magnification: 33000.

Table VIII   Final Synthesis Conditions of the Seed and Core–shell Latices Containing 25 wt % MAA

Seed Latex	S25
Initial charge	
Preseed particles (g)	15.56
$Na_2S_2O_5$ (g)	0.208
H_2O (g)	685.6
$(NH_4)_2S_2O_8$ (g)	0.029
Semicontinuous addition (4.5 h)	
St (g)	88.58
BuA (g)	50.05
MAA (g)	49.21
Aqueous solution	
S–C addit. (4.5 h)	
$(NH_4)_2S_2O_8$ (g)	0.119
NaOH (mol)	$7.3.10^{-3}$
H_2O (g)	110.3
Conversion at end of add.	0.78
pH	4.9
D_2	1320 Å
R_2	1.02

Core–Shell Latex	CS25
Initial charge[a]	
Seed particles (g)	31.48
St (g)	17.88
BuA (g)	11.92
H_2O (g)	682.4
$(NH_4)_2S_2O_8$ (g)[b]	0.40
Semicontinuous add. (3 h)	
St (g)	142.9
BuA (g)	95.26
Aqueous solution	
Semicontinuous add. (1 h)	
SDS (g)	0.084
NaOH (mol)	$17.6.10^{-4}$
H_2O (g)	17.6
pH	3.90
D_3	2670 Å
R_3	0.96

[a] Initial charge degased under nitrogen flow during 60 min and heated to 70°C.
[b] Added at 50°C.

which is not at the surface, is almost inaccessible (neutralization between 30 s and 24 h is low, 8 or 20%) or totally out of reach (45 or 30% of the total amount of MAA, depending on the latex).

Some seed latices containing 25 wt % of MAA have also been studied by this technique. The MAA percentage in the serum, for S25 seed latices prepared in the C1, C3, and C4 conditions of Table VII are shown in Table X. Again, the two methods dis-
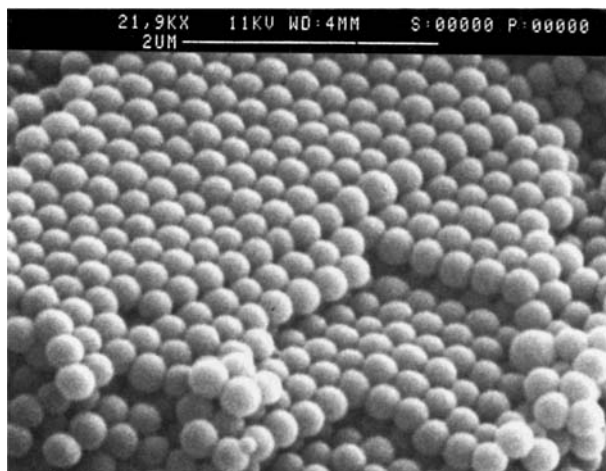
Figure 5 SEM picture of the CS25 core–shell latex. The bar represents 2 μm.

agree but, with both techniques, the MAA percentage in the serum is the same for all latices. Figure 6 presents the percentage of MAA neutralized as a function of time for the C3 and C4 S25 seed latices. The MAA at the surface is 35% in both latices; but, just below the surface, it is 13% for C3 and 19% for C4. The surface region is richer in MAA for C4; thus the core region is poorer.

DISCUSSION

The high amount of MAA at the surface of the particles (45%) and in the surface plus subsurface region (54 or 63%) for all final latices clearly indicates

Table IX   Methacrylic Acid Repartition in the Core–Shell Latices Determined by Sodium Hydroxide Titration

Core–Shell Latex	CS10	CS15	CS25
MAA in aqueous phase seed latex serum (%)		5	5
MAA in aqueous phase core–shell serum (%)	9.4	8.2	5.4
MAA in aqueous phase CS serum 100%—Y	2	5	6
MAA in particles Y (%)	98	95	94
MAA at surface of particles (%)	45	45	43
MAA subsurface (%) (neut. time 24 h)	53	53	64
MAA buried in particles (%)	45	42	30

