# High Solids Content Emulsions. IV. Improved Strategies for Producing Concentrated Latices

**M. SCHNEIDER,[1] C. GRAILLAT,[1] A. GUYOT,[1] I. BETRÉMIEUX,[2] T. F. MCKENNA[1]**

[1] LCPP-CNRS/ESCPE-Lyon, Bât 308F, 43 Blvd du 11 Novembre 1918, 69616, Villeurbanne Cedex, France

[2] ATOFINA, Cerdato, 27470 Serquigny, France

**ABSTRACT:** A new means of producing high solids content latices with low viscosity is presented. The replacement of water-soluble initiators that decompose to give charged free radicals is shown to perturb the stability of highly concentrated latices. Their replacement by an oil-soluble initiator during particle growth, then by an activated, water-soluble system to remove residual monomer has been shown to help significantly reduce the number of stable particles generated by homogeneous nucleation. Latices with 73% (v/v) solids have been produced with a bimodal particle size distribution (PSD) consisting of 900 and 110 nm particles. The viscosity of these latices can be as low as 300 mPa s$^{-1}$ at 20 s$^{-1}$. Despite the presence of water-soluble monomers, excellent control over the evolution of the PSD allows one to obtain highly reproducible results. In addition, latices produced with the new initiator system have a much lower water uptake and their viscosity is much less sensitive to changes in pH than is the case for latices produced using standard emulsion polymerization techniques. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1935–1948, 2002; DOI 10.1002/app.10514

**Key words:** emulsion polymerization; high solids content; low viscosity; oil-soluble initiator

## INTRODUCTION

As has been discussed in the literature,[1–3] high solids content latices (here taken to mean latices with a volume fraction of polymer of over 60%) can be produced by creating emulsion polymer bimodal or trimodal populations of particles. Concentrated latices with multimodal particle size distributions (PSDs) can be made by either: (1) creating seeds of different size, mixing them and then concentrating the polymer phase by a semi-batch feed, or (2) by nucleating a population of small particles in the presence of a concentrated monomodal or bimodal seed. Both methods have been used by Chu et al.[4,5] and more recently by Schneider et al.[3] to create latices with solids contents on the order of 65%, with low viscosities.

In earlier studies Schneider et al.[1–3] demonstrated that control of the PSD seems to be a key parameter in maintaining latex stability at high concentrations, reducing the amount of coagulum formed during the reaction, maintaining low viscosities, and ensuring the reproducibility of the final latices. One of the difficulties that they encountered was the composition of the system. The resulting polymer (which is the same as that investigated in the current study) served as a model recipe for pressure-sensitive adhesives, and had a final composition of 78% mass butyl acrylate (BA), 19.5% methyl methacrylate (MMA), and

2.5% acrylic acid (AA). Given that both the MMA and the AA are partially water soluble, it is likely that a certain amount of homogeneous nucleation will occur continuously throughout the different steps of the polymerization reaction. If the stabilization of the latex is correctly adjusted and the small particles are not stabilized, but rather flocculate onto the larger ones already present, we can benefit from this homogeneous nucleation, which will make the particles grow faster. If, on the other hand, the homogeneously nucleated particles are stabilized (in whole, or even for a short period of time), this can cause the surfactant that would otherwise be used to stabilize the large particles to be consumed by the unwanted small particles, thereby leading to either the formation of coagulum or the total loss of latex stability. Furthermore even if the breakdown of latex stability can be avoided, the formation of unwanted particles can change the PSD, which must be relatively well defined if we are to maintain low viscosities.[1,6–8]

It was shown in Part III[3] that by maintaining relatively low monomer concentrations in the reactor, by dispersing the initiator in the seeds at ambient temperature instead of at the reaction temperature, and by correctly choosing the balance between anionic (TA) and nonionic (TN) surfactants we can minimize, but not totally eliminate, the impact of this unwanted secondary nucleation. Because we are concerned with a polymer composed of partially water-soluble monomers, the only way to totally eliminate homogeneous nucleation would be to eliminate the free radicals from the aqueous phase, essentially by using an oil-soluble initiator.

However, another strategy could also be considered. It is common to find persulfate initiators used in emulsion polymerization, and in Parts I–III[1–3] the initiator of choice was ammonium persulfate (APS). However, in Part II[2] the authors also discussed the possibility of using a nonionic initiator such as $H_2O_2$/ascorbic acid (HPO/AscA) redox pair because this initiator system creates uncharged radicals that cannot help to stabilize homogeneously nucleated particles. This initiator system was used in only one experiment in that work with an insufficient quantity of AscA, which caused flocculation to occur as a result of an accumulation of unreacted monomer. Nevertheless, transmission electron micrographs of samples taken early in the reaction with the HPO/AscA initiator showed that far fewer small particles were

observed than was the case on a sample taken at a similar point of the reaction, but with a standard APS initiator.

Of course, other authors have studied emulsion polymerization with oil-soluble initiators.[9–11] However, these authors used either azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO), which are partially water soluble, and focused on either particle nucleation or polymerization kinetics, rather than on eliminating secondary nucleation. In the event that we want to accomplish this latter goal, it might be more interesting to test a more hydrophobic initiator that would remain (as much as possible) in the organic phase. As long as the quantity of radicals generated from an oil-soluble initiator and dissolved in the aqueous phase remains low, it seems that there is little risk of radical exit leading to homogeneous nucleation.[10] It is also usual practice to use either oil-soluble initiators or mixed initiators to consume traces of residual monomer at the end of a reaction.[12] In a slightly different vein, O'Callaghan et al.[13] used a mixed (APS + AIBN) initiator system to synthesize large particles of 1 to 7 $\mu$m in diameter. Their recipes contained large fractions of MMA (approximately 64% by mass of total monomers), which of course promotes homogeneous nucleation. These authors observed a tendency toward the formation of small, stable particles when APS was used alone. Replacing the APS by AIBN avoided the formation of a stable, secondary population of particles. However, if the charge density of the particles dropped too low, flocculation remained a problem.

In the current study we discuss modifications of the reaction scheme presented in Part III, where latices with approximately 65% by volume of polymer were produced, with viscosities of between 1000 and 7500 mPa s$^{-1}$ at a shear rate of 20 s$^{-1}$. The experimental protocol is discussed below, but the improvements presented herein focus on using different initiator systems to attenuate the impact of secondary nucleation on the viscosity and stability, and on a more appropriate choice of seed latices.

