

High Solids Content Emulsions. II. Preparation of Seed Latices

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ABSTRACT: The preparation of concentrated seed latices for use in bimodal and trimodal formulations is presented in the current work. Various recipes of surfactant and initiator were tested in order to allow us to control the number of particles produced during the nucleation stage. Following this, a semi-batch feed recipe that combined the use of oil-soluble initiators and pre-emulsified monomer was used to produce well-defined latices having well defined particle size distributions. It was found that the primary concern in maintaining latex stability and favorable viscosity was the reduction of undesirable secondary nucleation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1897–1915, 2002; DOI 10.1002/app.10512

Key words: high solids content emulsion; emulsion polymerization; seed latices; bimodal latices; trimodal latices; semibatch reactor

INTRODUCTION

Increasing the polymer content of a latices offers advantages such as reduced film drying times and reduced production and transport costs, although such an increase requires that special steps be taken in their preparation. Chu et al.^{1–3} showed that it was possible to carefully prepare bi- and trimodal latices with solids contents on the order of 65–70% with relatively low viscosities. However, it was also demonstrated in Part I of this series that the viscosity of a concentrated latex is very sensitive to the PSD (size and relative proportion of each population of particles), which means that strict control over this parameter must be observed at all times.^{4–6} It has been observed that low viscosity is obtained in a bimodal latex for a size ratio of $d_{p,L}/d_{p,S}$ between 7

and 8.^{5,6} It is not entirely clear what the preferred ratio of the size of small, medium, and large particles in a trimodal latex is, but the results of Schneider et al.⁴ suggest that we wish to maintain a ratio of large to medium particles in this range.

Processes for the production of multimodal latices can be grouped into one of two broad categories:

1. Nucleation of one or more populations of particles in the presence of larger seed particles. The seed particles can be either prepared *in situ* (see below) or added after being stored.
2. Mixture of two or three monomodal seeds with well-defined PSD, followed by a period of growth in a semibatch reactor.

Chu et al.^{1,2} used the first type of process to produce concentrated (up to 64.5% solids content w/w) bi- and trimodal terpolymer emulsions of styrene (Sty), butyl acrylate (BA), and methacrylic acid

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(MAA) with glass-transition temperatures (T_g) in the range of 20 to 50°C. The bimodal latices were created with a straight shot of surfactant followed by monomer addition. The trimodal latices were made by injecting a second seed latex at the same time as the components used to perform the secondary nucleation (i.e., a combination of the two). In both cases, it was important to inject the materials for renucleation and the second seed at the correct moment to obtain the correct particle size distribution (PSD) in the final latex.

Chu et al.^{1,2} used essentially water-insoluble monomers (except, of course, the trace amounts of MAA), which certainly helped to avoid unwanted homogeneous nucleation during the reaction stage. It is likely that when partially water-soluble monomers such as vinyl acetate (VAc) or methyl methacrylate (MMA) are used, homogeneous nucleation could occur throughout the emulsion polymerization, which would make maintaining control over the size and number of small particles very difficult. For instance, Urretabizkaia and Asua⁷ observed that secondary nucleation can occur during the semibatch growth stage from the moment that the feed stream is sent to the reactor. This also probably happens in the processes described in patents to Celanese Corp.,⁸ where they claim to produce a latex in the range of 65–70% solids with viscosities of $\eta \in 5000\text{--}10,000\text{ mPa s}^{-1}$. Similarly, and although it is not specifically stated, secondary nucleation is probably responsible for a multimodal PSD that allows BASF to claim to be able to produce solids contents on the order of 65–70%.⁹ One of the keys to the last process seems to be the formation of the seed latex *in situ*. The composition of the initial charge seems to be important. The reactor is initially loaded with monomer, water, water-soluble salts, and nonionic surfactants. No anionic surfactants are said to be used. This would favor the production of rather large particles in the seed.

Other companies have opted for the mixture of two seeds. Patents to Union Carbide¹⁰ and to Rohm GmbH¹¹ claim that they are able to make latices with solids contents on the order of 65–70%, by blending two seeds and making them grow by feeding in a highly concentrated feed stream of monomer, water, and eventually surfactant and initiator (we call this a *preemulsion*). In the Union Carbide patent¹⁰ the seed added in the later stage of reaction is, in fact, part of the original emulsion that is withdrawn in an early part

of the production. In the Rohm patent,¹¹ the second seed particles either are added as a shot or are continuously added in the preemulsion stream. In this patent, the authors claim that it is important that the ratio of the sizes of the seeds is important, and that it must be between 2 and 15. Although this is very vague, the fact that they mention it at all suggests that this is an important parameter. Additional patents to BASF in the early 1990s also claim a similar process and product.¹²

There is clearly industrial interest in producing multimodal latices to increase their solids content while maintaining relatively low macroscopic viscosities. The processes described in the patents are fairly complex and, regardless of whether they are of the sort seed + nucleation or seed + seed, it is clear that the production of at least one, highly concentrated seed latex is necessary.

Insofar as the production of multimodal latexes is concerned, our overall objective was to produce bi- or trimodal high solids content latices for use as pressure-sensitive adhesives, with a final composition of 78% mass BA, 19.5% MMA, and 2.5% acrylic acid (AA) ($T_g \approx -30^\circ\text{C}$) by either a combination of seeds or by nucleation in the presence of an initial dispersion. Regardless of whether we perform a renucleation step, we need relatively large (>500 nm) seeds, as well as seeds on the order of 250–300 nm (medium-size seeds). From an industrial point of view, it is desirable to do this as quickly as possible. Therefore, we want to be able to master the nucleation stage in such a way that we can make large particles rapidly and reproducibly. In the current study we concentrate on the preliminary steps: (1) characterizing the surfactants we will use in terms of the relationship between the number of particles (N_p) formed during nucleation, and their concentration; and (2) production of medium and large seeds for use in producing high solids content latices.

EXPERIMENTAL

The monomers BA, MMA, and AA, initiators ammonium persulfate (APS) or hydrogen peroxide (HPO) activated by ascorbic acid (AscA), NaHCO_3 , and sodium bisulfite were all obtained from Acros Organics (Geel, Belgium) and used as received. The anionic surfactant used in this study was Disponil® FES 32 IS (sodium salt of the sulfate of a polyglycol

Table I Recipes Used to Prepare Polymers for Analysis of Specific Surface Area of Disponil® Surfactants

	PMMA	PBA	PMMA-BA (20% MMA)	PMMA-BA (50% MMA)
Mass (g) of Each Component in Initial Charge				
MMA	199		44.6	114.0
BA		200	178.1	114.0
SDS	4.67	4.70	4.45	4.54
APS	1.49	1.48	0.36	0.36
H ₂ O	1779	1780	916.4	918.5
d_p (nm)	75	51		
N_p	4×10^{17}	13×10^{17}		
Mass (g) of Each Component in Feed Stream Reservoir				
MMA			178.3	456.2
BA			712.4	456.1
SDS			17.81	18.16
APS			3.24	3.24
H ₂ O			353.8	362.4
Length of addition phase				90 min
Length of finishing stage				30 min
Weight % polymer			46.2%	46.6%
d_p (nm)			119	134
N_p			5×10^{17}	3.5×10^{17}

ether) and the nonionic surfactant was Disponil® A 3065 (mixture of linear ethoxylated fatty acids). Both surfactants were supplied by Cognis (Meaux, France) and used as received.

The polymerizations were carried out in a 3-L jacketed glass vessel, equipped with feed pumps and an electronic balance that was used to measure the flow rate of the feed stream during semibatch operation. The jacket temperature was controlled by a thermostated water bath. Samples were withdrawn through a valve located at the bottom of the reactor and collected in vials containing hydroquinone. Particle size was measured with a Lo-C quasi-elastic light-scattering apparatus (Malvern Instruments), and solids contents were measured by thermogravimetry. A typical protocol for the semibatch copolymerization experiments is shown in Table I. Note that we used sodium dodecyl sulfate (SDS) in these experiments rather than TA or TN for reasons that are discussed below. Other possible variants on the recipes in Table I include the addition of Na₂S₂O₈ to activate the decomposition of APS, NaHCO₃ as a buffer, and AA as a functional comonomer, all at different points during the reaction. For reasons of brevity, modifications to the protocol in Table I will be discussed as we progress through the text.

The amount of coagulum formed during a reaction was measured by filtering the latex through a 100- μ filter at ambient temperature to avoid film formation (low T_g polymer). The coagulum thus recovered was rinsed with deionized water and dried in a vacuum oven at 110°C overnight. The mass of coagulum is reported with respect to the total amount of latex present at the end of the reaction.