Table X   Percentage of the Total Amount of Methacrylic Acid Introduced in the Latex that Can Be Found in the Serum of Various S25 Seed Latices[a]

Latex[b]	C1	C3	C4
τ_s		2.1%	1.8%
τ_p	7 ± 1%	6 ± 1%	6 ± 1%

[a] See Table VII for the meaning of C1, C3 and C4.
[b] τ_s, determination by direct titration of the serum and, τ_p, determination by difference between the total amount introduced and the total amount found in the particles.

that core–shell inversion effectively occurred. This process has already been mentioned several times in the literature. All authors emphasized that core–shell inversion is even more pronounced if mobility is increased in the particles and if the difference in hydrophilicity between shell and core is important.

For the polymerization of styrene on a poly-(methylmethacrylate) seed (Cho and Lee[11]), core–shell inversion was more pronounced with low molecular weight polymers. The synthesis of the hydrophobic polymer by a batch process[11,16] (where the monomers swell the particles, decreasing their viscosity) or in the presence of a solvent[11] also facilitates inversion. If the synthesis is performed at a temperature higher than the T_g of the polymer, mobility in the growing particles can be sufficient to allow inversion even in a semicontinuous process (where the particles are not swollen by monomers).[17]

The difference in hydrophilicity between the two polymers has to be high. If not, the initiator polar
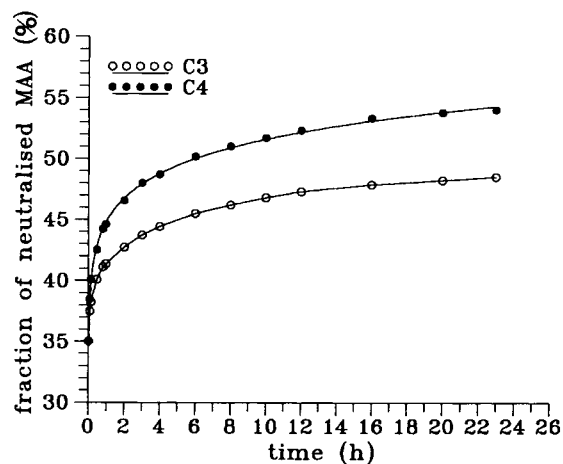

Figure 6   Percentage of MAA neutralized as a function of time for the C3 and C4 S25 seed latices (see Table VII for the meaning of C3 and C4).

groups at the end of the hydrophobic polymer hinder the core–shell inversion. In the case of the polystyrene–poly methylmethacrylate system[11] inversion only occurs if small amounts of persulfate initiator are used in the synthesis of polystyrene. For large amounts the latex has a direct core–shell structure. With medium amounts intermediate morphologies are observed.[11] According to Cho and Lee,[11] if very hydrophilic monomers like methacrylic or acrylic acid are used, the influence of sulfate end groups can be neglected.

Okubo et al.[16] have done some research that is similar to ours. They applied the principle of core–shell inversion to the synthesis of carboxylic latices without emulsifier. The seed was a St–BuA–MAA (82.5/11/6.5) terpolymer. The hydrophobic polymer was a St–BuA (88/12) copolymer. The hydrophobic–hydrophilic polymer weight ratio was 1/1. The poly(St/BuA) was synthesized at pH 9.5 to increase the hydrophilicity of the seed. If the styrene–butyl acrylate mixture is synthesized by a batch process, the MAA percentage at the surface of the particles is 56; it drops to 37 if a semicontinuous process is used. The batch polymerization of styrene–butyl acrylate at pH 2.2 leads to a concentration of MAA at the surface of 15%.

Inverted core–shell synthesis can give a better phase separation between the core and the shell than a direct core–shell synthesis as shown by Muroi et al.[17] on a poly(ethylacrylate-co-methacrylic acid) (90/10) and poly(methylacrylate-co-methacrylic acid) (90/10) system.