## 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

**Table I   Recipes for Preparation of Seeds**

|  | SEM9 | SEM21 | SEM23 | SEM31 | SEMM3 | SEMP2 | SEMP2 |
|---|---|---|---|---|---|---|---|
| | | | Seed Formation Recipe | | | | |
| Duration (min) | 44 | 48 | 50 | 50 | 17 | 10 | 60 |
| TA | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 18.9 | 6.4 |
| TN | 3.5 | 3.5 | 3.5 | 3.5 | 5 | 39.5 | 0 |
| BA | 80 | 80 | 80 | 80 | 80 | 70.9 | 210 |
| MMA | 20.1 | 20 | 20 | 22 | 20 | 17.7 | 52.4 |
| AA | — | — | — | — | — | — | 6.8 |
| $NaHCO_3$ | 1.8 | 1.9 | 1.8 | 1.8 | — | — | — |
| APS | 1.8 | 1.8 | 1.8 | 1.8 | 0.9 | 2.64 | 1.8 |
| $Na_2S_2O_5$ | — | — | — | — | 0.74 | — | — |
| $T$ (°C) | 70 | 70 | 70 | 70 | 70 | 80 | 70 |
| | | Characteristics at End of Seed Period (all reactions 10% solids content w/w) | | | | | |
| Solids content (% mass) | 10 | 10 | 10 | 10 | 10 | 6 | 22 |
| $d_p$ | 195 | 221 | 215 | 209 | 120 | 40 | 60 |
| $Z_{dp}$ | 0.05 | 0.07 | 0.06 | 0.06 | 0.04 | 0.3 | 0.1 |
| $N_p$ | $2.1 \times 10^{16}$ | $1.7 \times 10^{16}$ | $1.7 \times 10^{16}$ | $1.9 \times 10^{16}$ | $1 \times 10^{17}$ | $4.1 \times 10^{18}$ | $2.4 \times 10^{18}$ |
| | | | Preemulsion Recipe | | | | |
| Duration (min) | 552 | 436 | 255 | 259 | 423 | 66 | 100 |
| TA | — | — | — | — | — | 19.9 | 27.8 |
| TN | 15.6 | 15.8 | 15.9 | 16 | 30.7 | 41.6 | 49.3 |
| BA | 896 | 924 + 6.1 | 893 + 8 | 896 + 3.1 | 900 | 407 | 587 |
| MMA | 224 | 231 + 1.5 | 225 | 224 + 08 | 225 | 102 | 148 |
| AA | 31 | 34 + 0.2 | 32 | 30 + 0.1 | 31 | 13 | 19.5 |
| APS | 1.8 | 2 | 2 | 1.9 | 2.8 | — | 1.1 |
| BPO | — | — | 1.5 | — | — | — | — |
| DEAB | — | — | — | 1.12 | — | — | — |
| | | Characteristics at End of Reaction | | | | | |
| Solids (wt %) | 50 | 50 | 50 | 50 | 50.1 | 29 | 46 |
| $d_p$ | 510 | 500 | 513 | 480 | 270 | 60 | 95 |
| $Z_{dp}$ | 0.09 | 0.14 | 0.14 | 0.09 | 0.06 | 0.2 | 0.08 |
| $N_p$ | 1.7 | $1.9 \times 10^{16}$ | $1.7 \times 10^{16}$ | $1.8 \times 10^{16}$ | $1.1 \times 10^{17}$ | $4.8 \times 10^{18}$ | $2.1 \times 10^{18}$ |

[a] All quantities in grams active substance.

this study was Disponil® FES 32 IS (sodium salt of the sulfate of a polyglycol ether), and the nonionic surfactant (TN) was Disponil® A 3065 (mixture of linear ethoxylated fatty acids). TA contains 32%, and TN 65% by weight active material. (In the recipes listed in the tables below, the quantity of surfactant always refers to the mass of active material.) Both surfactants were supplied by Cognis (Meaux, France) and used as received. The initiators APS, BPO, and HPO/AscA were obtained from Aldrich (Steinheim, Germany) and used as received. Diethylazobutyronitrile (DEAB), an oil-soluble liquid phase initiator with decomposition kinetics similar to those of APS, was kindly supplied by ATOFINA (CRRA, Pierre Bénite, France). Its water solubility is 0.1%.