The surfactants were characterized in terms of their critical micelle concentration (cmc) values (deionized water at 20°C) and specific surface area. The cmc values were measured by titrated tensiometry (Krüss K12 tensiometer plus Krüss 665 Dosimat titrometer, Krüss, Germany). The cmc of the anionic surfactant (TA) was found to be 0.25 g/L and that of the nonionic surfactant (TN) was 0.2 g/L.

The specific surface areas (a_s) were measured by the method of Maron¹³ on polybutylacrylate (PBA) and polymethylmethacrylate (PMMA) homopolymers, as well as on copolymers with mass fractions of MMA of 0.2 and 0.5. The latter were prepared in a semibatch reaction. The homopolymers for this part of the study were prepared in batch using standard polymerization procedures, with a solids content of 10% by mass, 2.5% SDS

Table II Specific Surface Area of the Surfactants ($\text{\AA}^2 = 10^{-20} \text{ m}^2$)

	PBA	PMMA-BA (20% MMA)	PMMA-BA (20% MMA)	PMMA
TA	56	68	76	90
TN	80	85	90	94

(w/w with respect to monomer), and 0.75% APS (w/w with respect to monomer) as the free-radical initiator. The protocols for the preparation of the four polymers used in this step are presented in Table I. The final polymers were then diluted and passed over a mixture of cationic and anionic exchange resins to remove any residual ionic species from the surface of the particles. The conductivity was measured after each passage through the exchange resin bed. The latices were re-washed until the conductivity measurements became stabilized. The cmc of TA and TN were then measured in the presence of the washed latices, and the difference between the cmc in the presence of the latex and in pure water was used to calculate the specific surface area. To do this, one needs to know the molecular weight of the surfactants. NMR and mass spectroscopy measurements on the two surfactants yielded molecular weights of 464 for TA and 1022 for TN. Applying this method yielded values of specific surface area shown in Table II.

RESULTS AND DISCUSSION

Seed Formation

The synthesis of a seed latex will obviously start by a short batch nucleation stage. To avoid having to concentrate or dilute the latex formed during nucleation, it is important to have precise control over the number of particles formed per liter of emulsion (N_p). By forming the correct number of initial particles, which will serve as the original seed for either of the two means of creating concentrated latices that we discussed above, we will be able to develop a robust, reproducible process. In addition, if we choose to use the process whereby two seeds are blended and grown, then it is again important to be able to control precisely the number of particles nucleated in the batch stage. For these

reasons, we begin our study by looking at the influence of parameters such as the composition, concentration of functional monomer, of buffer and bisulfite, initiator, and surfactant(s) on particle nucleation.

All of the reactions discussed in this section were performed as described above, but with a final solids content of 10%. The rotation rate of the glass anchor agitator was fixed at 150 rpm, and the reaction temperature was either 70 or 80°C as specified.

Influence of the Surfactants

Given our objective to produce medium and large seeds as rapidly as possible, we did not consider the use of TA alone in the initial charge. It is well known that anionic surfactants produce relatively small particles, which is not useful for us because we would then be obliged to run a long semibatch period to grow them to the correct size. It is preferable to directly nucleate particles that are as large as possible in a short time, to avoid these long growth periods. In effect, preliminary experiments (not reported here) showed that it is very difficult to obtain particles larger than 120–130 nm with the anionic surfactant. For this reason we considered only TN or mixed surfactant systems.

Nonionic Surfactant. The seed step was begun with different concentrations of TN (2.5, 5, and 10 g L⁻¹). Of these recipes, only BG5 detailed in Table III is reported here because the others led to the formation of significant amounts of coagulum (≥ 500 ppm). The amount of coagulum increased as the concentration of TN decreased. Despite the high surfactant concentration in BG5 (about 40 times the cmc) and a temperature of 80°C (which causes the initiator to decompose rapidly¹⁴), the reaction was very slow and the particles were relatively large. (See Fig. 1) Note also from Table III that, even though coagulum formation was avoided in this particular experiment, the PSD is relatively broad. This, along with the results of the experiments at 2.5 and 5 g L⁻¹, also suggests that even at a surfactant concentration of 40 times the cmc, we did not undergo classical micellar nucleation and that significant amounts of particle agglomeration took place in the reactor. Clearly, if we wish to control the PSD during the nucleation stage with a reasonable amount of surfactant,

Table III Influence of the Nonionic Surfactant on Seed Formation^a

	TA	TN	APS	NaHCO ₃	AA	Na ₂ S ₂ O ₅	T (°C)	d_p (Z_{dp}) ^b	N_p (L ⁻¹)	Final pH
A1	0.01	1	0.3	0	3	0	80	185 (0.08)	2.8×10^{16}	2.3
A2		2.5						200 (0.09)	1.9×10^{16}	2.4
A6		10						175 (0.12)	4.0×10^{16}	2.5
B2	0.01	5	0.9	0	0	0	80	170 (0.14)	3.5×10^{16}	2.9
B1		10						150 (0.18)	5.0×10^{16}	2.8
A4	0.05	2.5	0.3	0	3	0	80	116 (0.09)	11×10^{16}	2.7
A5		5						126 (0.09)	8.8×10^{16}	2.9
A7		10						134 (0.09)	7.2×10^{16}	2.7
B9	0.01	3.5	1.8	1.8	0	0	70	216 (0.06)	1.7×10^{16}	8.3
BS7		5						193 (0.05)	2.0×10^{16}	8.8
BG5	0	10	1.8	1.8	0	0	80	211 (0.30)	1.8×10^{16}	2.9

^a Compositions given per 100 g monomer and 1000 g latex.

^b Z_{dp} = polydispersity index returned by Malvern Lo-C. $Z_{dp} < 0.1$ is considered to be a monodisperse latex.

we cannot hope to nucleate particles with TN alone.

Mixed Surfactant System. A similar series of experiments was run, this time using a small amount of anionic surfactant TA. The results are shown in Table III. First of all, it is clear that the addition of even a small amount of TA allows us to obtain relatively narrow PSDs, and no significant amount coagulum was found in the final products.

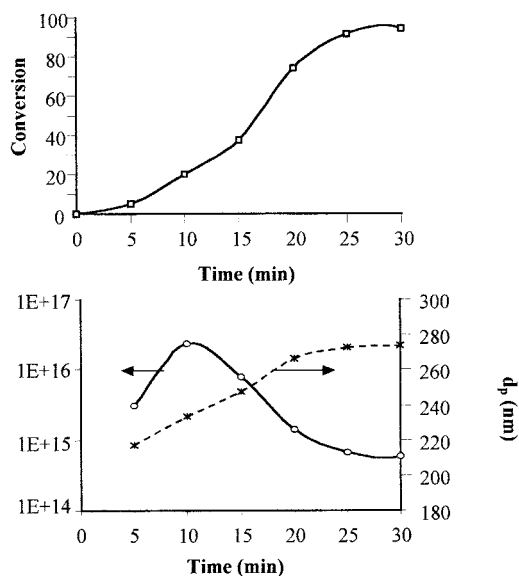


Figure 1 Evolution of the kinetics and granulometry of experiment BG5. Note that the continual decrease in N_p and growth of d_p throughout most of the experiment suggests that limited flocculation occurs on a significant scale.

Note that in these experiments, the TA was always present at concentrations well below its cmc. If we compare experiments A6, A7, and B1 to BG5, we can see that for the three experiments with a small amount of TA the final value of d_p was much lower as well. However, large changes in the concentration of TN have relatively little influence on d_p , whereas changes in the small amount of ionic surfactant (e.g., A7 versus A6) present in the reactor seem to have a significant effect on d_p . Changing [TN] from 2.5 to 10 g L⁻¹ (A4 to A7) led to an increase of 18 nm in the value of d_p , and if we compare A1 to A6, the value of d_p actually decreased by 10 nm when the surfactant concentration increased by a factor of 10. On the other hand, if we increased [TA] from 0.01 to 0.05 g L⁻¹, the particle size went from 200 to 126 nm (A2 to A4), or from 175 to 134 nm (A6 to A7).

The influence of the anionic surfactant on particle nucleation is clearly shown in Figure 2. In all cases, regardless of the concentration of TN, the number of particles formed is almost directly proportional to the quantity of TA added at low concentration (the exact exponent is 1.1).

Clearly a significant part of the TN does not directly participate in particle nucleation, which rather seems to be controlled by the amount of TA in the case of mixed surfactant systems. The proportionality found between N_p and TA is the same as that found by Novak¹⁵ for a similar monomer system. We discuss the influence of other parameters below, although the results of Figure 2 suggest that it is possible to “fine-tune” the number of particles by controlling the quantity of TA in the system.

