

# High Solids Content Emulsions. III. Synthesis of Concentrated Latices by Classic Emulsion Polymerization

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**ABSTRACT:** Two different methods of producing bi- and trimodal latices of a mixture of methyl methacrylate, butyl acrylate, and small amounts of acrylic acid were tested. It is shown that a combination of concentrating blends of seed particles by semibatch reaction, followed by a nucleation of small particles plus a second semibatch phase allowed us to obtain stable latices with solids contents over 65% and viscosities of below  $2500 \text{ mPa s}^{-1}$  with little coagulum formation. The key parameter in determining latex stability, coagulum formation, and viscosity appears to be the particle size distribution, and especially its modification attributed to secondary nucleation. Because it is not possible to eliminate water-soluble monomers from the polymerization recipe, secondary (homogeneous) nucleation must be minimized by careful addition of the free-radical initiator and choice of monomer feed flow rates. The nucleation of the third population in the trimodal latices is best accomplished with a mixed surfactant system because renucleation by anionic surfactant alone leads to detrimental changes in the particle size distribution (PSD) resulting from excessive flocculation of particles. In addition, it was found that the viscosity of the final products was not sensitive to small changes in the ionic strength of the latex, although neutralization to a pH of 6 effectively doubles the final latex viscosity. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1916–1934, 2002; DOI 10.1002/app.10513

**Key words:** high solids content emulsion; emulsion polymerization; particle size

## INTRODUCTION

High solids content latices, here taken to mean latices made by emulsion polymerization with a total polymer content greater than 60%, have been the object of growing interest over the past few years. Increasing the polymer concentration of a latex offers advantages such as reduced film drying times, and reduced production and transport costs. It has been demonstrated that it is possible to obtain latices with solids contents of

over 70% (v/v) by mixing together bimodal or trimodal particle size distributions.<sup>1–4</sup> However, producing a latex with a multimodal particle size distribution (PSD) is more difficult than producing a monomodal product, reaction times can be long, and the stabilization of the particles at different stages during the reaction can be delicate. In addition, 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.<sup>4</sup>

Despite the industrial interest in this subject, little information is available on the synthesis of high solids content latices in the open literature,

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and most of what is available is discussed in patents rather than in scientific journals. In what follows we present a brief review of the literature in this field, and then look at the synthesis of highly concentrated latices from an experimental point of view.

If we consider classic emulsion polymerization processes (i.e., slightly water-soluble monomers, with a water-soluble free-radical initiator), then there are two basic means of creating a multimodal concentrated latex:

1. Process 1: Mixture of two or three monomodal seeds with well-defined PSD, followed by a period of growth in a semibatch reactor.
2. Process 2: Creation of a seed latex, with growth of the seed latex particles during a semibatch reaction followed by one or two nucleations of secondary (and eventually tertiary) populations.

Process 2 (creation of a seed plus *in situ* nucleation) is the most widely discussed in the literature.<sup>1,2,5</sup> Generally speaking, the secondary nucleation is provoked by the injection of a shot of surfactant and rapid addition of monomer. Chu et al.<sup>1,2</sup> used this type of process to produce concentrated bi- and trimodal terpolymer emulsions of styrene (Sty), butyl acrylate (BA), and methacrylic acid (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. These authors were able to produce latices with solids contents of 64.5%, while retaining favorable viscosities ( $\eta = 100 \text{ mPa s}^{-1}$  at a shear rate  $\dot{\gamma} = 100 \text{ s}^{-1}$ ). However, they seemed to need up to 7% surfactant with respect to the total weight of monomer to stabilize the latices. They found that nucleation occurred only when the surface coverage of the seed latex was greater than 70%, and that, like the group of Chern et al.,<sup>5</sup> the moment at which the surfactant is injected and the quantity of surfactant used are critical.

Chern et al.<sup>5</sup> looked at the creation of bimodal latices of BA and MAA (95 : 5 w/w in the polymer, respectively), but limited their polymer concentrations to 50%. Like Chu et al. above, they found that the moment the secondary nucleation occurs is critical, the later it happens, the fewer new

particles they were able to nucleate. On the other hand, they also claim to have found that the concentration of surfactant has no effect on the number of particles nucleated. This conclusion is surprising and might be a result of the dynamic light-scattering technique used to measure the particle size. In effect, even though the authors announce a maximum error of 7% in the measurement of  $d_p$  (particle diameter), it is well known that QELS (quasi-elastic light scattering) is more sensitive to larger particles, and can actually miss some of the small particles in a bimodal system.

It is also likely that when water-soluble monomers such as MAA, 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 Asua<sup>6</sup> observed that secondary nucleation can occur during the semibatch growth stage from the moment that the feed stream is sent to the reactor.

As discussed in Part I,<sup>4</sup> a number of authors studied the rheology of bimodal and trimodal latices formed by combining blends of monomodal latices of different size. High solids contents can then be obtained by evaporating the aqueous phase.<sup>4</sup> Of course, this is not an economic alternative for the production of concentrated emulsions; however, a variant that consists of combining two monomodal seeds and then polymerizing them in a semibatch reactor until the desired PSD and/or solids content are obtained is possible. For instance, Chu et al.<sup>7</sup> prepared bimodal latices in this manner, with large particles being produced *in situ* by nucleation and semibatch growth and the small particles being injected at a moment during the reaction. They avoided micellar nucleation by ensuring that the free surfactant concentration remained below the critical micelle concentration (cmc). Homogeneous nucleation was not a problem because, even though they used MMA, it was present in relatively small amounts. They found that the  $d_p$  of both the large and small particles increased during the semibatch phase of the reaction, and that the number of particles of each population decreased. This process is relatively sensitive to flocculation, and the surfactant concentration must be strictly maintained at a minimum level to stabilize the particles.

The problem with this process of blending two latices is that it is difficult to maintain a signifi-

cant difference between the sizes of the large and small particles, which is an important parameter in terms of latex viscosity. 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.<sup>4,8,9</sup> 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 Part I<sup>4</sup> suggest that we wish to maintain a ratio of large to medium particles in this range. The total solids content of a blend of seeds will obviously be determined by the solids content of the seeds. A monomodal seed of medium-size particles (e.g.,  $d_p > 250$  nm) can comfortably have a solids content of 50–55% polymer, whereas for smaller particles, the limiting solids content will be lower.<sup>10</sup> The only way to get solids contents greater than 60% from a mixture or blend of seeds is therefore to feed pure monomer plus surfactant, or a highly concentrated preemulsion (here a preemulsion is a well-mixed solution of monomer, surfactant, and water), to make the particle phase grow without adding (significantly) to the amount of water in the reactor. The problem here is to finish with the correct PSD, given that the volumetric rate of change of smaller particles is greater than that of large particles at an equivalent value of  $\bar{n}$ . Therefore, if the second population is injected rather than nucleated, one needs to add a large quantity of monomer to increase the solids content to an interesting level. Also, because the seeds of smaller particles are more dilute than seeds of larger particles, the quantity of monomer to be injected (and thus the duration of the reaction) will be greater, the smaller the  $d_p$  of the particles in the second seed is.

There are, of course, other means of producing bi- and trimodal emulsions, including miniemulsion polymerization. A number of authors have considered this means of producing high solids content latices.<sup>11–14</sup> These studies show that progress has been made in applying the technique of miniemulsions. However, this method of polymerization requires special means of agitation and/or sonication to generate the polymerizable droplets,<sup>15,16</sup> which might be difficult to produce at an industrial scale. For this reason we focus on classic emulsion polymerization in the current study.

The patent literature contains many references to processes for the production of high solids content latices. A summary of some of the more interesting applications is presented in Table I. The original patents in this area date from the 1970s,

but it is not until the 1990s that we see intense activity, at least in terms of the number of patents taken out.

The earliest patent in this list, taken out by Celanese Corporation claims solids contents in the range of 65–70% with viscosities of  $\eta \in 5000$ – $10,000$  mPa s<sup>-1</sup> (no shear rate specified). The semibatch process in question consists of an initial seed that is grown by adding a highly concentrated feed stream containing 75–94% monomer. No data are available on the PSD, but given that the monomers cited in the example are partially soluble in the water phase (MMA, VAc), it is likely that there was a fair amount of homogeneous nucleation that broadened the PSD. This process can probably be classified as a seed plus *in situ* nucleation.

Other companies have opted for the mixture of two seeds (or variants thereof). For instance, the process described in the patent to Union Carbide consists of a seeded semibatch reaction where part of the initial seed is withdrawn from the reactor during the early stages of the reaction, then reintroduced at a later time. Although not particularly practical from an industrial point of view, the patent claims that the broad, bimodal distribution produced in this manner allows them to obtain solids contents of approximately 65%, with viscosities of 1000 to 3000 mPa s<sup>-1</sup> at 1 s<sup>-1</sup>. The Rohm patent also relies on a mixture of two seeds to form a bimodal latex: either the seeds can be premixed and then swollen with a semibatch feed or the seed of smaller particles can be added continuously with the preemulsion. The quantity of each seed must be properly adjusted, and the ratio of the size of large to small particles is between 2 and 15 (rather broad). Viscosities obtained in this manner are on the order of 10,000 mPa s<sup>-1</sup> at 1 s<sup>-1</sup> for a solids content of 69.5%. The patents to BASF dating from 1994 and 1995 (U.S. 5,340,858; 5,340,859; 5,350,787; 5,350,823; 5,405,693; 5,426,146), as well as those to Zeneca and Gencorp also rely on a blend of two seeds. The BASF patents claim solids contents on the order of 65–68% with viscosities of a few hundred mPa s<sup>-1</sup>. The latter two patents are, in fact, on the materials made by a standard process rather than the process itself.