The recipes for seed preparation are presented in Table I. The large ($d_p$ = 500 nm) and medium ($d_p$ = ±250 nm) seed latices were prepared as described in Part II,[2] with the exception that in the case of the large seeds a shot of either BPO or DEAB was added at the end of the nucleation stage, before the swelling and concentration of the particles was begun. This shot was prepared by mixing a fixed amount of DEAB with a small quantity of monomer to facilitate its transfer into the particles. The medium seed is SEMM3. In the case of the large seeds, the new recipes are compared with the previous seed recipes retained in Part III (SEM9 and SEM21). (See Fig. 1.) Care was taken to ensure that we were always operating under starved conditions for initiator injection. The final particle diameters were
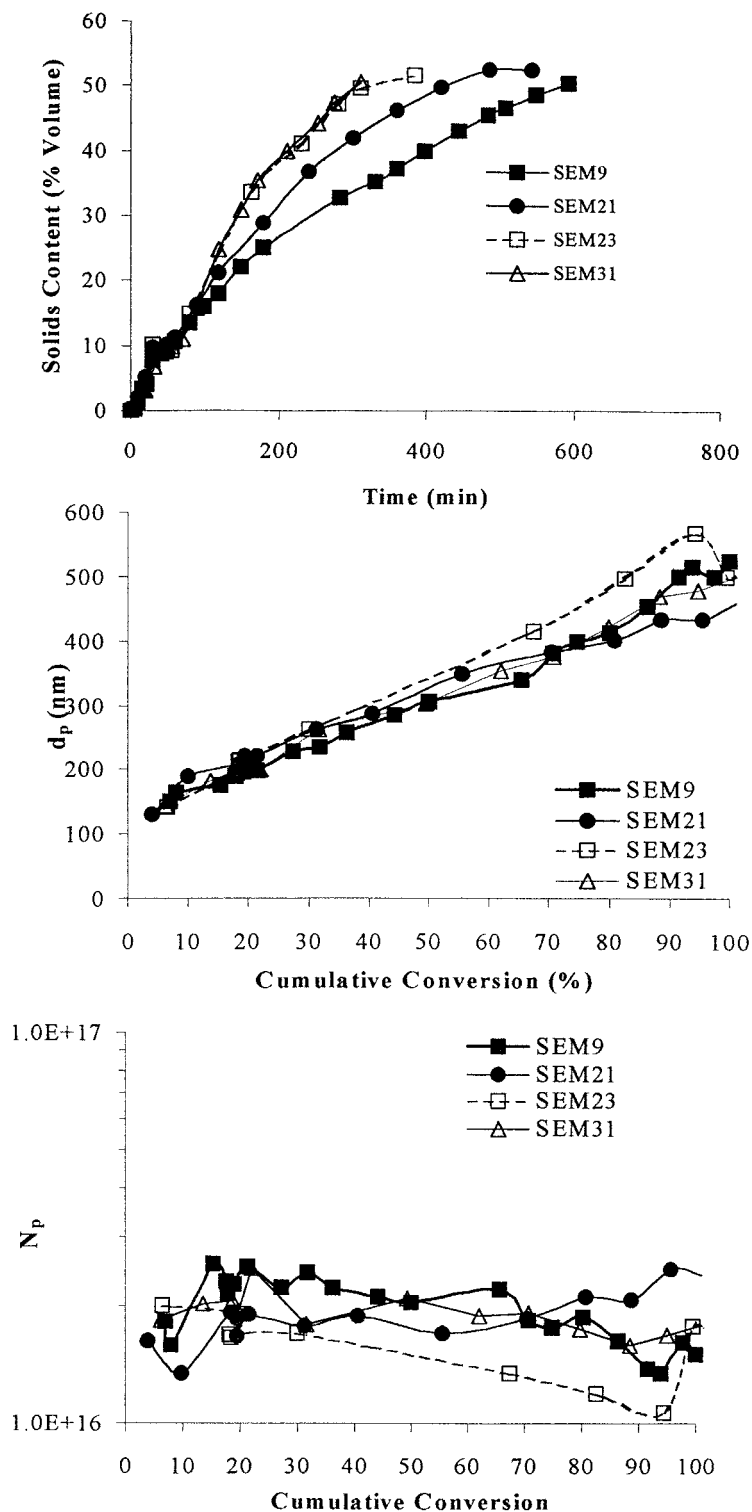
**Figure 1** Kinetics (rate of change of solids content = rate of accumulation of polymer) and evolution of the PSD for original seed recipes, and improved recipes using DEAB. Note that the conversion shown here is the cumulative conversion. This is defined with respect to the total amount of monomer that will be added by the end of the experiment (it is a quantity that cannot be calculated until the reaction is finished), and should not be confused with the overall or instantaneous conversion, which is defined with respect to the quantity of monomer added up to the instant at which the conversion is calculated.
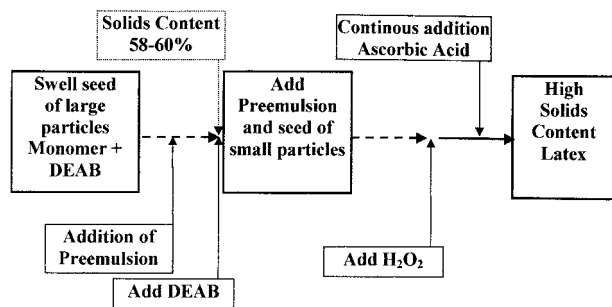
**Figure 2** Schema for the improved process for the production of high solids content latices.

$d_p$ = 60 nm for SEMP2 (30% v/v polymer) and $d_p$ = 95 nm (45% v/v polymer).

The process used is similar to that described in Part III.[3] The steps, shown in the schema in Figure 2, consist of the following:

- The seed of large particles is preswollen with a small amount of DEAB and a maximum of 5% monomer with respect to the total mass of polymer at 20°C and left overnight. It is not wise to put all of the DEAB that will be needed for the reaction into the seed at this point because it decomposes fairly quickly at 80°C.[14] An excess of initiator at this stage could therefore present problems of temperature control. For this reason, we add a portion of the initiator here and the rest when we add the second seed.

- The temperature is increased rapidly to 80°C, which begins the reaction, and a preemulsion of monomer (15–20% by weight), water, and surfactant is added. This preemulsion is fed for between 40 and 90 min until the solids content reaches between 58 and 60%. It is preferable to avoid exceeding this limit because the viscosity of a monomodal latex is sensitive to the solids fraction beyond this limit and can increase rapidly.[4] Also, unlike the preemulsion used in Part III,[3] that used here can contain small amounts of TA, given that the risk of secondary nucleation is greatly reduced.

- When the solids content of the seed is between 58 and 60%, a second seed of small particles (either one seed or a mixture of the two) is added after a short batch period and the addition of a shot of DEAB. The batch operation is to ensure that there are no monomer droplets. The addition of the seeds

can be in the form of either a shot or a semi-batch injection for a short period. Note that the seeds of small particles are not preswollen with monomer.

- A preemulsion (plus eventually a seed) is continually added to increase the solids content. However, because neither the small particles nor the preemulsion contain any initiator, the reaction theoretically proceeds only in the large particles. This should help us to control the PSD in terms of the ratio of the diameter of large to small particles (that we would ideally like to maintain between 6 and 8[1]), the proportion of large particles (a volume fraction of 0.8 is ideal[1]), and the reduction of secondary nucleation. Normally the preemulsion added in this stage is the same as that used in the initial step. The final solids content at the end of this step can be over 70%.

- This is followed by a finishing step, which lasts between 30 and 60 min, to consume the residual monomer in the large particles. However, because some of the monomer will obligatorily diffuse from the large to the small particles, we need to add an additional initiator. To finish the monomer in the particles, as well as in the aqueous phase, we use the couple HPO/AscA. Recall that this redox pair generates uncharged radicals and will therefore avoid altering the stability of the latex and the nucleation of additional particles.

All 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 is 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 Capillary Hydrodynamic Fractionation (CHDF) for the bi- and trimodal blends.