Core–shell inversion is not limited to seeded polymerizations. It can also occur in batch processes when, due to very different solubility and copolymerization parameters, the copolymer formed at the beginning of the synthesis is more hydrophilic than the one formed at the end.[18,19]

A problem of limited flocculation appeared in the synthesis of the S25 latex (Table VI). This phenomenon could be due either to poor stabilization of the particles or to the synthesis of a certain amount of hydrosoluble polymer, which gives rise to flocculation by "particle bridging." The first hypothesis seems unlikely because if SDS is added, flocculation still occurs, and S10 and S15 latices, synthesized under the same conditions, are stable. Stabilization, being due to the presence of MAA at the surface of the particles, should be even more efficient with an increased concentration of MAA. The "bridging hypothesis" is more likely. We showed (Table VI) that the problem could be solved by decreasing the concentration of initiator together with an increase of the amount of SDS.

The influence of the initiator concentration can be explained in the following way. In this polymerization, macroradicals ($RM_i^\bullet$) are formed in the aqueous phase. They can react with another radical in the aqueous phase:

$$RM_i^\bullet + RM_j^\bullet \rightarrow RM_{i+j}R$$

$$\text{or} \quad RM_i^\bullet + R^\bullet \rightarrow RM_iR$$
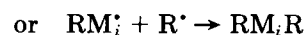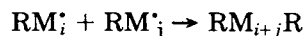
forming water-soluble polymer or be captured by a particle. Polymerization in the aqueous phase involves mainly MAA. The macroradicals can remain soluble until they reach rather high degrees of polymerization when the MAA content is high.[20] The rate of capture of macroradicals by particles is proportional to their concentration in the aqueous phase:

$$R_c = k_1[RM_i^\bullet]$$

The rate of termination of macroradicals in the aqueous phase is proportional to the square of their concentration:

$$R_T = k_2[RM_i^\bullet][R + RM_i^\bullet]$$

An increase in the initiation rate corresponds to an increase in the radical concentration in water. Termination in water is then favored in comparison with capture by particles: A greater amount of water-soluble polymer is formed.

The SDS probably adsorbs on the water-soluble macroradicals to form a kind of charged complex similar to a polyelectrolyte.[21] Electrostatic repulsions between these complexes inhibit termination reactions in the aqueous phase. The capture of the SDS–macroradical complexes by particles is less hindered by electrostatic repulsions due to the important volume difference between a particle and a complex.[22] The SDS effect on the flocculation phenomenon is about as important as the effect of the initiator concentration as shown in Table VI. When synthesis A is compared with synthesis B (same initiation rate but increase in SDS) or E (decreased initiation rate and no SDS), the decrease in R_2 is very similar. The two effects have to be combined in order to avoid flocculation (synthesis C).

Under certain conditions, nucleation of new particles occurred during the CS25 latex synthesis. We showed that the rate of monomer addition in the S25 seed latex synthesis determined this nucleation phenomenon: a slow addition (6–8 h) gave rise to

nucleation whereas a fast addition (4.5 h) avoided it. To a lesser extent, the rate of monomer addition during the CS25 synthesis also played a role in the other way: a 7.5-h addition time limited the nucleation observed with a 3-h addition time. The origin of this nucleation will be discussed in this section.

All the 25 wt % MAA latices were stable whatever new particles were nucleated or not. The interpretation of the results also explains this stability. The amount of SDS in the medium is far too low (0.11 g/L) to account for the stability of the latex and for the nucleation of new particles. On the other hand, a weak quantity of initiator was used in this step in order not to perturb the core–shell inversion. Thus, the initiator residues at the end of the St–BuA copolymers cannot stabilize new particles of hydrophobic polymer. Stabilization of new particles can only be due to a certain amount of hydrophilic p(St–BuA–MAA) terpolymer at their surface.