The patent to BF Goodrich claims to be able to produce solids contents of up to 75–80%, although the viscosity of these products is so high as to make them impractical (300,000 mPa s<sup>-1</sup> at 0.1 s<sup>-1</sup> for a solids content of 79%). The final particle

**Table I Patents on Multimodal, High Solids Content Latices**

| Patent Number  | Date (month.year) | To                   | Title  |
|----------------|-------------------|----------------------|--|
| FR 1.603.046   | 04.71             | Celanese Corporation | Procédé de préparation d'émulsions à haute teneur en matières solides  |
| US 4,130,523   | 12.78             | Union Carbide        | High solids latices  |
| DE 3147008     | 06.83             | Rohm GmbH            | Procédé de préparation de dispersions aqueuses bimodales de polymères à haute concentration  |
| US 5,340,858   | 08.94             | BASF                 | Aqueous polymer dispersions  |
| US 5,340,859   | 08.94             | BASF                 | Aqueous polymer dispersions  |
| US 5,350,787   | 09.94             | BASF                 | Aqueous polymer dispersions  |
| US 5,350,823   | 09.94             | BASF                 | Copolymers crosslinking at room temperature  |
| US 5,405,693   | 04.95             | BASF                 | Aqueous polymer dispersions  |
| US 5,426,146   | 06.95             | BASF                 | Aqueous polymer dispersions  |
| WO 96.11234    | 04.96             | BF Goodrich          | High solids copolymer dispersion from a latex and its use in sealants  |
| WO 96.19536    | 06.96             | Zeneca resins        | Aqueous polymer emulsions  |
| CA 2179681     | 01.97             | GenCorp Inc.         | Bimodal latex binder   |
| EP 818471.A1   | 01.98             | BASF                 | Verfahren zur Herstellung von wässrigen Polymerdispersionen mit bimodaler Teilchengrößen verteilung                                  |
| WO 98.07767    | 02.98             | BASF                 | Production of highly concentrated adhesive dispersions and their use   |
| WO 98.16560    | 04.98             | BASF                 | Method for the manufacture of low-viscosity aqueous polymer dispersions with a polymer   |
| DE 19645427 A1 | 05.98             | BASF                 | Verfahren zur Herstellung niedrigviskoser wässriger Polymerisatdispersionen mit polymodaler Verteilung der Polymerisatteilchengrößen |

size in these latices is very high for emulsion systems, with typical values being:

- from 5 to 30% (w/w) of particles with a  $d_p$  between 50 and 700 nm
- from 20 to 70% (w/w) of particles with a  $d_p$  between 700 nm and 4  $\mu\text{m}$
- from 5 to 75% (w/w) of particles with a  $d_p > 4 \mu\text{m}$

Although these values are rather high, the ratios of  $d_p$  of each population and the proportions are similar to those found to minimize the viscosity in Part I.<sup>4</sup> Their process is simple: an initial charge containing between 40 and 68% (very high for a monomodal charge) of particles with an average  $d_p > 500$  nm is placed in the reactor, and the particles are then swollen by the addition of monomer feed. The addition of monomer provokes a secondary nucleation of new particles, and limited flocculation throughout the reaction leads to

an increase in the size of the particles. It is very likely that this process is difficult to master in that it will be sensitive to problems of flocculation, and it is also likely that the PSD is not very well controlled.

All of the above-mentioned processes rely on:

- well-adapted (time-varying) feed profiles of preemulsions and/or initiator to control particle growth and secondary nucleation.
- an equilibrium between homogeneous nucleation and limited flocculation.
- specific surfactant technology (Dowfax surfactants are widely cited).
- specific initiators ( $\text{H}_2\text{O}_2$  plus an activator, or persulfate initiators seem to be the most common).

Generally speaking, these early patents demonstrate the feasibility and interest in producing bimodal latices, but do not help to understand

how to control the PSD. What is clear is that it is the control of the PSD and the relationship between the PSD and the viscosity that are important (see also Part I<sup>4</sup>).

The remaining BASF patents (EP 818471.A1, WO 98.07767, WO 98.16560, DE 19645427 A1) do not rely on the use of several dispersions. Patent WO 98.07767 does not specifically refer to multimodal latices. However, given that the final solids content is on the order of 65–70% and Brookfield viscosities are between 600 and 3500 mPa s<sup>-1</sup>, it is highly likely that the PSD is at least bimodal. This is possible for several reasons:

- the initial charge does not contain ionic surfactants but does contain water-soluble salts, both of which point to the formation of large particles during an initial batch nucleation step.
- the initiator feed during semibatch operation is time varying and carefully chosen, so a sudden increase in the free-radical concentration could provoke secondary nucleation.
- the monomer feed rates are well controlled and an increase in the monomer concentration, coupled with a high concentration of radicals, could provoke secondary nucleation. In addition, the monomers specified are relatively water soluble.

On the other hand, patent WO 98.16560 clearly indicates that the final latex has a multimodal PSD with low viscosity. In this case, the process uses functional monomers (e.g., AA) and the pH is varied throughout the reaction. Varying the pH leads to a modification of the surface charges on the particles, and thus the electrostatic stabilization of the particles and the water solubility of the functional monomers. The formation of water-soluble polymers (e.g., PAA) can help to favor either homogeneous or micellar nucleation, and thus lead to the formation of a multimodal PSD.

Although patent DE 19645427 A1 is similar to the preceding one, only the composition of the polymers seems to change for different types of applications. The final patent, EP 818471.A1, is the only one that we have found that claims to use a miniemulsion that is mixed with an initial seed of PS to form a bimodal latex. BASF claims it is possible to obtain solids contents of 60–70% with viscosities of 180 to 660 mPa s<sup>-1</sup> at a shear rate of 250 s<sup>-1</sup>.

It is clear from the scientific and patent literature that it is possible to produce high solids

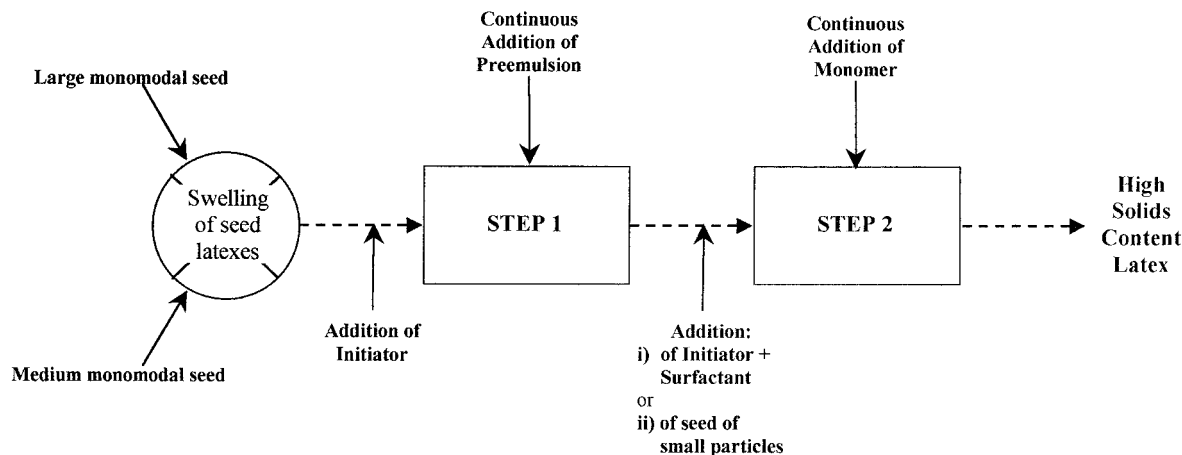
content latexes with a multimodal PSD, either by a blend of seed latices that are then grown to the desired point or by secondary nucleation in the presence of larger particles, or eventually by a combination of the two. The processes described in the patents are fairly complex and seem to rely on homogeneous nucleation, and occasionally controlled flocculation, to tailor the PSD. It is not clear to what extent the results of these processes are reproducible: it is one thing to design a process to broaden the PSD of a latex; it is something entirely different to be able to really control this broadening.

Our objective in the rest of this report is 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% AA ( $T_g \approx -30^\circ\text{C}$ ) either by a combination of seeds or by nucleation in the presence of an initial dispersion. To do so we set out to develop a mechanistic understanding of how both to mix and grow the seed latices (see Part II of this series), to produce high solids latices by the “blending” process, and to attempt to develop a systematic view of how to perform the secondary nucleation in a reproducible manner for the second process.