## RESULTS AND DISCUSSION

### Production of Large Seeds

In fact, the large seeds are simply monomodal latices that contain a predetermined number of particles with a fixed average diameter. Classic
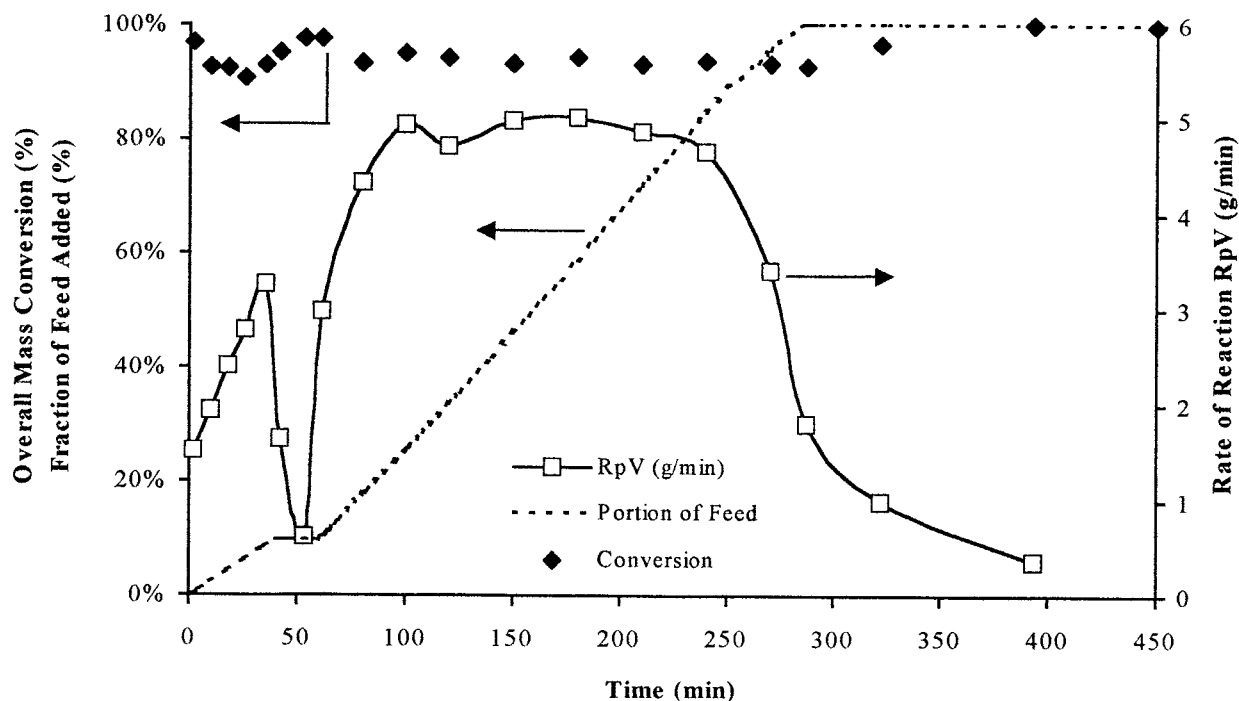
**Figure 3** Conversion, rate of reaction, and feed addition rate for run TR38. The rate of reaction remains constant for most of the bimodal growth period. The overall mass conversion is the instantaneous conversion (relative to the amount of monomer added to the reactor, and not the same as the cumulative conversion in Fig. 1).

emulsion copolymerization methods were used in Part II[2] to create seeds of 500 nm that are used as the basis for the production of multimodal products. As was the case for the high solids content latices, the key to obtaining a well-defined seed in a minimum amount of time is to control the PSD. Runs SEM23 and SEM31 are similar in composition to the original seed recipes (SEM9 and SEM21), with the exception that we added a shot of BPO (SEM23) or DEAB (SEM31) at the end of the nucleation stage. As we can see from Figure 1 the addition of the oil-soluble initiators significantly accelerates the rate of reaction, and allows us to increase the semibatch feed rate of the preemulsion. Reaction times are reduced by almost a factor of 2, down to 4 h from 9 and 7 h for SEM9 and SEM21, respectively. Also, the polydispersity index returned by the Malvern Lo-C QELS indicates that we can consider the PSD to be monodisperse. We therefore use the modified seed recipe in the rest of the work presented here.

### Latex Production

The process described in the previous section offers several advantages. In principle it should allow us to control the PSD and, in particular, the size of the population of large particles more easily than we could with a "standard" emulsion process. The reason for this is that, during the first part of the bimodal step, growth is essentially isolated in the large particles, and limited to the small particles only at the end when we change initiators. In addition, with the vast majority of the initiator being found in the particle phase, almost no secondary nucleation should occur, and the number of particles should vary little with respect to that fixed during the blending step. It should be pointed out that the seed latices undergo a long finishing period to eliminate the residual persulfate initiators. It is this that allows us to isolate the growth in the different parts of the latex.

A typical experiment is illustrated in Figure 3 for run TR38. The batch periods correspond to the plateaux in the feed addition rate. It can also be seen that the feed rates have been adjusted so that the rate of polymerization is constant during the semibatch phase.

In this new process configuration, one of the more delicate steps is that of radical generation

during the final finishing stage. In cases where only DEAB was used and no additional initiator was injected, it quickly became apparent that it was not possible to consume all of the residual monomer. This is most likely attributable to the fact that some MMA and AA remain in the water phase, and that a small fraction of the monomer in the preemulsion has gone to swell the small particles. The addition of a extra shot of DEAB would allow us to consume what remains in the small particles, but not what is in the aqueous phase. For these reasons, it was decided to test a water-soluble initiator, either APS or the couple HPO/AscA.

In run TR35, a solution of APS was used for the finishing stage. Despite the advanced conversion of the reaction and the low levels (less than 5%) of monomer, this provoked a massive coagulation in the reactor. In effect, the amount of coagulum in the latex just before the injection of APS was approximately 1000 ppm, and after injection it was 96,000 ppm. This difficulty is probably the result of the rapid decomposition of the APS at 80°C, much in the same way as was noted in Part III for the concentration of the seeds. The APS is simply not dispersed quickly enough throughout the reactor, so we get local increases in radical concentration and rapid nucleation. However, because there is not enough surfactant in the system, these freshly nucleated particles begin to flocculate onto larger particles, and probably absorb a portion of the surfactant used to stabilize the latter, thus further perturbing the stability of the latex. This solution was obviously abandoned.

In runs TR36–TR38, HPO was used with AscA to enhance its decomposition. The advantage of HPO is that it produces uncharged free radicals, which do not help to stabilize homogeneously nucleated particles. In addition, given that its deactivation is, in effect, controlled by the quantity of AscA present in solution, the HPO can also be evenly dispersed throughout the reactor *before* the activator is added. This system can then be adequately controlled by injecting a shot of HPO and then adding AscA semibatch-wise. Free radicals are generated as long as there is AscA in solution. Although this offers the advantage of allowing us to disperse the HPO, it also means that we need to carefully determine the rate of addition of the activator. The impact of the rate of addition of the AscA is shown in Figure 4, where we can see that if the AscA is added too quickly (e.g., in 15 min, run TR37), we cannot remove all of the residual monomer. On the other hand, in

run TR38, the acid was added over the course of 1 h, thereby maintaining a steady flux of radicals and ensuring that we obtain high conversions.