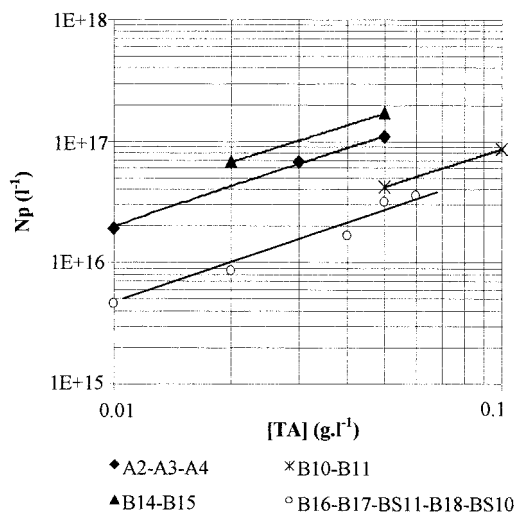


Figure 2 Plot of $\ln(N_p)$ as a function of the concentration of anionic surfactant for different experiments. The slope for all of the lines is very close to 1.1.

Influence of Other Species on Particle Formation

The influence of the concentration of initiator, buffer, and $\text{Na}_2\text{S}_2\text{O}_5$ are summarized in Table IV.

APS. The influence of the initiator concentration on the rate of polymer is rather strong, as shown in Figure 3. We can see from Table IV that this is not the result of a change in the number or size of particles nucleated, because $N_p \in 1.7\text{--}2.1$

$\times 10^{16}$ for all three experiments. Note, however, that these three experiments were performed with NaHCO_3 in the aqueous phase, the effect of which was to alter the pH and to increase the ionic strength of the emulsion. This, in turn, might mask any additional electrostabilizing effect that could come from the negatively charged SDS, thereby eliminating any influence that SDS might have on stabilizing the particles.

NaHCO₃. Experiments B13, B7, and B8 demonstrate that, as we increase the concentration of the buffer in the aqueous phase, the particles that are nucleated are bigger and less numerous, which results from an increase in the ionic strength of the latex as the quantity of NaHCO_3 increases. Such an increase favors the controlled flocculation of small particles onto larger ones.

Sodium Bisulfite. $\text{Na}_2\text{S}_2\text{O}_5$ is commonly used to activate the decomposition of persulfate initiators. The mechanism by which this occurs is rather complex and depends to a certain extent on the acidity of the latex.¹⁶ Basically it accelerates the formation of radical by an oxidation–reduction reaction. If we compare experiments B13 and B4 in Table IV, we can clearly see that adding sodium bisulfite to the initial charge leads to a significant decrease in the size of the particles, and to an almost threefold increase in the number

Table IV Influence of Different Parameters on Seed Formation

	TA	TN	APS	NaHCO_3	AA	$\text{Na}_2\text{S}_2\text{O}_5$	T (°C)	d_p (Z_{dp})	N_p (L^{-1})	Final pH
BS11	0.04	3.5	1.8	1.8	0	0	80	207 (0.06)	1.7×10^{16}	8.9
BS12			0.9					185 (0.07)	2.0×10^{16}	8.9
BS12b			0.45					180 (0.04)	2.1×10^{16}	8.5
B13	0.01	5	0.9	0	0	0	70	146 (0.08)	5.6×10^{16}	2.9
B7				0.9				177 (0.08)	3.2×10^{16}	8.9
B8				1.8				191 (0.08)	2.4×10^{16}	8.7
B15	0.05	5	0.3	0	0	0	80	102 (0.06)	17.0×10^1	2.6
A5					3			126 (0.09)	8.8×10^{16}	2.9
B13	0.01	5	0.9	0	0	0	70	146 (0.08)	5.6×10^{16}	2.9
B4				0		0.75		107 (0.07)	15.0×10^1	2.3
B6				0.9		0.07		177 (0.09)	3.2×10^{16}	8.8
B13	0.01	5	0.9	0	0	0	70	146 (0.08)	5.6×10^{16}	2.9
B2							80	170 (0.14)	3.5×10^{16}	2.9
B7	0.01	5	0.9	0.9	0	0	70	177 (0.08)	3.2×10^{16}	8.9
B3							80	288 (0.34)	0.7×10^{16}	8.3
B9	0.01	3.5	1.8	1.8	0	0	70	216 (0.06)	1.7×10^{16}	8.3
B16							80	311 (0.05)	0.6×10^{16}	8.9

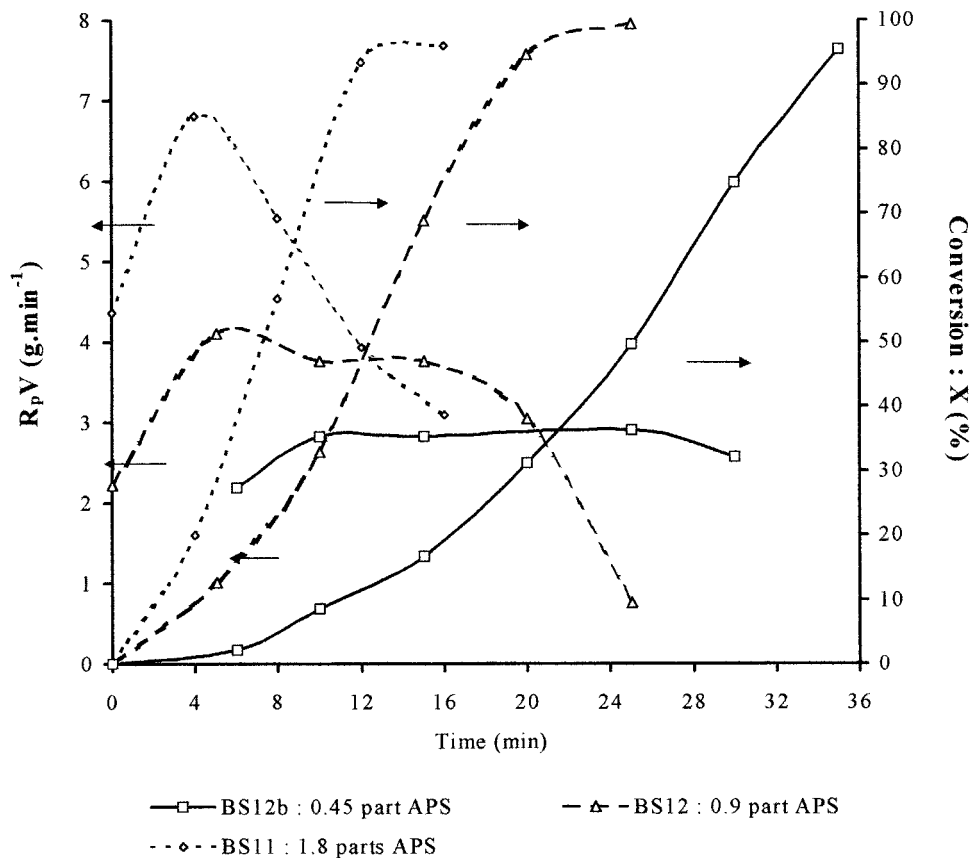


Figure 3 Evolution of the kinetics (total rate of polymerization $R_p V$, and overall mass conversion X) as a function of time and initiator concentration for experiments BS11, BS12, and BS12b. Conditions: 80°C, 3.5 g TN, 0.04 g TA, 1.8 g NaHCO₃.

of particles nucleated. This is not surprising, given that in the absence of a buffer, we expect the TA to contribute to the electrostabilization of the growing particles. Therefore, the higher concentration of negatively charged sulfate and sulfonate ions obtained with the bisulfite led to more stable particles. However, this effect seems to be masked, at least for low bisulfite concentrations, when the NaHCO₃ buffer is added. This can be seen if we compare B4, B6, and B13. One would expect the addition of a small amount of bisulfite to slightly increase the number of particles in B6 with respect to B4. However, because we also added sodium carbonate, the effect of the buffer was stronger than the effect of the bisulfite, and we created fewer larger particles. In fact, B6 and B7 are almost identical in terms of particle size and number (Fig. 4).