## EXPERIMENTAL

The composition of all of the latices used in this study was (by weight) 78% BA, 19.5% MMA, and 2.5% AA. All materials were obtained from Acros Organics (Geel, Belgium) and used as received. The anionic surfactant (TA) used in this study was Disponil<sup>®</sup> FES 32 IS (sodium salt of the sulfate of a polyglycol ether) and the nonionic surfactant (TN) was Disponil<sup>®</sup> A 3065 (mixture of linear ethoxylated fatty acids). Both surfactants were supplied by Cognis (France) and used as received. TA contains 32% and TN 65% by weight active material. (Note that in the recipes listed in the tables below, the quantity of surfactant always refers to the mass of active material.) The initiator was ammonium persulfate (APS).

Seed latices were prepared as described in Part II.<sup>10</sup> Medium-size seeds were on the order of 250 nm in diameter and large seeds were 500 nm in diameter. Both seed latices, with a volume solids content of 50%, were monomodal [as far as can be told with a fixed-angle QELS Malvern Lo-C (Malvern Instruments); see Schneider and McKenna<sup>17</sup> for difficulties associated with the mea-



**Figure 1** Schematic of processes for production of high solids content latices.

surement of the particle size distribution]. 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.

The average particle sizes of the latices were measured using a Malvern Lo-C quasi-elastic light-scattering device for the monomodal products and a capillary hydrodynamic fractionation (CHDF) for the bi- and trimodal blends.

## PRODUCTION OF HIGH SOLIDS CONTENT LATICES

The processes considered here consist of either of the following:

1. Process 1: mixing two or three seeds of different size particles (see Part II<sup>10</sup>) at concentrations of 50% polymer (v/v) for large ( $\geq 500$  nm) and medium ( $\approx 250$  nm) seeds, and of 35–45% for small ( $\leq 100$  nm) seeds, and polymerizing the mixture in a semibatch reaction to solids contents of up to 65% (v/v).
2. Process 2: creating a population of small particles *in situ* by injecting surfactant, initiator, and monomer into a latex of larger particles.

These two alternatives are summarized in Figure 1, and can be used to create either bimodal or trimodal latices. In the first case, the medium

seed is not added before STEP 1, and we add and swell only the large particles. The appearance of small particles, whether by seed or by nucleation, is always accompanied by an addition of monomer. This can be done in the form of either a preemulsion (preemulsified mixture of monomer, surfactant, and less than 15% water) or a pure monomer. The use of a preemulsion has the advantage of stabilizing the emulsion because it contains surfactant. On the other hand, this same surfactant can also help promote the stabilization of homogeneously nucleated particles. Also, the fact that the preemulsion contains a small amount of water means that adding it dilutes the latex and thus slows down the concentration of the emulsion. The choice of whether to add pure monomer or a preemulsion will thus be a trade-off between the need to stabilize the latex, on the one hand, and control over the PSD and speed of concentration, on the other.

In Figure 1, STEP 1 and STEP 2 refer to semi-batch polymerizations in which the particles grow. As was the case in the seed-preparation stage,<sup>10</sup> it is necessary to correctly adjust the monomer and stabilizer feed flow rates, as well as the radical flux. This will be especially delicate in the case of bi- and trimodal latices, in that we do not know *a priori* what portion of the added monomer is consumed by the small particles. It has been shown that, at least for this system of monomer, the rate of polymerization seems to depend strongly on the size of the particles.<sup>18</sup> Furthermore, for a given final solids content, the less monomer we add in STEP 2, the higher the solids content must be after STEP 1. Also, the ratio between the amounts of monomer added in STEP

1 and STEP 2 determines the ratio of the diameters of the different particle populations in the latex, which in turn exerts a strong influence on its viscosity.<sup>4</sup>

Let us look at each of the different steps outlined in Figure 1.

### Process 1: Preparation of a Large Seed and Mixing with a Smaller Seed (STEP 1)

In a bimodal latex, the ratio of the  $d_p$  of each population and its relative quantity is important in terms of maintaining control over the final viscosity. As mentioned above, the optimal ratio of large to small particle diameter in a bimodal latex is between 6 and 8, with a volume fraction of approximately 80% large particles (with respect to total polymer content). The difficulty is to obtain high solids content in an acceptable period of time. If we mix large (e.g.,  $d_p \geq 600$  nm) particles with a seed small enough to maintain this ratio, the addition of the small seed would dilute the mixture, and thus impose a long reaction time in STEP 2. Adding a larger, more concentrated seed would shorten reaction times, but mean that the particle size ratio would be more on the order of 3 to 4, rather than the 6–8 that corresponds to the lower viscosity. In the interest of maintaining reasonable reaction times, we will concentrate on this second option, and hope that we can produce latices with acceptable viscosities.

#### Preparation of the Large Particle Seed

*Preliminary Swelling.* Before beginning the semibatch addition of the preemulsion, it is preferable to swell the seed latex/latices with approximately 5% (with respect to polymer in seeds) monomer. This allows us to begin the semibatch stage more or less at a steady state (in Part II, it was found that maintaining an instantaneous conversion of  $\pm 95\%$  allowed us to avoid accumulation of monomer and to maintain homogeneous nucleation at an acceptable level<sup>10</sup>). Also, it is well known that it is easier to add monomer to a slightly swollen latex than it is to a “dry” one, so preswelling avoids the risk of the undesirable accumulation of monomer at the beginning of the feed step.

*Initiator Injection.* Although seemingly trivial, the injection of initiator into the reactor at the beginning of the feed step (just before STEP 1 in Fig. 1) turns out to be important. If the initiator is

added before the semibatch feed begins, in a small quantity of water, it was found that it is better to inject the initiator solution into the swollen latex before raising the temperature of the reactor to 70°C. If we inject initiator into the hot reactor, it does not have time to be evenly dispersed, and a rapid decomposition in a small zone leads to an increase in the local concentration of initiator and thus radicals. This increase in radical concentration provokes a local nucleation of a large number of small particles. However, because there is not enough surfactant to stabilize the new particles at the injection point, we get a local breakdown of stability and subsequent formation of coagulum. One might think that this is also attributable in part to an increase in the local ionic strength resulting from the formation of negatively charged  $\text{SO}_4^{\bullet-}$  radicals. However, it should be recalled that the electronic double layer expands as the temperature increases, and the effect of generating these negatively charged radicals would be compensated for by the temperature. In addition, we tested this hypothesis by adding enough NaCl solution at 70°C to reproduce the same rapid variation in ionic strength after the completion of a reaction, and observed absolutely no formation of coagulum. Therefore, it can be concluded that variations in the ionic strength are not responsible for the difficulties encountered when injecting the initiator at high temperature.

These problems can be partially circumvented by adding a very dilute solution of initiator throughout the semibatch stage in the preemulsion (at the risk of accumulating it during the reaction).

If we preswell a seed containing 500-nm particles, our objective is to grow the latex until  $d_p$  is between 600 and 700 nm at a solids content of 55–60%. As shown in Part II,<sup>10</sup> it is unwise to attempt to increase the solids content of a monomodal latex much beyond this point because of problems associated with the interpenetration of the electronic double layers of the particles. As in the seed-preparation step, we wanted to maintain total control (insofar as this is possible) over the number of particles to optimize the rheological properties of the final product. These particles will then be combined with a population of smaller particles to form a bimodal latex.

The large seed latex used in all of these experiments is SEM21, a monomodal latex of particles with a  $d_p$  of 500 nm and a solids content of 50% (w/w). The recipe for the preparation of SEM 21 is recalled in Table II. The recipes for increasing the

**Table II Preparation of Large Seed Latex SEM21**

| Seed Formation Recipe                         |                      | Preemulsion Recipe                 |                      |
|---|----------------------|------------------------------------|----------------------|
| Duration (min)                                | 48                   | Duration (min)                     | 436                  |
| TA  | 0.01                 | TN                                 | 15.8                 |
| TN  | 3.5                  | BA                                 | 24 + 6.1             |
| BA  | 80                   | MMA                                | 231 + 1.5            |
| MMA   | 20                   | AA                                 | 34 + 0.2             |
| NaHCO <sub>3</sub>                            | 1.9                  | APS                                | 2                    |
| APS   | 1.8                  | Characteristics at end of reaction |                      |
| Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> | —                    | Solids wt %                        | 50                   |
| T (°C)  | 70                   | $d_p$                              | 500                  |
| Characteristics at end of seed period         |                      | $Z_{dp}$                           | 0.14                 |
| $d_p$   | 221                  | $N_p$                              | $1.9 \times 10^{16}$ |
| $Z_{dp}$                                      | 0.07                 |                                    |                      |
| $N_p$   | $1.7 \times 10^{16}$ |                                    |                      |

size and solids content of the seed latex are listed in Table III.