Another of the difficulties encountered with the classic emulsion process for high solids was the reproducibility of the runs. In Part III, it was shown that, although the kinetics (the rate of polymerization and conversion) were reproducible, it was very difficult to reproduce the PSD and viscosity. However, as shown in Figure 5, the reduction in secondary nucleation achieved here means that the process is very reproducible. In the two runs compared in Figure 5, the PSD of both are very similar, as is the viscosity. The viscosity measured for TR40 was 300 mPa s$^{-1}$ at a shear rate of 20 s$^{-1}$, and that of TR41 was 320 mPa s$^{-1}$ at the same shear rate. The final polymer content was 70.2% (final solids content including surfactant was over 72%) for both runs. Although presented only in Table II, runs TR38 and TR42 are also highly reproducible and yield the same results in terms of kinetics, PSD, and viscosity (820 mPa s$^{-1}$ at $\dot{\gamma} = 20$ s$^{-1}$ for TR38 and 900 mPa s$^{-1}$ for TR42) at solids content of 73%.

As discussed in Part I[1] and in Chu et al.[6] and Greenwood et al.[7,8] the viscosity of multimodal products is a key quality parameter, and we want to keep it as low as possible. With standard emulsion polymerization processes, we were able to obtain solids content of approximately 65% and viscosities of less than 2500 mPa s$^{-1}$ at 20 s$^{-1}$. We obtained similar solids contents for runs TR36 and TR37, but with viscosities one order of magnitude lower. Moreover, in all of the runs presented in Table II the viscosity remained below 1000 mPa s$^{-1}$ for all but one of the runs (TR39), where it was 1200 mPa s$^{-1}$. This improvement in both viscosity and solids content is obviously attributable to an improved control over the PSD and a better adaptation of the PSD in terms of viscosity.

As mentioned above, it has been shown that, for a given solids content, the viscosity of a bimodal dispersion of particles will be lowest when: (1) the large particles represent approximately 80% of the volume of the dispersed phase, and (2) the ratio of the diameter of the larger to that of the small particles is between 6 and 8. In the case of a trimodal latex, it is more difficult to quantify the relationship between the three populations.[11] Nevertheless, it was found experimentally that the ratio between small and large particles should remain the same, and that the volume fraction of large particles should still be on the order of 75–
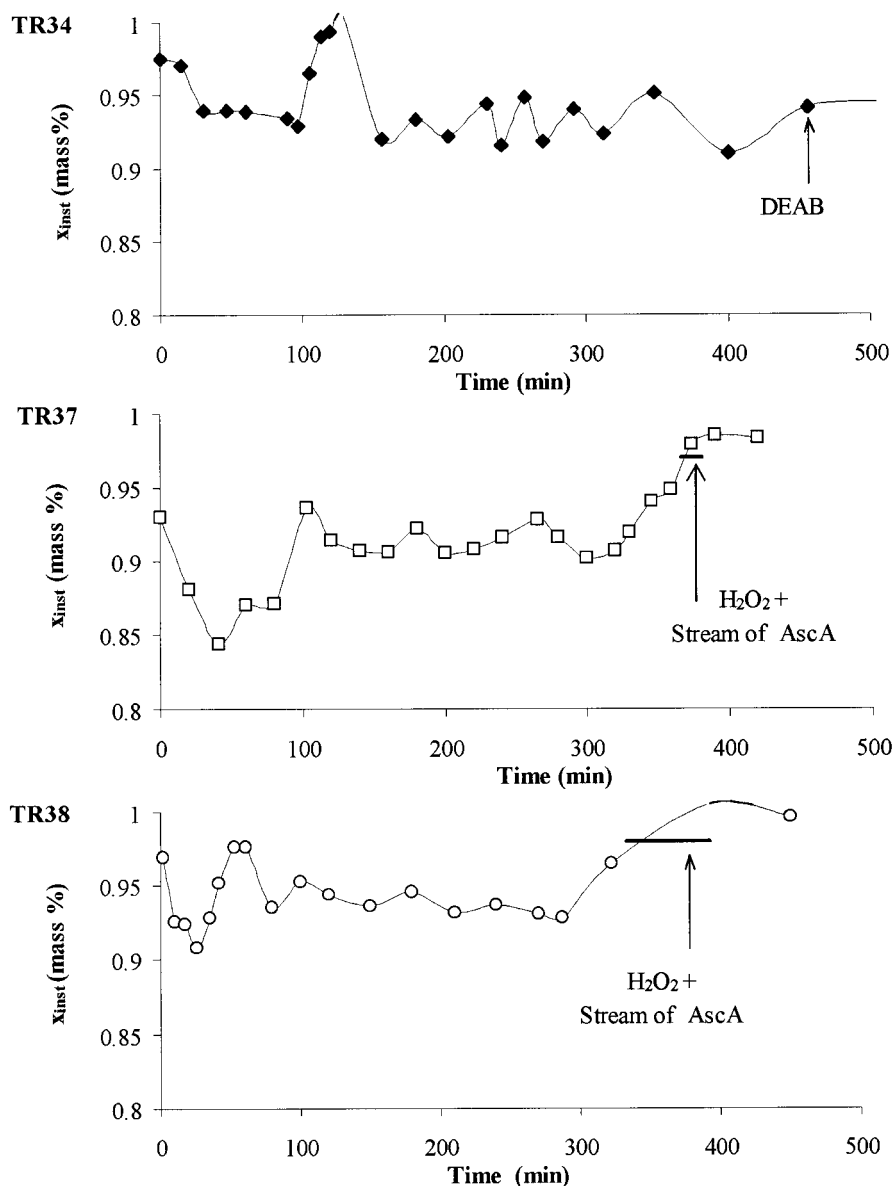
**Figure 4** Instantaneous conversion as a function of time for runs TR34, TR37, and TR38 showing the influence of how the postinitiation of the reaction influences the finishing stage. In TR34 a shot of DEAB is added. In TR37 $H_2O_2$ is injected with a very brief feed of an AscA feed stream (solid line). In TR38, the postinitiation is as in TR37, but the feed of AscA lasts longer.