The new particles that appeared in the CS25 latex synthesis could result from the growth of very small particles already present in the seed. To check this point, TEM pictures of the seed latices were taken (Fig. 4), but no small particles could be detected.

Another possibility is that water-soluble polymer formed in the seed synthesis could stabilize new particles of p(St–BuA). But the MAA content of serums of various S25 seeds was measured (Table X), and no differences could be detected in latices giving rise to new particle nucleation or not.

The only difference we found between "nucleating" and "nonnucleating" latices is in the MAA repartition in the particles (Fig. 6). For C4 latices (nonnucleating) the inside of the particles is slightly poorer in MAA than for C3 (nucleating) (monomer addition time is 8 h for C3 and 4.5 h for C4, see Table VII). We propose the following interpretation of the nucleation phenomenon. The styrene–butyl acrylate monomer mixture polymerizes in domains inside the seed particles. In the nucleating latices this region is relatively rich in MAA, thus being incompatible with the p(St–BuA). Some p(St–BuA) domains can coalesce, forming particles with protuberances. Under the influence of agitation, these protuberances may break and produce small particles of p(St–BuA) surrounded by hydrophilic p(St–BuA–MAA) terpolymer, which stabilizes them. The breakage of these small particles is made easier by the softness of the monomer-swollen particles. In this case the swelling ratio is about 200%. If the hydrophobic monomers are added more slowly (7.5 h instead of 3 h), the swelling ratio is much less and breakage is limited. In the nonnucleating latices the core is poorer in MAA, the compatibility with p(St–

BuA) is better, the driving force for protuberance formation is smaller, and it does not occur.

Okubo et al.[23] polymerized a St–BuA mixture (88/12) on a p(St–BuA–MAA) seed (82.5/11/6.5). Particles with protuberances are formed at pH 9.5 for a batch addition of the hydrophobic monomers. A semicontinuous addition of the monomers limits the formation of protuberances. At pH 2.2, spherical particles are formed even in a batch process. According to Okubo et al.,[23] protuberances result from the incompatibility between the p(St–BuA) and the p(St–BuA–MAA) and from the low viscosity inside the particles. At pH 2.2, MAA is not dissociated, which limits the incompatibility between the two phases. Even at pH 9.5, no breakage is observed by Okubo et al. probably because the size increase from the seed particles to the core–shell ones is much less in their case (factor 2) than in ours (factor 10).

CONCLUSION

An inverted core–shell synthesis allowed us to synthesize latices with 10, 15, or 25 wt % MAA in the shell. These three latices all have the same particle diameters and narrow size distributions. They only contain very small amounts of emulsifier (SDS). The stability of the latices and the high percentage of MAA found at the surface of the particles (45%) indicate that the core–shell inversion procedure succeeded.

The synthesis of the latices with 10 and 15 wt % MAA in the shell was relatively easy, but it was more difficult with 25 wt % MAA. The synthesis of the S25 seed showed the importance of the initiation rate in the semicontinuous polymerization of monomer mixtures with high amounts of hydrosoluble monomer. A high rate of production of radicals gives rise to the synthesis of relatively large amounts of water-soluble polymer, which provokes particle flocculation.

In the CS25 core–shell synthesis new particles were nucleated due to the incompatibility of the polymers in the core and in the shell. A faster addition rate of the monomer mixture in the seed synthesis limited this incompatibility and nucleation could be avoided. This incompatibility problem did not appear in the CS10 and CS15 latex synthesis because of the lesser amount of MAA.

These latices appear to be suitable ones for our purposes provided they have the expected surface structure. The surface has to be an homogeneous layer of p(St–BuA–MAA) terpolymer with no core copolymer showing through. A good way of con-

trolling the homogeneity of the surface structure of the core–shell particles is to compare the surface properties of the seed and core–shell particles. If they are similar, the core–shell particle surface is correct. We already have some experimental evidence by soap titration that it is the case. Further work is currently in progress in our laboratory to confirm this important point.

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