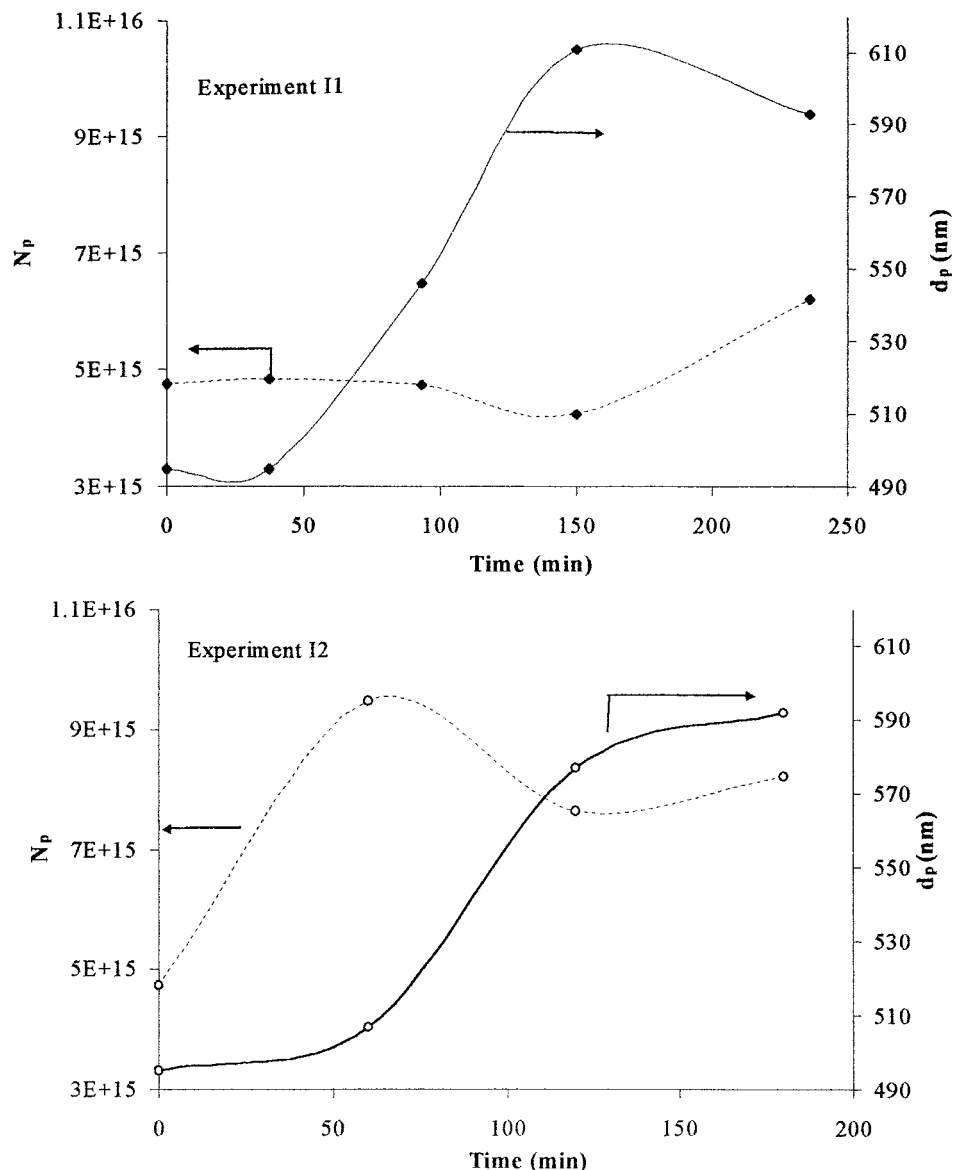
If we compare the performance of runs I1 and I2 (see Fig. 2), despite a small amount of nucleation that appears to occur at the beginning of each run, the particles attained  $d_p = 593$  nm for I2 without a significant amount of (observable) nucleation or coagulation near the end of the experiment, whereas for run I1 this is not the case.

Other than this, the two runs were very similar. The concentration of TN in the preemulsion is high enough to maintain a surfactant surface coverage of between 80 and 90% in both cases (enough to comfortably stabilize the existing particles, without creating micelles), and the conversion remained very close to 95% throughout the experiments. The only other difference was the solids content, which increased to 58.7% for I2

**Table III Recipes for Increasing the Solid Content of Large Seeds**

| STEP 1                            | I1                   | I2                   | I3                   | I5                   | I6                   | I8   |
|-----------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|------|
| Blend of seeds                    |                      |                      |                      |                      |                      |      |
| Total mass (g)                    | 499                  | 999                  | 1000                 | 496                  | 398                  | 499  |
| wt % large                        | 100                  | 100                  | 100                  | 100                  | 100                  | 91   |
| wt % medium                       | —                    | —                    | —                    | —                    | —                    | 9    |
| Mass monomer used to swell seed   | 13                   | 26                   | 26                   | 12.9                 | 10.4                 | 15   |
| APS solution                      |                      |                      |                      |                      |                      |      |
| Mass H <sub>2</sub> O (g)         | 9.5                  | 19.1                 | 18.7                 | 9.3                  | 9.1                  | 18.1 |
| Mass APS (g)                      | 0.55                 | 1.12                 | 1.13                 | 0.56                 | 0.56                 | 1.18 |
| Preemulsion composition           |                      |                      |                      |                      |                      |      |
| Total mass (g)                    | 435                  | 538                  | 789                  | 535                  | 571                  | 823  |
| Mass monomer (g)                  | 326                  | 404                  | 600                  | 405                  | 435                  | 823  |
| Mass TN (g)                       | 8.05                 | 7.37                 | 8.39                 | 11.32                | 7.14                 | 8.72 |
| Mass APS (g)                      | 0.67                 | 0.8                  | 1.2                  | 0                    | 0                    | 0    |
| Feed duration (min)               | 308                  | 195                  | 307                  | 308                  | 308                  | 424  |
| Particle characteristics          |                      |                      |                      |                      |                      |      |
| Theoretical                       |                      |                      |                      |                      |                      |      |
| $N_p$                             | $4.1 \times 10^{15}$ | $8.2 \times 10^{15}$ | $8.2 \times 10^{15}$ | $4.1 \times 10^{15}$ | $3.3 \times 10^{15}$ | —    |
| $d_p$ (nm)                        | 632                  | 584                  | 623                  | 660                  | 703                  | —    |
| Measured particle characteristics |                      |                      |                      |                      |                      |      |
| $N_p$                             | $4.7 \times 10^{15}$ | $7.6 \times 10^{15}$ | —                    | $5.2 \times 10^{15}$ | $5.1 \times 10^{15}$ | —    |
| $d_p$ (nm)                        | 593                  | 592                  | —                    | 607                  | 607                  | —    |





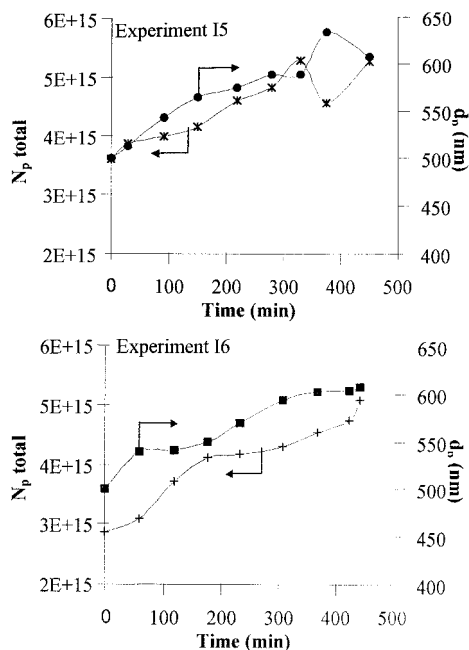
**Figure 2** Evolution of particle size and number for experiments I1 and I2. Final solids content: 61.5% for I1 and 58.7% for I2.

and to 61.5% for I1. However, the particles were slightly smaller than projected in I1 (the experiment ran longer and there was 3% more polymer formed) because of the secondary nucleation. To circumvent this, two alternatives were tested:

1. I3 reproduced run I1, but with a lower concentration of TN in the preemulsion, to avoid stabilizing the homogeneously nucleated particles.
2. I5 reproduced run I1, but no APS was added during the semibatch period.

As indicated in Table III, I3 terminated in total flocculation. In fact, I3 flocculated near the end of the experiment at 61% total solids content, which indicates that there is not a large excess of TN in run I1, and that we should maintain the same level of TN in the rest of the experiments.

Reduction of the APS in the preemulsion did not seem to pose a particular problem. The conversion remained well above 90% throughout the semibatch phase, so we were generating an acceptable flux of free radicals. In fact, we were able to add preemulsion for a few minutes more than



**Figure 3** Evolution of  $N_p$  and  $d_p$  for runs I5 and I6. Conditions are similar to those for I1 with no APS in the preemulsion. Final solids content: 63.2%.

we did in I1, thereby attaining a solids content of over 63% (see Fig. 3). This last point suggests that we were experiencing some homogeneous nucleation. As shown in Table III, the “theoretical” particle diameter (i.e., that which we would obtain if  $N_p$  remained unchanged with respect to that of the seed latex) was 660 nm, whereas the final value at the end of run I5 was “only” 607 nm. Moreover, 63% solids was a fairly high level to attain without having a small amount of small particles. Given that the final size was measured with a fixed-angle QELS apparatus, it is entirely possible that the device did not “see” the small particles present in the latex. Because the volume of polymers in the particle phase is proportional to the cube of  $d_p$ , a mass balance suggests that, in fact, over half of the polymer produced during the semibatch phase of I5 was not in the large particles that grew from those present in the seed.