80%. If we consider the results in Table III, we can see that the theoretical PSDs of the different latices are close to these criteria. The bimodal latices TR40 and TR41 adhere the most closely to both and have the lowest viscosity. As shown in Part I[1] and Greenwood et al.[7,8] increasing the ratio of the particle diameters from 8 to 12 (runs TR38 and TR39) leads to a slight increase in the viscosity for the same solids content. Also, the trimodal latices created here are slightly more

viscous than the bimodal latices and seem to be more sensitive to changes in the PSD than are the bimodal latices. However, if we compare runs TR39, TR43, and TR44 we can see that the viscosity is lower when the ratio of the diameter of the large to that of the medium particles is 7.2 (TR43) than when it is 2.6 (TR39) or 1.7 (TR44).

This evidence (low viscosity, reproducible runs) suggests that it is entirely possible to control the PSD (to within reasonable limits) by using the
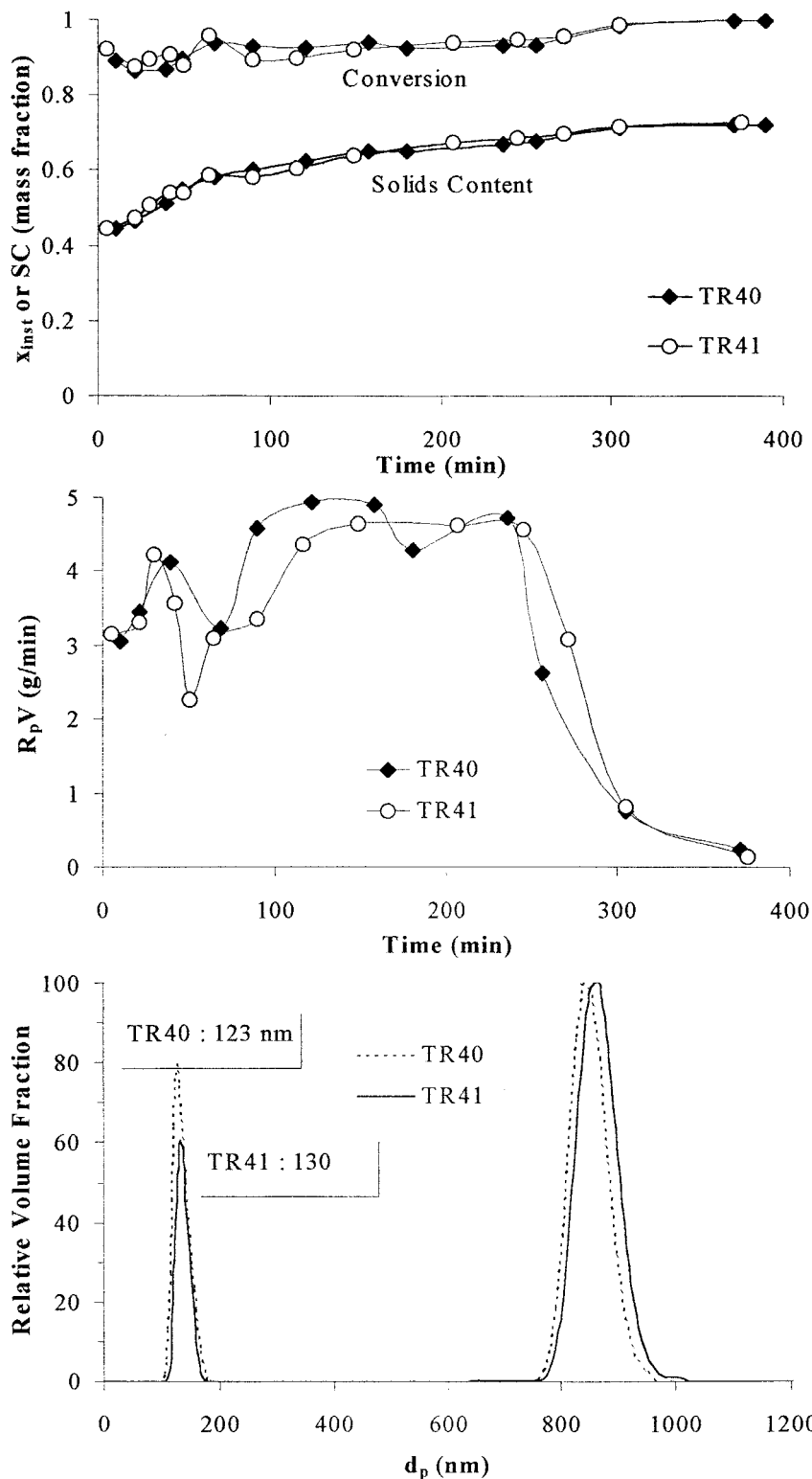
**Figure 5**   Reproducibility of high solids content runs TR40 and TR41. Expected sizes were 110 and 900 nm for the small and large populations, respectively. For TR40 the size of the large population was $d_p = 840$, and for TR41 it was $d_p = 866$.