Temperature. The influence of the reaction temperature (tested only at two levels) can also be

seen in Table IV. It can be seen that the number of particles is higher at lower temperatures, and that this effect is even stronger when the ionic strength of the medium is stronger (pH > 8 in the presence of the buffer). It is not immediately evident exactly why this happens, but a possible explanation lies in the increase in the ionic strength (c.f. B13 and B2 with no buffer) attributed to the increase in the quantity of sulfate radicals in the water phase. It is possible that at higher temperatures, we were initiating more, very small particles that autoflocculate onto each other to produce what appears to be fewer, larger particles than we obtained at lower temperatures. This idea is supported by the fact that at low to moderate ionic strengths (pairs B13/B2, and B7/B3), the polydispersity index is much higher at 80°C than that at 70°C. For the pair B9/B16, we did not see an increase in the polydispersity index because the ionic strength is so high that all of the small particles in the medium flocculated onto the

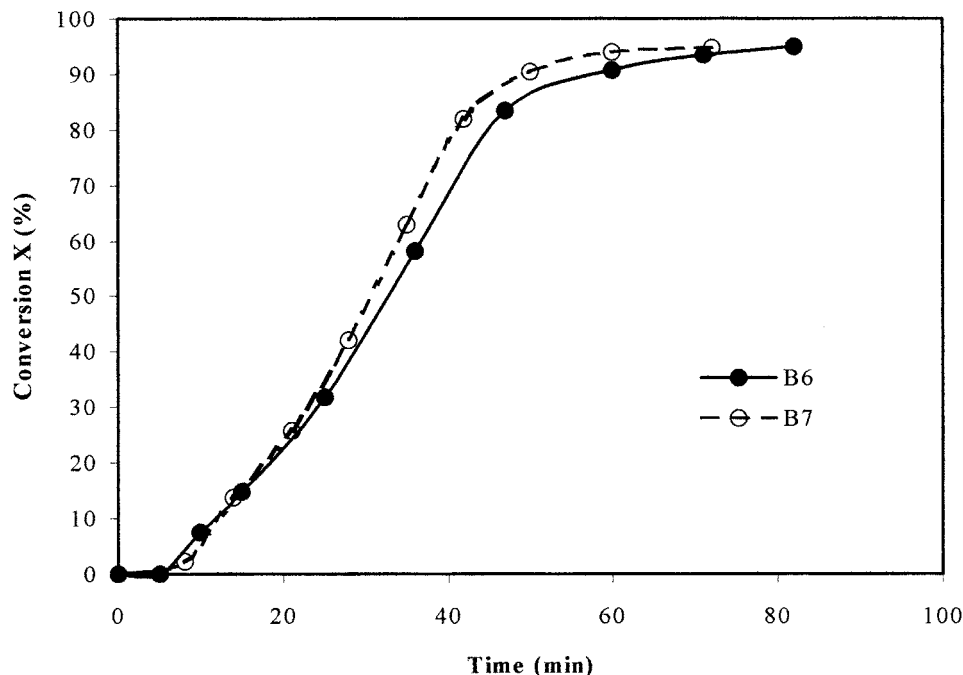


Figure 4 Comparison of the kinetics of experiments B6 and B7. B6 has a trace amount of bisulfite (0.07 g/100 g monomer), whereas B7 does not. Both have 0.9 g NaHCO_3 (w.r.t. 100 g monomer).

larger ones, which in turn reduced the width of the PSD. Note also that the buffer masked the effect of changing initiator concentration for the experiments BS11, BS12, and BS12b, which likely results from the fact that for these last three experiments the concentration of ionic surfactant was four times higher than it was for the experiments where we looked at the influence of the temperature. For this reason, the number and size of the particles in B13/B2, B7/B3, and B9/B16 is more sensitive to the presence of the sulfate ions. Of course, the effect of the temperature is not limited only to the decomposition of the initiator; it can also have an effect on the solubility of MMA in the aqueous phase, and on the mobility and affinity of the surfactant.

Conclusion

In this section, we looked at the nucleation phase of an MMA-BA copolymer to understand the relationship between the different components of a model industrial recipe and the nucleation of particles. The motivation for this was to produce seed latices of different sizes for high solids content emulsions. The experiments presented here show that it is preferable to nucleate the seeds with a

mixed surfactant system containing trace amounts of TA well below its cmc.

PRODUCTION OF CONCENTRATED SEED LATICES

It is difficult to know *a priori* how the different seeds will grow, once they have been blended, without an exact model for particle growth and stability. In a previous study, Chu et al.³ succeeded by blending seed latices on the order of 100, 250, and 500 nm. The experimental data and simulations of Schneider et al.⁴ showed that for bimodal latices, a diameter ratio of 6–8 provided the highest solids content at low viscosity. In addition to controlling the particle size, we must produce seeds that are as concentrated as practical. To obtain an estimate of what this upper limit on the concentration of a monomodal latex would be, we calculated the thickness of the electronic double layer around the particles, then calculated the maximum concentration of particles permissible to avoid interpenetration of the double layers.

Let us denote the volume fraction of polymer in a latex by ϕ , which is a function of the number of N_p , d_p , and the total volume of latex:

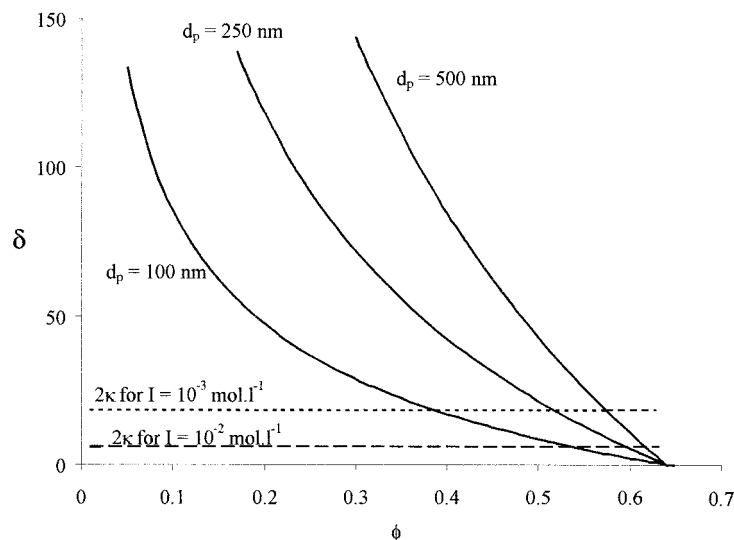


Figure 5 Distance between uncharged particles δ as a function of volume fraction for different particle sizes (solid lines). The straight dotted lines are twofold thicker than the electric double layer at two different ionic strengths. The intersection of the curves and straight lines represents the maximum volume fraction of latex possible in a monodisperse emulsion.

$$\phi = \frac{1}{V} N_p \frac{\pi}{6} d_p^3 \quad (1)$$

If the thickness of the electronic double layer is denoted by δ , then the relationship between the maximum admissible volume fraction ϕ_{\max} , the particle size, and δ is

$$\phi_{\max} = \frac{1}{V} N_p \frac{\pi}{6} (d_p + \delta)^3 \quad (2)$$

In the case of randomly packed spheres, ϕ_{\max} is on the order of 0.64. In an experimental evaluation of the latex viscosity, Schneider et al.⁴ found that for a monomodal latex of 600 nm, particles exhibited a ϕ_{\max} of 0.66, probably because the latex was not perfectly monodisperse. Because the difference between the two values is small, we continue to use $\phi_{\max} = 0.64$ and suppose that the latex is monodisperse. The thickness of the electronic double layer δ can be calculated as follows¹⁷:

$$\delta = \sqrt{\frac{\varepsilon k_B T}{8 \pi e^2 N_A I}} \quad (3)$$

where ε is the dielectric constant of water (continuous medium), k_B is the Boltzmann constant,

T is the absolute temperature, I is the ionic strength, e is the charge of a single electron, and N_A is Avagadro's number. The thickness of the layer is independent of the particle size and therefore has a relatively larger impact when the particles are small. In practice the ionic strength of our latices varies between 10^{-3} and 10^{-2} mol L⁻¹, which corresponds to values of δ between 9 and 3 nm; that is, the higher the ionic strength, the more compact the double layer.

As we can see in Figure 5, the double layers of the 100 nm start to interpenetrate at a volume fraction $\phi_{\max} = 0.38$ for an ionic strength of 10^{-3} mol L⁻¹, whereas those of 500 nm particles begin to interpenetrate at $\phi_{\max} = 0.57$ for the same value of I . At higher ionic strengths, the maximum volume fraction is, of course, higher because the double layers are compacted. This suggests that the seed recipe should probably have a relatively high ionic strength, and, as we saw above, one of the means of obtaining this is to use a buffer and to perform the reaction at high pH.

The production of large and medium seeds should also obligatorily be done in semibatch processes. The semibatch phase should be run under starved feed conditions to limit secondary nucleation and to improve the stability of the latices.