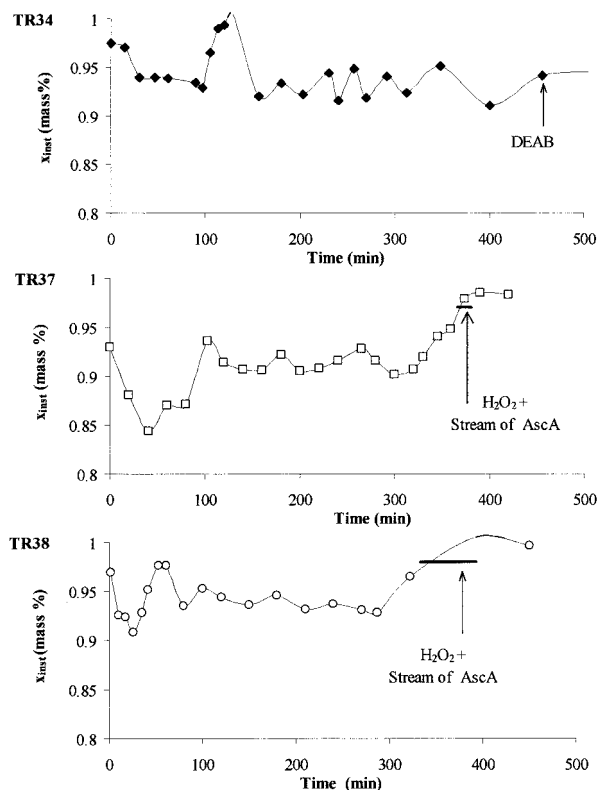
Therefore, neither of the two solutions proposed above seems to help us resolve the problem of homogeneous nucleation, so we will be obliged to do our best to limit its impact on the quality of the intermediate latices and use recipe I5 to prepare the large particle portion of the mixture.

#### Growth of a Mixture of Two Seeds

The results of a rheological study<sup>4</sup> suggest that the viscosity will be lowest for volume fractions of

large particles on the order of 0.8. Given that the volume fraction of medium and small particles increases more rapidly than that of the larger particles, we fixed the composition of the mixture to be preswollen at 91% large particles and 9% medium particles. Although it would be interesting to explore a range of other mixtures, we limited our study to this one composition.

We used these results to maintain the surface coverage of the latex at between 80 and 90%, and did not feed any APS in with the preemulsion. As we can see from the results of experiment I8 in Table III, simply by polymerizing the bimodal mixture of large and small seeds, we were able to achieve a solids content of 65%. Unfortunately, the viscosity of this mixture was very high (the final latex had a viscosity of 30,000 mPa s<sup>-1</sup> at a shear rate of  $\dot{\gamma} = 20 \text{ s}^{-1}$ ). The reason that the viscosity was so high is probably attributable to a poorly adjusted PSD. Although it is likely that we were not far from the optimal proportion of large to small particles, it is not at all clear what the PSD was in this latex. Unfortunately, no information is available on the evolution of the PSD of run I8; however, as an example, we can consider



**Figure 4** Evolution of the PSD for step 1 of run TR7 (Table IV) as a function of time, as measured by CHDF.

STEP 1 of run TR7, which is similar to run I8. This portion of the experiment led to the production of a latex with a final solids content of 68% (66 parts polymer, 2 parts surfactant), with a moderate viscosity of  $2500 \text{ mPa s}^{-1}$  at a shear rate of  $\dot{\gamma} = 20 \text{ s}^{-1}$ . However, there was also a moderate amount of coagulum formation, with 1000 ppm of coagulum being formed during the reaction. Figure 4 shows the evolution of the PSD during STEP 1 of TR7 as measured by CHDF, which provides a good indication of how the PSD evolves as a function of time. It can be seen that the large particles grow from 500 to around 650 nm (volume increase of just over double), and that the small particles grow from 270 to about 430 nm (volume increase of a factor of 4). Note that this increase in volume of each population means that the large particles represent approximately 83% of the total volume of polymer in the latex, close to the rheological optimum. On the other hand, the ratio of particle size is not particularly favorable ( $d_{p,L}/d_{p,S} = 1.5$  instead of 6–8).

The experiments presented here are only an example of several runs that yielded similar results. It can be seen that by correctly blending latices of different sizes, we can grow the particles and concentration of the dispersion to solids contents well above 65%. These results also suggest that homogeneous nucleation has a significant impact on the polymerization during STEP 1, regardless of whether we are attempting to concentrate a single monomodal latex or a blend of two. Small amounts of homogeneous nucleation seem unavoidable with the recipes used here, but clearly it needs to be minimized because breakdown of the overall latex stability seems to be associated with conditions that provoke large amounts of secondary nucleation.

### Process 2: *In Situ* Nucleation of Small Particles (STEP 2)

In this step, we create a second or third population of small particles, to attempt to further increase the solids content of the latex issued from STEP 1. In theory this should help to decrease the viscosity of the latex, or at least allow us to increase the solids content without dramatically increasing the viscosity.<sup>3,4</sup>

After STEP 1, a solution of surfactant, water, and initiator is injected over a short period of between 2 and 7 min into a latex prepared according to the recipes developed in the previous section. Once this injection is complete, an injection

of a mixture of pure monomer is slowly added to the reactor over the course of 30–150 min, always ensuring that we remain under starved conditions. The recipes are summarized in Table IV.

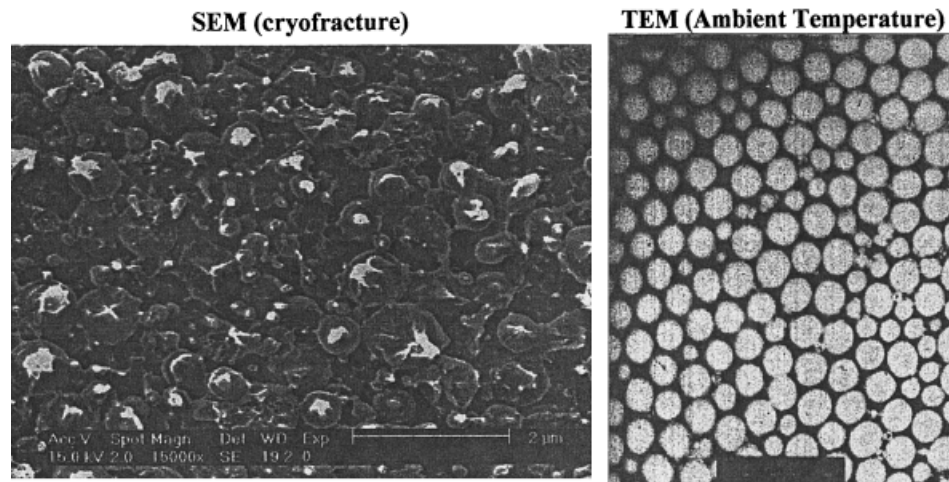
As an example of some of the difficulties encountered during the analysis of these experiments, consider the results shown in Figure 4 and Figure 5. Here we see the analysis of the PSD of different samples of the final latex issued from run I8 using CHDF. Apparently these measurements are not very reproducible. In fact, one of the measurements does not even indicate the presence of any small particles with a  $d_p$  less than 200 nm, particles that are clearly visible on the micrographs in Figure 5. Of course the micrographs also give a less than perfect representation of the granulometry of the latex as well, given that the final  $T_g$  of latex TR7 is approximately  $-40^\circ\text{C}$ . In the case of the cryofracture SEM, the particles are slightly drawn, even though the fracturing was done at  $-90^\circ\text{C}$ . The TEM images were taken on a sample at ambient temperature, so the latex has formed a film. Therefore, as suggested in Schneider and McKenna,<sup>17</sup> care must be taken in using CHDF (or any other technique) in the analysis of multimodal latices. In what follows, we will use an average of at least two measurements of CHDF per sample (unless otherwise stated), to attempt to attenuate the importance of eventual variability on the PSD measurements. This, of course, makes it difficult to judge the reproducibility of these experiments.

### Choice of Surfactants

The logical choice for the renucleation of particles in the last step would be to use an anionic surfactant (TA). However, as can be seen in the final results of runs TR10, TR12, TR13, and TR14, using TA alone leads to the production of very viscous ( $\geq 50,000 \text{ mPa s}^{-1}$  at  $20 \text{ s}^{-1}$ ) latices; in fact, in certain cases the viscosity was too high to allow it to be measured with our viscosimeter. Interestingly enough, in these runs, the latices that are clearly bimodal before the injection of TA develop a monomodal PSD immediately after the injection of surfactant, and remain so throughout STEP 2. This is illustrated for runs TR13 and TR14 in Figure 6. We can verify that this observation is not an artifact of the CHDF measurements because we cannot detect any particles smaller than 200 nm in the TEM micrographs shown in the same figure. It appears that the injection of surfactant actually produces a con-