**Table II   Recipes and Results of Characterization for Bimodal Latices**

| | TR34 | TR36 | TR37 | TR38 | TR40 | TR41 | TR42 | TR43 | TR44 |
|---|---|---|---|---|---|---|---|---|---|
| **Seed preparation** | | | | | | | | | |
| Mass first seed[a] | 401.3 g | 400 g | 401 g | 401 g | 350 g | 352 g | 400 g | 400 g | 403 g |
| Added water | 101 g | 100 g | 66.4 g | 0 | 54 g | 54 g | — | — | 82 g |
| Added monomer[b] | 9.91 g | 9.98 g | 9.84 g | 9.74 g | 8.88 g | 8.84 g | 9.55 g | 10 g | 10 g |
| DEAB | 4.52 g | 4.6 g | 4.6 g | 4.54 g | 4.35 g | 4.35 g | 4.6 g | 4.5 g | 4.8 g |
| **First preemulsion** | | | | | | | | | |
| Total mass preemulsion 1[c] | 441 g | 407 g | 286 g | 133 g | 234 g | 243 g | 133 g | 133 g | 315 g |
| % Monomer[b] | 80% | 82% | 85% | 86% | 85% | 85% | 86% | 85% | 86% |
| % Nonionic surfactant | 1.4% | 1.52% | 1.8% | 2.68% | 1.87% | 1.87% | 2.68% | 2.91% | 2.72% |
| % Ionic surfactant | — | 0.06% | 0.08% | 0.14% | 0.08% | 0.08% | 0.14% | 0.15% | 0.13% |
| Duration preemulsion 1 feed (min) | 97 min | 91 min | 82 min | 40 min | 49 min | 50 min | 40 min | 40 min | 40 min |
| Mass DEAB at end step 1[d] | 0.98 g | 4.36 g | 4.25 g | 4.55 g | 3.82 g | 4.2 g | 4.74 g | 4.5 g | 4.6 g |
| Duration intermediate finishing (min) | 18 min | 27 min | 23 min | 18 min | 11 min | 14 min | 20 min | 20 min | 20 min |
| Mass second seed[e] | 193 g SEMP2 | 286 g SEMP2 | 299 g SEMP2 | 309 g SEMP2 | 289 g SEMP3 | 284 g SEMP3 | 285 g SEMP2 | 583 g SEMP2 + SEMP3 | 588 g SEMP2 + SEMP3 |
| **Second preemulsion + finishing stage** | | | | | | | | | |
| Total mass preemulsion 2 | 666 | 861 g | 997 g | 1210 g | 985 g | 991 g | 1203 g | 1955 g | 1801 g |
| % Monomer[b] | 80% | 82% | 85% | 86% | 85% | 85% | 86% | 85% | 85% |
| % Nonionic surfactant | 1.4% | 1.52% | 1.8% | 2.68% | 1.87% | 1.87% | 2.68% | 2.91% | 2.72% |
| % Ionic surfactant | — | 0.06% | 0.08% | 0.14% | 0.08% | 0.08% | 0.14% | 0.15% | 0.13% |
| Duration preemulsion 2 feed (min) | 272 min | 214 min | 215 min | 225 min | 191 min | 225 min | 225 min | 200 min | 200 min |
| Mass DEAB at end of step 2 | 2 | — | — | — | — | — | — | — | — |
| Mass $H_2O_2$ in solution (20 wt %) | — | 1.28 g | 1.17 g | 1.78 g | 1.85 g | 1.51 g | 1.73 g | 1.81 g | 1.79 g |
| Mass AscA added (in g $H_2O$) | — | 0.3 g (in 5.7 g) | 0.41 g (in 5.6 g) | 0.44 g (in 5.6 g) | 0.41 g (in 5.1 g) | 0.42 g (in 5.6 g) | 0.44 g (in 5.6 g) | 0.44 g (in 5.6 g) | 0.43 g (in 5.5 g) |
| Duration of AscA addition (min) | — | 15 min | 15 min | 90 min | 60 min | 60 min | 60 min | 60 min | 60 min |
| Total surfactant in final latex (wt %) | 1.6% | 1.9% | 2.2% | 2.8% | 1.8% | 1.8% | 2.8% | 3.2% | 1.1% |

[a] All recipes used SEM31 in seed except SEMM3 for TR44.
[b] Monomer always in proportion 80 : 20 (BuA : MMA by weight).
[c] The difference is water.
[d] Added as a shot in all experiments except TR41 and TR42 where it is added with a second seed.
[e] Added at same time as preemulsion 2.

**Table III  Properties of Bimodal and Trimodal Latices**

| | Final Solids[a] (% Mass) | Predicted $d_p$ (% Mass of Each Population) | Final Viscosity (mPa s$^{-1}$ at 20 s$^{-1}$) |
|---|---|---|---|
| TR38 | 73.1 | 75nm (15%) | 820 |
| TR42 | 72.9 | 900nm (85%) | |
| TR40 | 72.2 | 110nm (15%) | 300 |
| TR41 | 72.6 | 900nm (85%) | |
| TR39 | 73.1 | 75nm (15%) | 1200 |
| | | 350nm (5%) | |
| | | 900nm (80%) | |
| TR43 | 73.1 | 75nm (15%) | 700 |
| | | 125nm (5%) | |
| | | 900nm (80%) | |
| TR44 | 71.3 | 75nm (15%) | 900 |
| | | 350nm (5%) | |
| | | 590nm (80%) | |

[a] Includes approximately 1.8–2.5% surfactant (see Table II).

modified initiator system and feed policy proposed here. Of course, given the limitations of the measurement of the PSD, even with techniques as powerful as CHDF,[15] it is difficult to be entirely certain that we are obtaining exactly the PSD that we want, especially in terms of the proportions of particles of different sizes. Nevertheless, given that we are mixing independently characterized seeds in known proportions, we can combine this information with a mass balance (i.e., we know what we should expect) to follow the PSD. For example, the PSD in Figures 5 and 6 show the results of the CHDF analyses of runs TR40, TR41, and TR42. The measured particle sizes agree very well with the expected values of $d_p$ (Table III). If we accept that there is no error in the measurement of the average particle size of the small particles, then there is less than 20 nm between the expected and measured particle diameters. The large particle diameters are slightly smaller than would be expected if all of the monomer reacted inside them: between 840 nm for TR40 up to 866 nm for TR41 and TR42. Nevertheless, the particle growth seems to be close to what is expected, and at least as importantly, highly reproducible. The proportions of the different populations are more difficult to quantify, but the different analyses run provide values of the volume fraction of large particles between 75 and 90%, again in line with the expected values.

Further evidence for the lack of reaction in the aqueous phase comes from a characterization of

the molecular weight of hydrosoluble polymers, although it would be desirable to do this on a purified serum isolated from one of the bimodal or trimodal latices. Unfortunately, it was not possible to separate the small particles from the serum, even by centrifugation at 20,000 rpm combined with freeze–thaw treatment. For this reason it was decided to perform this operation on medium-size particles, both of which are "grown" from SEMP3. SEMM3 is prepared as in Part II,[2] using APS during the growth stage, and SEM32 is prepared in the same way, but replacing the APS with the same quantity of DEAB. Both SEMM3 and SEM32 have $d_p$ = 275 nm and a solids content of 50%. The sera were easily isolated, and analyzed in an aqueous phase GPC using low molecular weight polyethylene oxide standards. The raw chromatograms are shown in Figure 7. Clearly, both latices contain the same hydrosoluble material (as discussed in Part III,[3] the molecular weight of this substance is greater than that of TN, so we are sure that it is not a surfactant); however, in SEM32, we have significantly less hydrosoluble material, which further supports the idea that we have reduced the presence of radicals in the aqueous phase, and have very little reaction taking place there (the small amount of hydrosolubles present in SEM32 could very well come from the preparation of SEMP3).