Table V Recipes Used in Preparing Seeds of Large and Medium Particles

	SEM7	SEM8	SEM9	SEM11	SEM12	SEM12b	SEM21	SEM23	SEMM3
Seed Formation Recipe									
Duration (min)	35	45	44	16	27	36	48	50	17
TA	0.01	0.01	0.01	0.01	0.04	0.04	0.01	0.01	0.01
TN	5	5	3.5	3.5	3.5	3.5	3.5	3.5	5
BA	80.1	80.2	80	80	80	80	80	80	80
MMA	20.2	20.1	20.1	20	20	20	20	20	20
NaHCO ₃	1.8	1.8	1.8	1.8	1.8	1.8	1.9	1.8	—
APS	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	0.9
Na ₂ S ₂ O ₅	—	—	—	—	—	—	—	—	0.74
T (°C)	70	70	70	70	80	80	70	70	70
Characteristics at end of seed period (all reactions 10% solids content w/w)									
d_p	193	210	195	207	184	185	221	215	120
Z_{dp}	0.07	0.06	0.05	0.05	0.09	0.04	0.07	0.06	0.04
N_p	2×10^{16}	1.2×10^{16}	2.1×10^{16}	1.7×10^{16}	2.4×10^{16}	2.3×10^{16}	1.7×10^{16}	1.7×10^{16}	1×10^{17}
Preemulsion Recipe									
Duration (min)	570	540	552	298	347	358	436	255	423
TN	25.2	12.4	15.6	19.6	19.7	20	15.8	15.9	30.7
BA	699	701	896	896	910	906	924 + 6.1	893 + 8	900
MMA	185	175	224	224	224	227	231 + 1.5	225	225
AA	25	25.4	31	32	32	32	34 + 0.2	32	31
APS	1.08	1.1	1.8	1.8	0.9	0.45	2	2	2.8
BPO	—	—	—	—	—	—	—	1.5	—
Characteristics at end of reaction									
Solids wt %	40	40	50	50	50	50	50	50	50.1
d_p	250	490	510	250	380	410	500	513	270
Z_{dp}	0.18	0.1	0.09	0.27	0.22	0.9	0.14	0.14	0.06
N_p	9×10^{16}	1.4×10^{16}	1.7×10^{16}	1.5×10^{17}	4.1×10^{16}	3.2×10^{16}	1.9×10^{16}	1.7×10^{16}	1.1×10^{17}

Production of Large Seeds

With the objective of obtaining a latex with a solids content of 50% and a d_p of at least 500 nm from a latex with an initial charge on the order of 10% solids, we need to obtain approximately 1.8×10^{16} particles per liter of emulsion (or to obtain particles with a $d_p = 200$ nm at the end of the nucleation stage). The recipes discussed in this section are summarized in Table V.

Choice of Nucleation Conditions

Because we wish to obtain a seed with as narrow a PSD as possible, we need to eliminate the possibility of secondary nucleation. It was shown above that these objectives can be obtained with a mixed surfactant system by carefully adjusting the quantity of ionic surfactant in the mixture. Also, we saw that adding a certain amount of buffer to the reactor contents helps us to obtain

large particles during seed formation by decreasing the electrostatic repulsion between the particles and favoring the flocculation of small onto larger particles. Because NaHCO₃ causes the pH to increase to above 8, use of a buffer can create an environment in which the AA will be present in its dissociated form. Given that this would, in turn, favor homogeneous nucleation, it was decided to adjust the polymerization recipe, and to add the AA exclusively during the semibatch phase and to avoid using NaHCO₃ in this same phase. We therefore chose to use the conditions of experiment B9 for the nucleation stage.

Semibatch Phase

The production of large and medium seeds must be done in semibatch processes. The semibatch phase should be run under starved feed conditions both to limit secondary nucleation and to

improve the stability of the latices. It was found that the instantaneous conversion should be at least 90% during the semibatch stage; otherwise, secondary nucleation occurred. This secondary nucleation often led to a partial, or even total, loss of latex stability, given that the feed stream did not contain enough surfactant to stabilize the newly formed surface area. It would be possible, of course, to increase the quantity of nonionic surfactant in the feed stream, but this is also undesirable from the standpoint of product quality because we wish to maintain the surfactant concentration at less than 3% with respect to total monomer content.

The presence of anionic surfactant in the initial charge was necessary to promote nucleation. On the other hand, because we wish to avoid just that during the growth of the particles in the semibatch phase, the semibatch feed stream should contain only nonionic surfactant (TN). Although not shown here, secondary nucleation was observed in the several experiments run with TA in the feed stream. Furthermore, it was also necessary to find the trade-off between loss of stability at low TN concentrations and poor product quality and eventual renucleation at high TN levels in the feed stream. As can be seen from Figure 6, the final quality of the seed can be very sensitive to the amount of TN in the feed. The only difference between experiments SEM7 and SEM8 is that the semibatch feed in SEM7 contains twice as much surfactant as that of SEM8. Interestingly enough, the two experiments exhibit very similar evolutions of conversion versus time, even though N_p continues to increase throughout the semibatch period for SEM7 and remains (more or less) constant for SEM8. The reasons for the constant rates are twofold. First of all, we are operating at high instantaneous conversions, so the concentration of monomer in the particles and, consequently, the rate of reaction are not very high. Second, as shown by Ouzineb et al.,¹⁸ the value of \bar{n} is higher in large particles than that in smaller ones. Therefore, the rate of polymerization is probably dominated by the large particles already present in the system, and the smaller particles created by secondary nucleation polymerize more slowly.

The quantity of TN used in SEM8 is "correct," insofar as maintaining the original number of particles is concerned, and the final solids content was 40–10% below the desired limit. Because this experiment lasted approximately 10 h and the

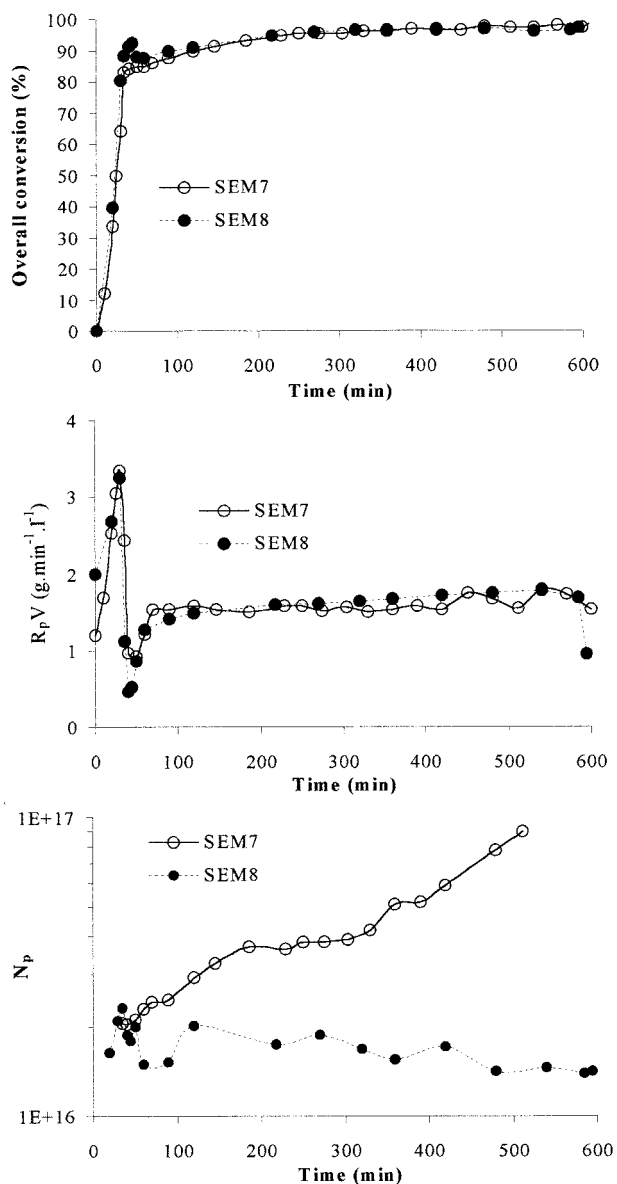


Figure 6 Influence of the concentration of TN in the feed stream during semibatch operation. Recipes for SEM7 and SEM8 are given in Table V.

instantaneous conversion remained well above 90%, it was decided that rather than prolong the semibatch stage, we would attempt to increase the solids content by increasing the flow rate. The results of SEM9, shown in Figure 7, show that increasing the flow rate by 25% allowed us to attain a solids content of 50% in the same time that it took to achieve a level of 40% in SEM8. There appeared to be a small amount of secondary nucleation at the beginning of the semibatch period of SEM9; however, the number of particles