**Table IV Recipes for *In Situ* Nucleation of Small Particles**

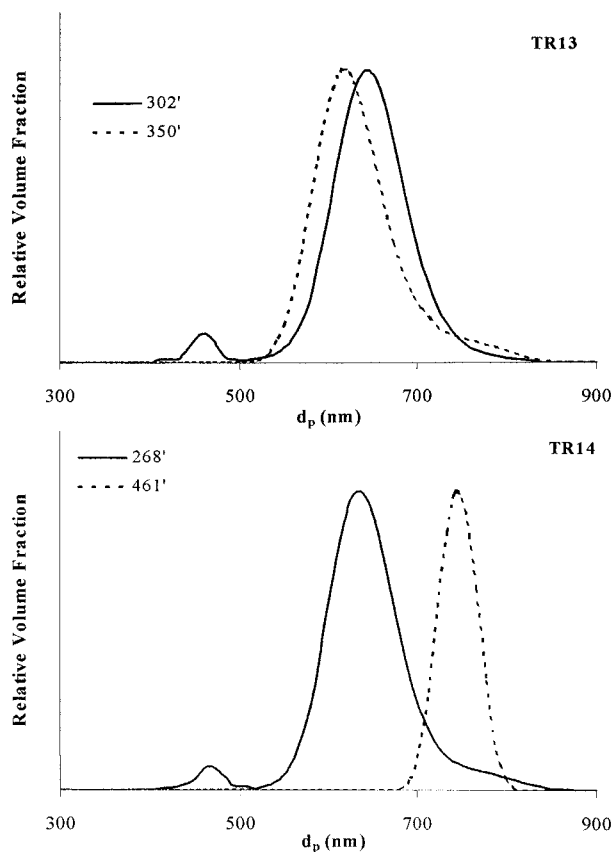
| STEP 1   | TR7  | TR10    | TR12    | TR13    | TR14    | TR17 | TR19 | TR20 | TR21 | TR22 | TR23b | TR26 |
|--|------|---------|---------|---------|---------|------|------|------|------|------|-------|------|
| Blend of seeds   |      |         |         |         |         |      |      |      |      |      |       |      |
| Total mass (g)   | 498  | 498     | 494     | 495     | 502     | 494  | 494  | 502  | 502  | 506  | 496   | 999  |
| wt % large   | 91   | 91      | 91      | 91      | 91      | 91   | 91   | 91   | 91   | 91   | 91    | 100  |
| wt % medium  | 9    | 9       | 9       | 9       | 9       | 9    | 9    | 9    | 9    | 9    | 9     | —    |
| Mass monomer used to swell seed                                    | 13   | 13.2    | 13      | 13.6    | 13.7    | 13   | 13   | 13.4 | 13.4 | 13.9 | 13.4  | 26   |
| APS solution   |      |         |         |         |         |      |      |      |      |      |       |      |
| Mass H <sub>2</sub> O (g)  | 28.6 | 20.6    | 17.9    | 17.8    | 18.0    | 27.7 | 7.6  | 7.43 | 7.43 | 7.32 | 17.73 | 19.0 |
| Mass APS (g)   | 1.05 | 1.09    | 1.07    | 1.07    | 1.07    | 1.03 | 1.0  | 1.03 | 1.03 | 1.02 | 1.04  | 1.1  |
| Preemulsion composition  |      |         |         |         |         |      |      |      |      |      |       |      |
| Total mass (g)   | 913  | 889     | 817     | 828     | 833     | 914  | 455  | 439  | 439  | 437  | 838   | 538  |
| Mass monomer (g)   | 680  | 665     | 613     | 620     | 624     | 680  | 346  | 334  | 334  | 333  | 621   | 404  |
| Mass TN (g)  | 16.6 | 9.6     | 8.8     | 8.86    | 9.0     | 16.7 | 8.51 | 8.25 | 8.25 | 8.18 | 8.79  | 7.37 |
| Feed duration (min)  | 540  | 510     | 312     | 311     | 332     | 484  | 194  | 195  | 195  | 220  | 305   | 190  |
| Feed flow (g/min)  | 1.69 | 1.74    | 2.62    | 2.66    | 2.51    | 1.89 | 2.35 | 2.25 | 2.25 | 1.99 | 2.63  | 2.82 |
| STEP 2   |      |         |         |         |         |      |      |      |      |      |       |      |
| Surfactant injection   |      |         |         |         |         |      |      |      |      |      |       |      |
| Total mass (g)   | 56.0 | 34.7    | 34      | 34      | 34.7    | 56.9 | 42.3 | 42.8 | 42.8 | 48.0 | 56.9  | 92   |
| Mass TA (g)  | 4.96 | 4.9     | 9.3     | 4.76    | 3.13    | 4.95 | 3.68 | 3.74 | 3.74 | 10.0 | 4.86  | 18.2 |
| Mass TN (g)  | 8.83 | —       | —       | —       | —       | 8.89 | 6.74 | 6.79 | 6.79 | 6.81 | 8.87  | 21.9 |
| Mass APS (g)   | 0.17 | 0.18    | 0.18    | 0.18    | 0.17    | 0.18 | 0.17 | 0.17 | 0.17 | 0.18 | 0.17  | 0.32 |
| Feed duration (min)  | 2    | 2       | 2       | 4       | 4       | 7    | 5    | 5    | 5    | 2    | 7     | 2    |
| Monomer injection  |      |         |         |         |         |      |      |      |      |      |       |      |
| Total mass (g)   | 164  | 246     | 158     | 158     | 167     | 163  | 147  | 148  | 184  | 156  | 162   | 400  |
| Feed flow (g/min)  | 2.05 | 4.92    | 4.05    | 3.86    | 3.89    | 1.9  | 4.91 | 1.51 | 1.56 | 1.38 | 3.88  | 2.1  |
| Feed duration (min)  | 80   | 50      | 39      | 41      | 43      | 86   | 30   | 98   | 118  | 113  | 42    | 190  |
| Duration of finishing period (min)                                 | 70   | 30      | 60      | 60      | 80      | 40   | 60   | 60   | 60   | 70   | 70    | 70   |
| Theoretical polymer content (wt %)                                 | 66.1 | 68.9    | 67.2    | 67.2    | 67.3    | 66.1 | 64.9 | 64.7 | 65.8 | 64.6 | 66.3  | 64.1 |
| Total surfactant content (wt %)                                    | 2.06 | 1.09    | 1.18    | 0.88    | 0.77    | 2.08 | 1.98 | 1.99 | 1.58 | 2.14 | 1.43  | 2.29 |
| Apparent viscosity at 20 s <sup>-1</sup><br>(mPa s <sup>-1</sup> ) | 2500 | >50,000 | >50,000 | >50,000 | >50,000 | 7500 | 5400 | 1000 | 9000 | 1700 | 8000  | 2000 |
| Quantity of coagulum (ppm)   | 1000 | 20,000  | 20,000  | 20,000  | 20,000  | 1000 | 700  | 650  | 750  | 700  | 5000  | 600  |



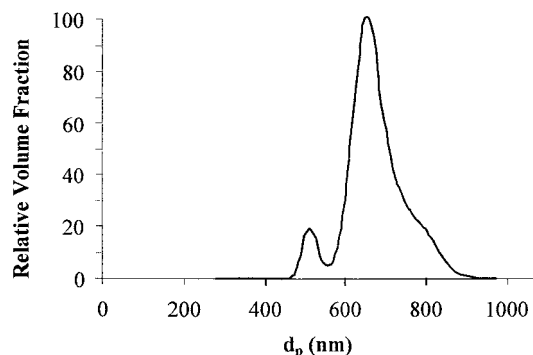
**Figure 5** Cryofractured SEM micrographs and TEM images for the final latex of run TR7, comparable to CHDF results in Figure 4.

trolled flocculation in the latex, especially at lower TA concentrations, and this modification of the PSD is accompanied by the increase in viscosity noted above. This is not surprising, given that it has been clearly demonstrated that, all other things being equal, the viscosity of a truly bimodal latex will be lower than that of a monomodal latex with the same solids content. Increasing the concentration of TA alone will, of course, favor the compression of the electronic double layer, and thus slightly reduce the electrostatic repulsion between large particles, while at the same time increasing the number of small particles that are nucleated. These events would reduce the stability of the latex, and to restore a certain level of stability, either the large particles could flocculate onto each other (thus creating a coagulum) or the small particles could flocculate either onto other small particles or onto the larger ones.

Changing the composition of the surfactant, injected to create the small population, changes this result. For instance, the only difference between run TR23B and run TR13 is that both TA and TN are added to nucleate small particles (same amount of TA in both, but an additional amount of TN in TR23B). As we can see from comparing Figure 7 to Figure 6, even though the CHDF does not detect small particles (which can be seen in TEM images not shown here), it does detect the medium-size particles issued from STEP 1 for TR23B. In addition, as we can see from Table IV, the viscosity of TR23B, although not negligible, is significantly lower than that of



**Figure 6** Evolution of the PSD of latices issued from step 1 of runs TR13 and TR14, before and after injection of TA surfactant, to create small particles. In both cases, secondary nucleation appears to have destabilized the latex and caused the smaller particles to flocculate onto the larger ones.



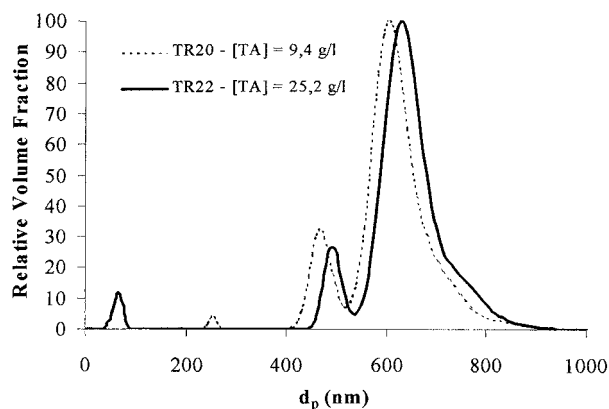
**Figure 7** CHDF analysis of the PSD of TR23B *after* injection of mixed surfactants to nucleate small particles. Unlike the case presented in Figure 6, renucleation with mixed surfactant does not provoke nearly as much limited flocculation, and the population of medium-size particles remains visible in the PSD analysis.

TR13, and we form only a fraction of the amount of coagulum in the TR23B. Thus, the presence of TN seems to significantly modify the stability of the system. It is possible that the addition of TN to the mixture changes the balance between electrostatic and steric stabilization by causing the TA already present to be redistributed in the system, possibly into the aqueous phase, where the latter would help to promote renucleation. The choice of how much TA and TN to add (because it is clear that we cannot add TA alone, and that adding TN alone will not necessarily lead to nucleation; see, e.g., Part II<sup>10</sup>) is a difficult one to make. For instance, if we compare TR20 and TR22 (2.5 times more TA in TR22), we can see from Figure 8 that the higher the concentration in TA, the smaller the particles that are nucleated. Aside from that, this factor does not seem to exert an important influence on the formation of coagulum (about the same for both reactions), nor on the viscosity (slightly higher for TR22, but still lower than that observed for the previous reactions).

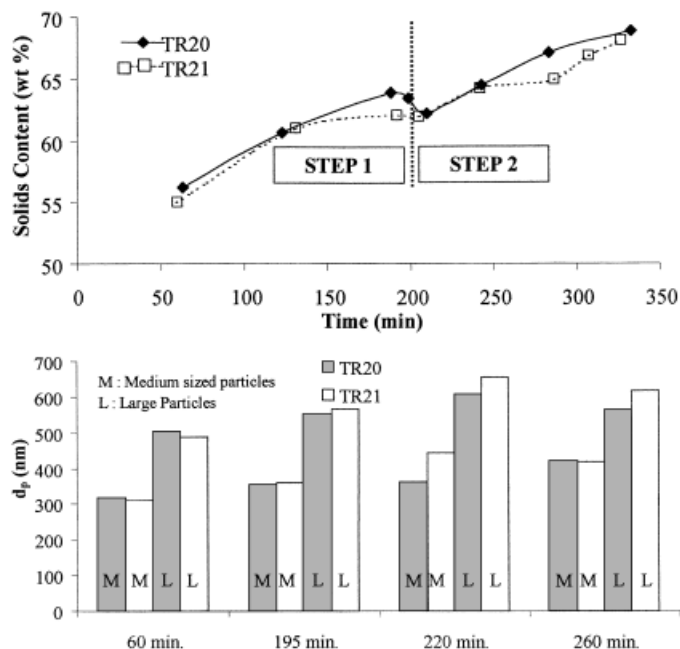
As we mentioned above, reproducibility can be a problem. For instance, TR20 and TR21 are two runs with the same composition and similar modes of operation, with the difference that the quantity of pure monomer added during the second step of the runs is slightly lower in TR20. Nevertheless, the rate of addition of monomer in the two experiments is similar, so we could expect to see similar behavior during most of the reaction. As we can see from Figure 9, the profiles of conversion and solids content seem to be reproducible, and, insofar as we can have confidence in

the exactitude of the measurements of the CHDF, the evolution of the characteristic value of  $d_p$  for the medium and large populations also seems to be reproducible; however, the CHDF did not detect the small particles nucleated during STEP 2 that we can see in the TEM micrographs. The results of the viscosity measurements led us to believe that somewhere during STEP 2, there is a difference in the granulometry of the small particles. In effect, the viscosity at  $20 \text{ s}^{-1}$  of TR21 is  $9000 \text{ mPa s}^{-1}$ , whereas that of TR20 is only  $1000 \text{ mPa s}^{-1}$ . Of course, the solids content of TR21 is approximately 1% higher than that of TR20, and it was shown in Part I<sup>4</sup> that the viscosity is sensitive to changes in this parameter at high solids content. Nevertheless, similar fluctuations have been observed in otherwise identical experiments. For example, TR7 and TR17 are nominally identical, although their viscosities varied by a factor of 3 for the same solids content (66.1%). The viscosity of TR17 is  $7500 \text{ mPa s}^{-1}$  at a shear rate of  $20 \text{ s}^{-1}$ , and that of TR7 is 2500. Note that the solids content of TR21 is just under 66%, but that its viscosity is  $9000 \text{ mPa s}^{-1}$ .

These results underline the point made above: the viscosity and, to a large extent, the stability and formation of coagulum in these systems are basically governed by some secondary nucleation process. Given the complex nature of the real PSD of the latices produced here, coupled with the difficulty that we had in measuring the exact PSD with certainty, it is very difficult to offer absolute proof for this point. Nevertheless, there is enough evidence to help infer that this is the case.



**Figure 8** PSD of runs TR20 and TR22. Both runs were done with mixed surfactant injection at the beginning of step 2.



**Figure 9** Reproducibility of the kinetics and granulometry of runs TR20 and TR21.

### ***Influence of Monomer Flow Rate in STEP 2***

It is difficult to determine whether the flow rate of monomer in STEP 2 is important. Indeed, one might expect that a high flow rate could lead to a higher concentration of MMA in the water phase, and thus to an increase in the amount of homogeneous nucleation that occurs. Increasing the concentration of MMA in the water phase also helps to increase the amount of micellar nucleation taking place, given that the oligoradicals formed in the aqueous phase cannot exceed the critical length for entry into the particles, but can also be captured by micelles (or enter into the particles). The number of particles formed by micellar nucleation is directly proportional to the number of primary particles. It is also important to consider the partitioning of the monomers between the aqueous phase and the droplets: if the monomer fed to the reactor does not enter rapidly into the particles, then the flux of newly formed particles will be higher than that if it does.

If we consider runs TR19 and TR20, it can be seen that even when the composition of the feed stream during STEP 2 is identical, the fact that we reduced the flow rate of monomer from 4.9 to 1.5 g/min in TR20 corresponds to a reduction in the viscosity at 20 s<sup>-1</sup> (1000 versus 5400 mPa s<sup>-1</sup>). A similar observation can be made if we compare runs TR7 and TR8, where increasing the

flow rate from 2.1 g/min in TR7 to 6.7 g/min in TR8 corresponds to a viscosity increase from 2500 to 7000 mPa s<sup>-1</sup> at 20 s<sup>-1</sup>. On the other hand, TR7 and TR17, which have the same recipes and flow rates, show similar differences in viscosity from one run to the next. More work could be done on this point in the future.

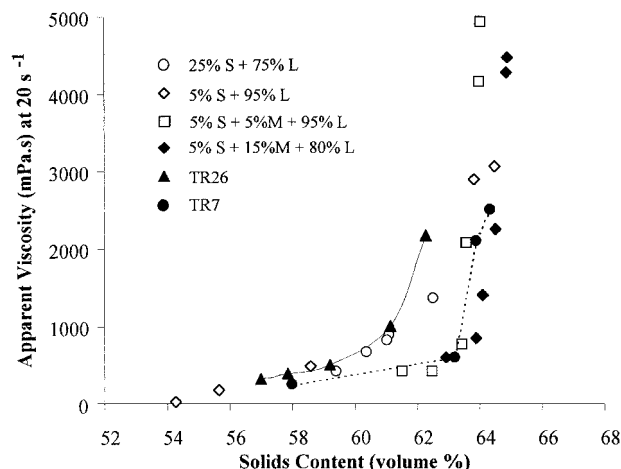
### **Latex Viscosity**

Of the trimodal latexes produced here, TR7 and TR26 seem to be the most interesting in terms of concentration and viscosity. According to the analysis of the PSD (combination of CHDF and TEM) of TR7 presented above, the PSD of this trimodal latex contains:

- a volume fraction of between 2 and 15% small particles ( $40 < d_p < 340$  nm)
- a volume fraction of between 2 and 18% medium particles ( $340 < d_p < 530$  nm)
- a volume fraction of between 75 and 90% large particles ( $530 < d_p < 1000$  nm)

In the case of TR26, only a CHDF analysis was available (recall that this can overlook the smallest particles in the latex):

- a volume fraction of between 2 and 10% small particles ( $50 < d_p < 125$  nm)



**Figure 10** Viscosity of latices TR7 and TR26 compared to that of well-characterized blends prepared by evaporation (in the blends, the particle diameters of the small (S), medium (M), and large (L) particles are  $d_p^S = 60$ ,  $d_p^M = 340$ , and  $d_p^L = 600$  nm, respectively).

- a volume fraction of between 75 and 90% large particles ( $500 < d_p < 1000$  nm)

The viscosities of these two latices are compared with those measured in Part I (blends of known PSD mixed and concentrated by evaporation) in Figure 10. In the case of TR7, the viscosity as a function of the solids content suggests that its PSD is similar to that of blends B3 and B6, which is also validated by the CHDF measurements. This means that at least one-third of the monomer injected during STEP II is consumed in forming the small particle population. In fact, it is probably higher than this, given that a number of the small particles formed by nucleation will flocculate onto the larger ones. TR26 on the other hand behaves more like blend B1, composed of 25% small particles and 75% large particles.