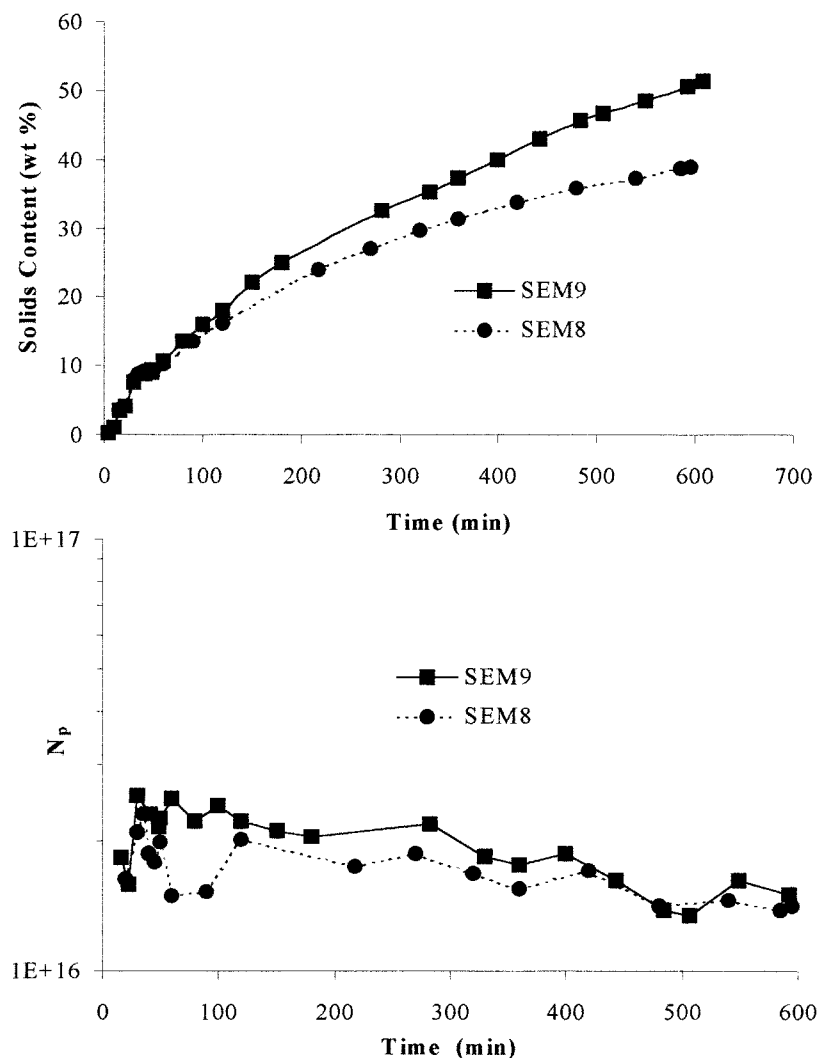


Figure 7 Results of SEM9 compared to results of SEM8. Changing the flow rate in SEM9 allows us to make the same particles as SEM8, but at a higher solids content and more rapidly.

decreased slightly throughout the experiment, allowing us to obtain 1.7×10^{16} particles per liter of emulsion at the end of 10 h. Note that the small amount of renucleation and limited flocculation led to a slight broadening of the PSD during the course of the experiment. The Lo-C QELS indicates that the polydispersity of the latex at 300 min is slightly above 0.1. Nevertheless, the limited flocculation helped to narrow the distribution by the end of the reaction. In terms of PSD and solids content, the results of SEM9 were quite satisfying and were highly reproducible (see Fig. 8).

However, from an industrial point of view the seed formation is relatively long, and it would be

useful to reduce the length of the semibatch period. Increasing the semibatch feed rate of monomer alone is not possible because this would lead to significant secondary nucleation and loss of stability. However, it might be possible to:

1. increase the monomer feed rate combined with a slightly higher concentration of TN
2. increase the flux of radicals to the particle phase
3. increase the rate of monomer consumption by an increase in the reaction temperature

All of these potential solutions are dangerous because, if not executed correctly, they could pro-

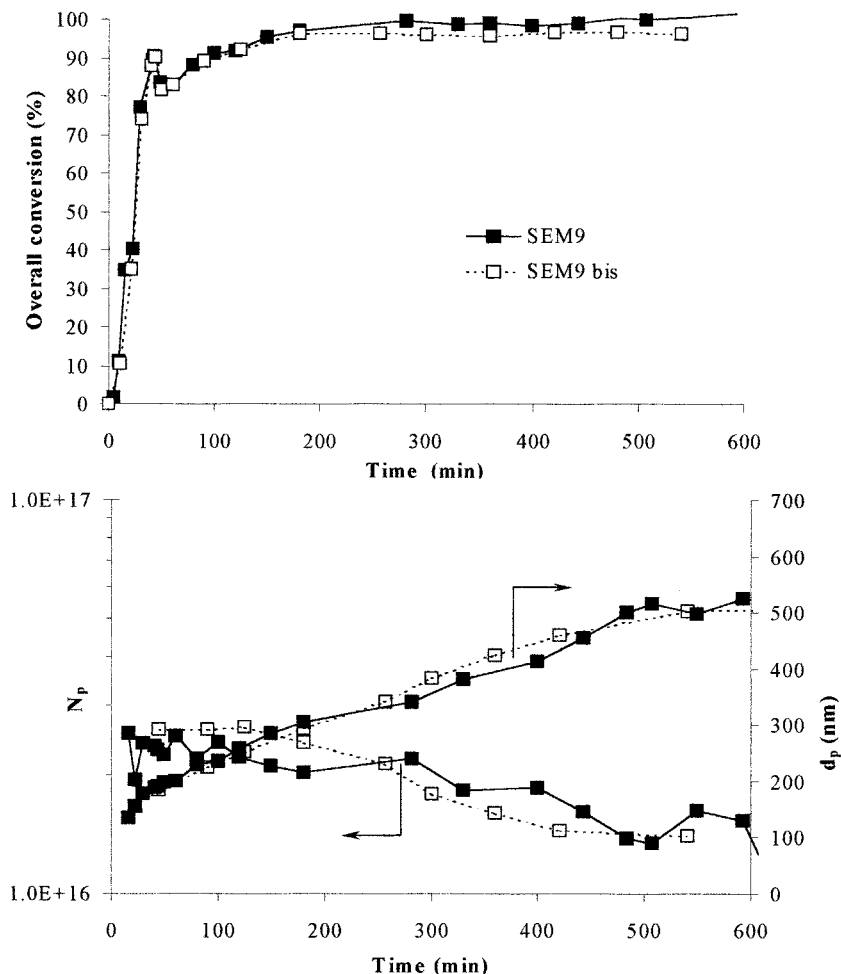
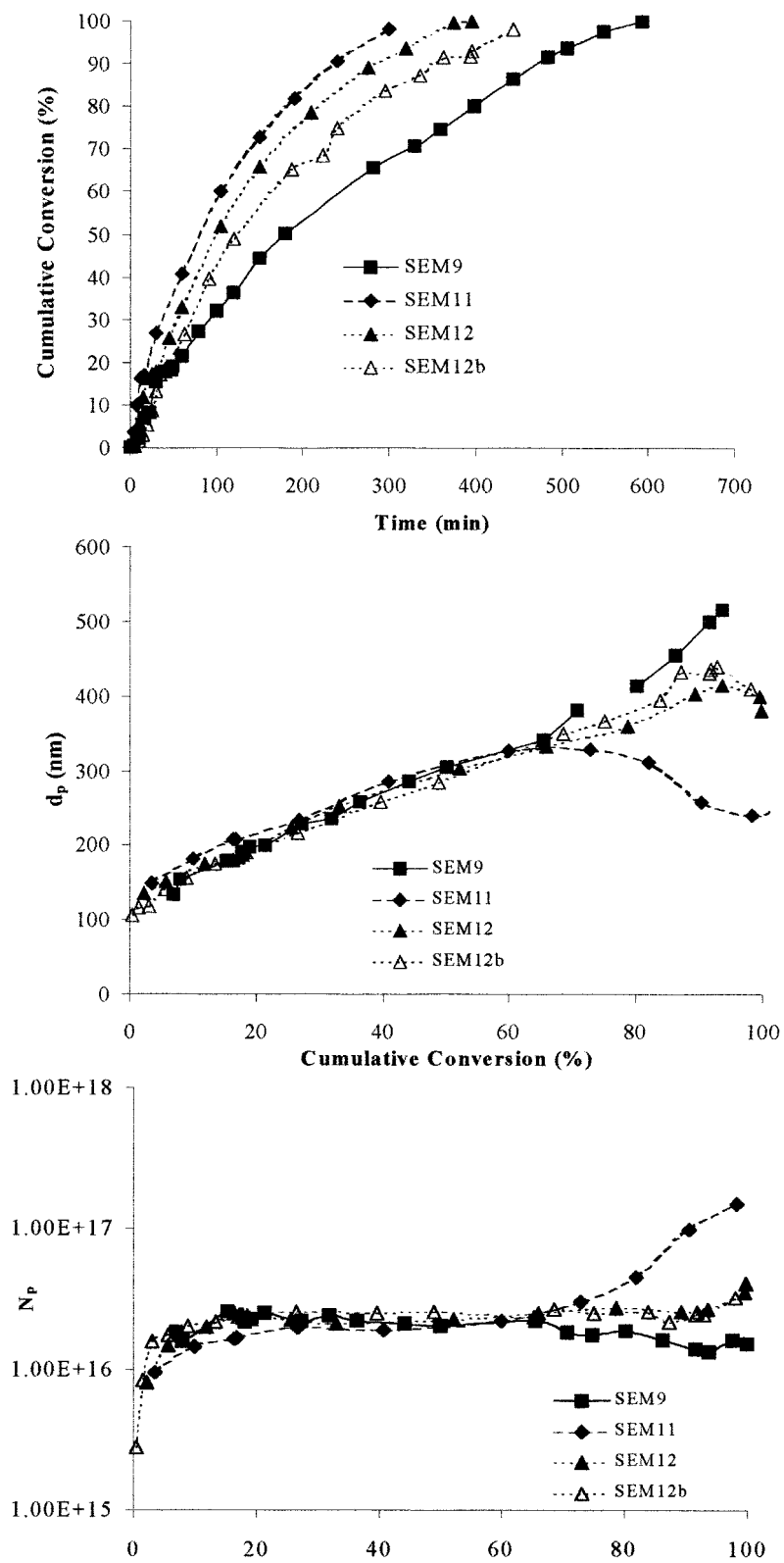