In addition to the PSD, a certain number of other parameters can influence the viscosity of these latices, including changes in the ionic strength, the pH, and the concentration of hydrosoluble polymers. We will use latex TR26 to study the influence of changes in these parameters on the latex viscosity.

### Ionic Strength

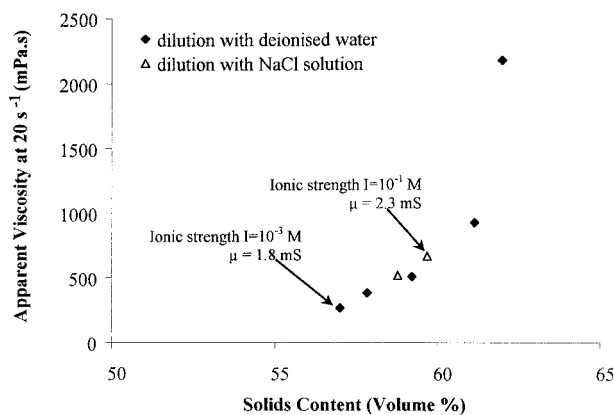
When a latex is stabilized by an ionic surfactant, the stability is a strong function of the ionic strength. As shown by eq. (1), increasing the ionic strength compresses the double layer around the

particle, where the thickness of the electronic double layer  $\delta$  can be calculated as follows<sup>19</sup>:

$$\delta = \sqrt{\frac{\epsilon k_B T}{8 \pi e^2 N_A I}} \quad (1)$$

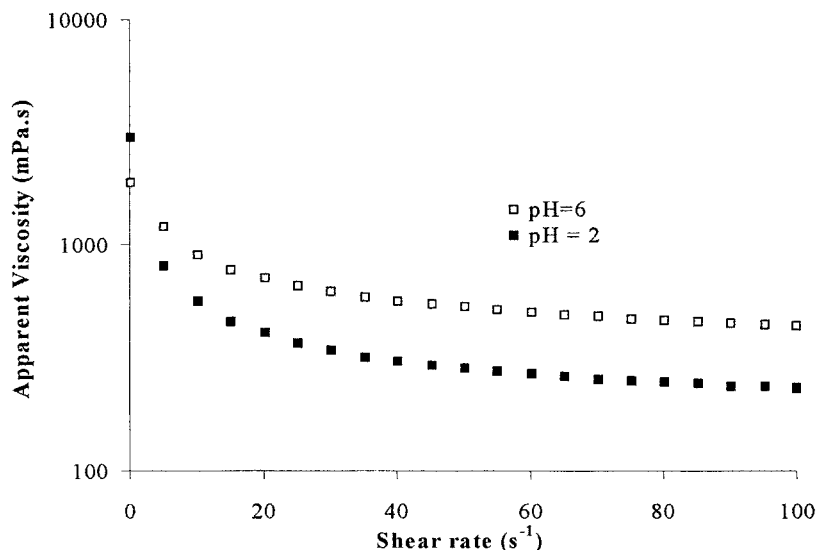
where  $\epsilon$  is the dielectric constant of water (continuous medium),  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $I$  is the ionic strength,  $e$  is the charge of a single electron, and  $N_A$  is Avagadro's number. The thickness of the layer is independent of the particle size, and will therefore have a relatively larger impact when the particles are small. As long as the ionic strength remains below the critical coagulation concentration (CCC), the latex remains theoretically stable, and an increase in the ionic strength should actually provoke a decrease in the viscosity, in that the interaction between particles (or the effective diameter of the particles) decreases.

The situation is, of course, more complex in the multimodal latices we produced because the stabilization is mixed (with a strong proportion attributed to steric or nonionic surfactants). The ionic strength is estimated at approximately  $10^{-1}$  mol/L, and its conductivity in its natural state was 1.5 mS. As was done in Part I,<sup>4</sup> the latex was diluted to determine the evolution of viscosity as a function of total solids content. The only difference here is that to study the effect of the ionic strength, the latex was diluted with either deionized water or with a  $7.7 \times 10^{-1}$  mol L<sup>-1</sup> NaCl solution. We can see from Figure 11 that dilution with water and with salt solution leads to the same viscosity at  $20 \text{ s}^{-1}$ . On a macroscopic scale,



**Figure 11** Effect of the ionic strength on the viscosity of latex TR26 as a function of volume fraction of polymer.





**Figure 12** Viscosity of latex TR26 at pH 2 (normal) and neutralized at pH 6.

these recipes are robust to reasonable changes in the ionic strength. This is not surprising, given that the thickness of the double layer of the original latex is already on the order of 1 nm, so increasing the ionic strength (provided we remain below the CCC) should not have a significant influence on  $\delta$ , and thus on the viscosity.

#### *Water Soluble Polymers/Oligomers*

The presence of hydrosoluble polymer chains could influence the overall viscosity of a latex either by increasing the viscosity of the continuous phase or by acting as a thickening agent if it carries a charge. Because the pH of the latex in its normal state is between 2 and 3, we are well below the  $pK_a$  of AA, and any hydrosoluble PAA chains should not be in an ionic state. Thus, we would expect that if hydrosoluble species do indeed exert an influence on the viscosity of the final latex, it would be attributable to an increase in the viscosity of the aqueous phase.

To test this idea, we separated a certain amount of the serum from a large sample of latex TR26 by ultracentrifugation, freeze-thaw, and filtration on a 100-nm filter. Although it was not possible to ascertain how much water-soluble material was in the serum, GPC analyses showed that there were indeed molecules larger than those of TN present in the serum. Measurement of the viscosity of the serum on a low shear viscosimeter (graciously provided by

the Laboratoire de Physicochimie Macromoléculaire at the ESPCI in Paris, France) showed that, despite the presence of these large water-soluble molecules, it was not possible to distinguish between the viscosity of the serum and that of deionized water. Therefore, it is unlikely that the formation of hydrosoluble molecules increases the viscosity of the continuous phase, and that they do not increase the overall viscosity of the final latex.

#### *Influence of the pH*

Figure 12 shows that, unlike the previous two parameters, the pH does indeed exert an effect on the viscosity of latex TR26. As noted above, increasing the pH to above the value of the  $pK_a$  of AA causes the latter to become ionized. This has the effect of increasing the electroviscous effect of the PAA chains absorbed onto the surface of the particles. These chains can unfold and, because they are charged, they increase the interaction between neighboring particles, and eventually between the particles and the continuous phase. The ionization of the polyacid chain ends also has the effect of compacting the electronic double layer around the particles, but, as we saw above, this effect is negligible in our case.

Note also that the neutralization of the latex was done by adding a 1N solution of NaOH, which had the effect of diluting the latex to 60.4%. The nonneutralized latex was therefore diluted to the

same solids content with deionized water, which explains the slight difference in viscosities between Figure 11 and Figure 12.

## CONCLUSIONS

We analyzed different methods for producing bi- and trimodal latexes at high solids contents using two different semibatch processes, and showed that it is possible to produce latices with solids content of over 65% with viscosities of less than 2500 mPa s<sup>-1</sup> at 20 s<sup>-1</sup>. The common thread running through all of the experiments is that the final viscosity, amount of coagulum, and overall stability during production are all directly correlated with secondary nucleation. If care is taken to eliminate this phenomenon as much as possible, it is easier to produce large particles, to make less coagulum, and to retain the stability of the latex during the reaction. On the other hand, the influence of secondary particle formation on the final viscosity is more ambiguous. In the process of the swelling of 500-nm seeds, it appears that secondary nucleation helps us to obtain solids contents of over 60% at moderate viscosities. However, in multimodal systems, the beneficial effect of a small amount of secondary nucleation is less clear. This suggests that success in producing high solids content, multimodal latices involves mastering the evolution of the PSD as much as possible. On the other hand, difficulties associated with measuring precise, reliable PSDs make it difficult to obtain useful information about this important parameter. Nevertheless, a certain degree of success is attainable if:

- APS initiator is mixed with the seed latex at ambient temperature, with the mixture being heated, once dispersion of the initiator is complete. It is thought that this eliminates massive nucleation on a local scale, and thereby reduces the tendency to form coagulum.
- In the case of a trimodal latex, small gains in solids content can be made by nucleating a third population of small particles with a mixture of TA and TN. The use of anionic surfactant (TA) alone leads to loss of control over the PSD.

The influence of the rate of addition of monomer to the trimodal latices is less clear. Some

evidence exists to suggest that slower rates of addition correspond to lower viscosities and lower amounts of coagulum. However, given that less secondary nucleation also means less coagulum and lower viscosities, and that lower monomer concentrations in the reactor also mean less secondary nucleation, this is likely. However, uncertainties arising from limited reproducibility make it difficult to draw a firm conclusion on this point.

Note also that the PSDs used in this work are not necessarily optimal. Further work needs to be done on this point before identifying an optimal recipe for the production of high solids content products. However, the most important improvement seems to be the need to find a means of reducing secondary nucleation. If the composition of the polymer is fixed by end-use applications, we cannot simply eliminate water-soluble monomers. On the other hand, the use of either non-ionic initiators or initiators that are soluble only in the organic phase might go a long way to helping us control this point. This will be discussed in Part IV of this series.<sup>20</sup>

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