Figure 8 The recipe defined by SEM9 is quite reproducible, as shown by the excellent agreement between the two replicate runs shown here.

voke secondary nucleation and thus a deviation of the PSD from the desired values.

If we were to increase the reaction temperature from 70 to 80°C, this would of course have a significant effect on a number of parameters, especially on the decomposition of the initiator. However, as we saw above, we identified conditions in experiment BS11 that allow us to produce seeds with the same characteristics as those of experiment B9 (seed composition for SEM9). The experiment SEM11 is similar to SEM9 in that we use BS11 to obtain the same seed characteristics, and then feed in the same preemulsion as for SEM9, but for 5 h rather than 9 h. As we can see from Table V, this increase in temperature with no adjustment of the feed composition provoked a massive renucleation, and the final particle size

in SEM11 is 250 nm (less than half that of SEM9), there are almost 10 times as many particles, and the PSD is quite broad. Because the surface coverage remained between 55 and 75% throughout the experiment, renucleation is mostly attributable to an excess of radicals combined eventually with a slight increase in the amount of AA and MMA dissolved in the aqueous phase at the higher temperature (MMA solubility increases from 16 to 18 g/L only, so this effect is probably not very important, especially given that we are working under starved conditions and the absolute monomer concentration is very low), rather than to an excess of surfactant. Because APS decomposes four times faster at 80°C than at 70°C,¹⁴ there will be significantly more radicals in the aqueous phase, and the oligoradicals termi-



nating in $\text{SO}_4^{\bullet-}$ will stabilize a fair number of the homogeneously nucleated particles, thereby preventing them from flocculating onto the larger ones.

To attempt to benefit from the increased rate of polymerization at 80°C but without the problem of renucleation, the above-mentioned experiment was repeated with lower initiator concentrations in the preemulsion. Two experiments were run with one-half (SEM12) and one-quarter (SEM12b) the initiator concentration of SEM9 in the preemulsion. As we can see from Figure 9, the lower the radical flux, the less problematic secondary nucleation becomes. However, even for SEM12b (which has the highest final particle size), d_p remains below the 500 nm mark, and, as we can see from Table V the polydispersity index is still higher than that for SEM9. In addition, significant amounts of coagulum were found in SEM12 and SEM12b (1200 and 1500 ppm, respectively, versus 400 for SEM9). It was therefore concluded that increasing the temperature was not going to allow us to prepare 500 nm faster than was found possible with SEM9.

However, there is no reason for us to limit ourselves to the use of APS, and it therefore seemed useful to investigate the use of a water-soluble initiator that decomposes to yield uncharged radicals. For this we chose to use H_2O_2 , which decomposes to yield HO^\bullet radicals. The underlying idea is that the uncharged radicals would not stabilize homogeneously nucleated particles, which would flocculate onto the larger particles already present. Of course, it is necessary to adjust the composition of the initial charge if the APS is replaced by the hydrogen peroxide. It was found that increasing the TN to 11.5 g was sufficient (experiment B24). Unfortunately, massive flocculation occurred during the semibatch stage because the ascorbic acid (catalyst for the decomposition of H_2O_2) was consumed before the end of the experiment. Nevertheless, this experiment provided some results. As can be seen from Figure

10, transmission electron micrographs of two samples of latex, one formed with APS, the other with H_2O_2 , show that significantly fewer small particles are present in the final product when we use the initiator yielding uncharged radicals. We are clearly forming far fewer stable small particles with the water-soluble peroxide. We will return to the idea of using the $\text{H}_2\text{O}_2/\text{AscA}$ couple in Part III of this series.¹⁹

An alternative to using a water-soluble non-ionic initiator would be to rely partially on an initiator such as BPO that is soluble in the organic phase, to increase the flux of radicals in the particle, and thus accelerate the reaction, without promoting homogeneous nucleation. To test this idea, two experiments, SEM21 and SEM23, were run. The temperature and compositions in these reactions are identical to those of SEM9 (up to now, our "best" reference), except that a shot of BPO dissolved in a few grams of monomer is added at the end of the nucleation stage. Care must be taken to avoid adding the BPO while there is still enough monomer in the reactor to allow droplet formation when the monomer in the shot is added to the system. In addition, the feed rate of preemulsion is increased in these two experiments (7 h for SEM21 and 4 h for SEM23 versus 9 h for SEM9). Because the radical concentration in the particles is higher, we should be able to consume the added monomer more rapidly.

It can be seen from Figure 11 that d_p and N_p are very similar for all three experiments and, although the polydispersity of the PSD is slightly above 0.1 for the two experiments with BPO, this value still remains acceptable. It is therefore possible to reduce the synthesis time of our large seed latices to approximately 5 h from the 10 h found for SEM9. Although the problem of secondary nucleation is not totally eliminated, a judicious choice of recipe and reaction conditions allows us to control it.

Figure 9 Reduction in radical flux resulting from reduction in initiator concentration. The concentration of APS in SEM11 is equal to that in SEM9 (but added in 5 h instead of 9 h). The concentration in SEM12 is half that of SEM9, and in SEM12b it is a quarter of that in SEM9 (added in 5.5 h for SEM12 and SEM12b). Clearly, the lower the radical flux, the less important the phenomenon of secondary nucleation. Note that here we have used cumulative rather than overall conversion. This is the conversion with respect to the entire mass of preemulsion to be added, rather than the mass of preemulsion actually added.

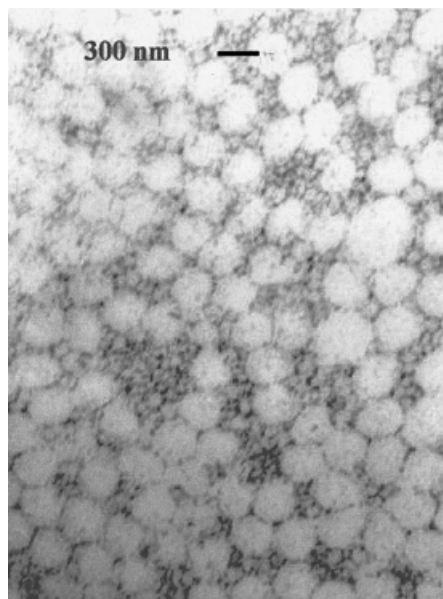


Figure 2.19 : MET – échantillon de l'expérience SEM16 (amorçage APS) prélevé au bout de 404 minutes

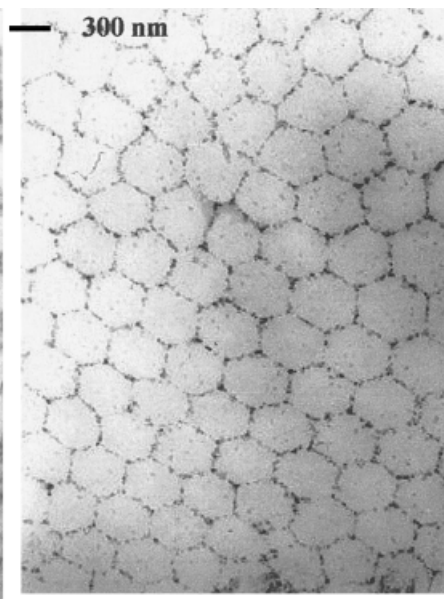


Figure 2.20 : MET – échantillon de l'expérience SEM17 (amorçage H₂O₂) prélevé au bout de 180 minutes

Figure 10 Transmission electron micrographs of latex samples formed with APS (left) and with H₂O₂ (right). There are significantly fewer small particles formed with the initiator yielding uncharged radicals. Phosphotungstic acid was used as a marker to allow us to detect the small particles in the film (observation at room temperature). Particles are nonspherical because they form a film at room temperature, given that the T_g of the latex is approximately -30°C .

Medium and Small Seed Production

The production of small and medium seeds is much easier than that of the large seeds, given the size of the particles involved: 250 nm for medium and between 50 and 100 nm for the small particles.

Medium Particle Seeds

Because we still require 50% solids content, we need to produce these seeds in a semibatch system. However, because the particles are smaller, we do not need the same number of particles to yield a d_p of 250 nm at 50% solids, but rather we start with a larger number of smaller particles. A quick calculation shows that we want approximately 10-fold more particles than that for the large seeds, with a diameter on the order of 110 nm. Experiment B4 provides the correct conditions for this preparation. SEMM3 shows the final recipe chosen for the semibatch phase. The reasoning for the rate of addition, temperature,

and composition is as above. No attempt was made to finely optimize the recipe farther.

Seed Characterization

Partitioning of AA

Given that the final pH of the system is between 1.5 and 3 for the seeds retained, it is useful to know how much AA is to be found on the surface of the particles, especially if the seeds need to be neutralized at a later stage. In the case of the large seeds, SEM9 was retained for analysis. Although we used the recipe in SEM23 for ulterior studies on the production of concentrated latices, it is supposed that the presence of BPO (the only difference between the two) had little effect on the partitioning of the acid. SEMM3 was used for the medium-size seeds. The method used to measure the quantity of acid on the surface of the particles is well known, and details can be found in the literature.^{3,20,21} Measurement of the concen-

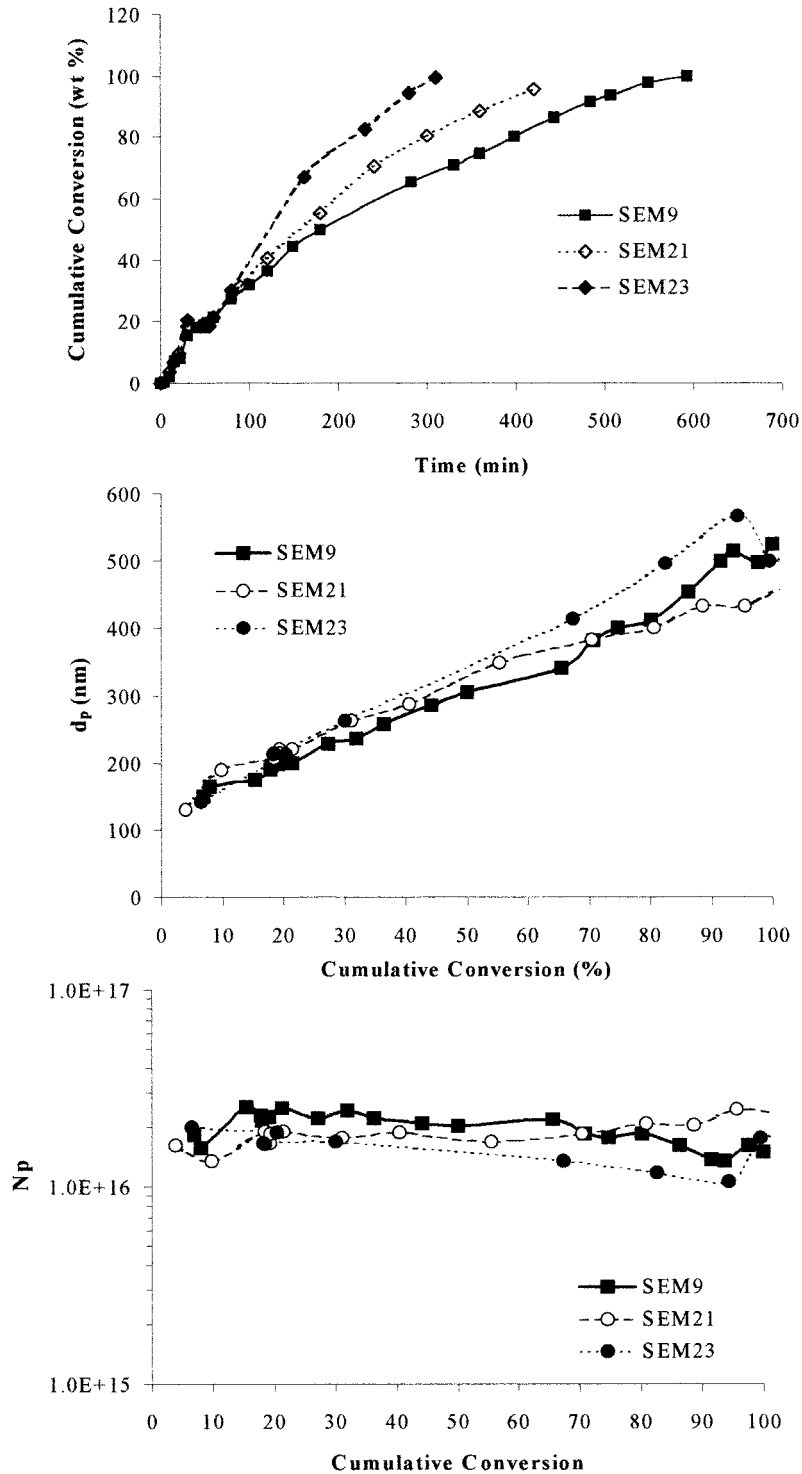


Figure 11 Evolution of the cumulative conversion (see caption Fig. 9), d_p , and N_p for SEM21 and SEM23, compared to that of SEM9, to demonstrate the effect of adding a shot of BPO dissolved in monomer at the end of the nucleation stage. Feed times: 550 min for SEM9, 436 min for SEM21, and 255 min for SEM23.

Table VI Partitioning of Acrylic Acid in the Large and Medium Seeds

	Large Seed: SEM9	Medium Seed: SEMM3
d_p	500 nm	270 nm
pH of final latex	2.1	2.9
Conductivity of final latex	1.77 mS/cm	2.40 mS/cm
% (w/w) of AA on particle surface	9.2%	12.0%
Charge density	31.7 $\mu\text{C}/\text{cm}^2$	20.2 $\mu\text{C}/\text{cm}^2$
% (w/w) of AA in serum	10.8%	19.6%

tration of acid in the serum was performed by separating the serum by ultracentrifugation, and then analyzing the serum in the same way as we did for the latices. The results are shown in Table VI.

Viscosity

The rheological profiles of the two seeds are shown in Figure 12. The seed latices exhibit a slight tendency toward shear thinning, and their viscosities at low shear remain low. As expected, the viscosity of the large particle seed is slightly lower than that of the medium particle seed.⁴

CONCLUSIONS

We have presented a systematic study of the synthesis of large- and medium-size monomodal seed latices for use in preparing highly concentrated,

multipopulated emulsions. The viscosity of these latices is fairly low, which is important, given that they will be blended and further grown to modify the PSD in a subsequent stage. Low viscosity ensures that mixing of the different seeds and/or added monomer, initiator, and surfactant will be dispersed as uniformly as possible in the final product. These recipes also yielded stable emulsions. In effect, the average particle size and polydispersity of the medium-size particles remained unchanged after several months of storage at ambient temperature.

It was demonstrated that the rate of reaction during the semibatch step can be significantly increased through the use of an organosoluble initiator, and that the stabilization of homogeneously nucleated particles can be reduced if a nonionic water-soluble initiator is used in place of the more traditional persulfate initiators.

These products and concepts will be put to use in Part III of this series for the production of latices with low viscosity and with solids contents on the order of 65%.

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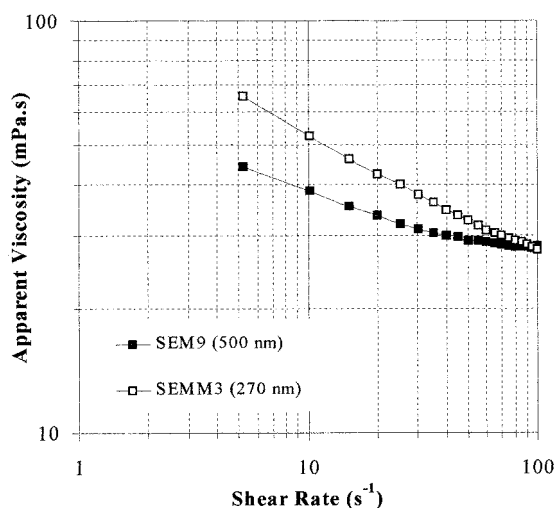


Figure 12 Rheological profiles of medium (SEMM3) and large (SEM9) seeds in a Couette viscometer.

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