**Latex Characterization**

Because the recipe used for the preparation of latices proposed here is different from that in Part III, it is interesting to compare the physical prop-
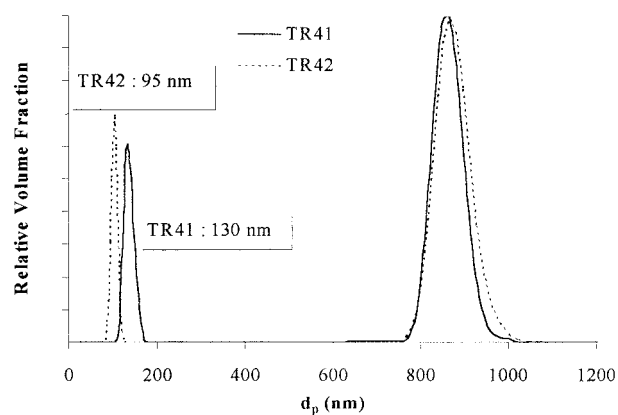


**Figure 6**  CHDF analysis of the PSD of runs TR41 and TR42. Expected $d_p$ values were 110 and 900 nm for TR41, and 75 and 900 nm for TR42. The size of the large population in both runs was $d_p$ = 866 nm.
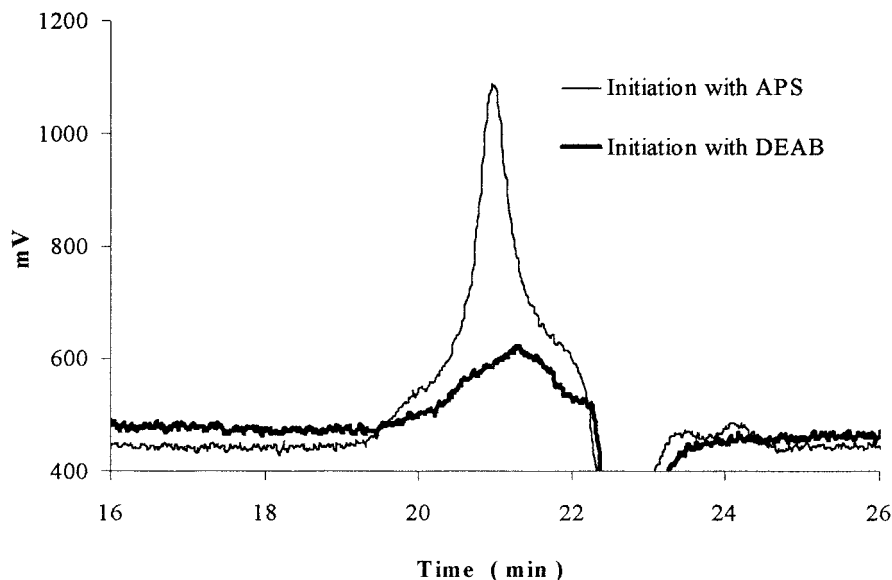
**Figure 7** Raw GPC signal for the sera recovered from SEMM3 (with APS) and SEM32 (with DEAB). The quantity of hydrosoluble material is greater in SEMM3.

erties of the latices in terms of the influence of the pH on the viscosity and water uptake of films made from the different products, the molecular weights, and mechanical properties of the films.

To look at the influence of pH on the viscosity and water uptake, we will compare two latices: TR26, prepared using the emulsion process proposed in Part III, and TR36 (Table III). Latex TR26 is a bimodal latex with a poorly controlled PSD made up of particles of 60 and 600 nm. Both latices have a pH in the neighborhood of 2 at the end of the reaction, and are neutralized to pH 6 using a $1N$ solution of NaOH. Because there are two acids that need to be neutralized in TR26 (AA, in the serum and on the particle surface, and $H_2SO_4$, created by the decomposition of the APS), the neutralization step dilutes TR26 to a solids content of 60.4%. Given that TR36 contains no sulfuric acid, the neutralization step dilutes it to only 62.4%.

Viscosity measurements were performed on the raw and neutralized latices (all values reported here are for a shear rate of 20 s$^{-1}$). At a pH of 2, the viscosity of TR26 was found to be 400 mPa s$^{-1}$ and at a pH of 6, 700 mPa s$^{-1}$.[3] On the other hand, in its slightly diluted state, latex TR36 had a viscosity of 90 mPa s$^{-1}$ at a pH of 2 and 100 mPa s$^{-1}$ at a pH of 6. Apparently the neutralization does not affect the viscosity of the latices produced with the new recipe nearly as much as it does for the latices made with a normal

emulsion process. If the two latices had a different quantity of AA on the surface of the particles, this might explain the difference in the impact of neutralization on the latices. However, when a dosage of acid groups was performed on SEMM3 and SEM31 (with APS and DEAB, respectively), 12% of the acrylic acid groups were found on the surface of the particles in both latices. Thus, it would appear at first glance that electroviscous effects attributed to the unfolding of the acid chains on the surface are not responsible for this difference in sensitivity. However, if we consider that the surface area of TR26 is at least 1.5 times that of TR36 (maybe even more because of the poor control of the PSD and the presence of undetectable small particles), then, even so, it is possible that this attribute could explain this observation.

Films of the same thickness were made from the same four latices (TR26 and TR36, both at pH = 2 and pH = 6). Samples were cut from each of the films and placed in bottles filled with deionized water. The samples were occasionally withdrawn, wiped with a paper napkin, and weighed to follow the water uptake of the polymers. As can be seen from Figure 8, the neutralized films absorb less water than do the films prepared from the untreated latices, which is most likely the result of a higher concentration of acrylic acid on the surface of the particles. It is also clear that the films made with DEAB also absorb significantly less water than do those made using APS. This
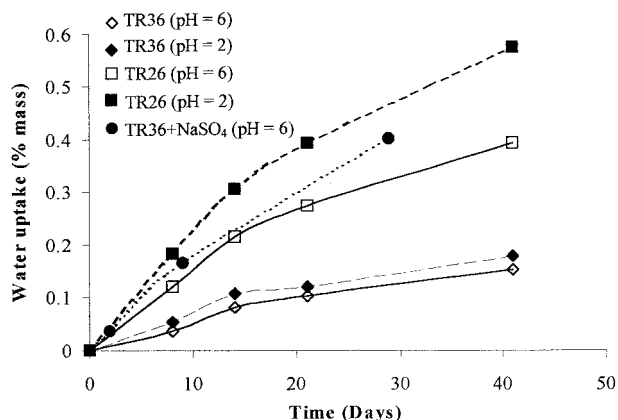
**Figure 8** Water uptake of films made from two latices, each at two different degrees of neutralization.

could be explained by the presence of undecomposed APS in the latter case. This could help form hydrophilic zones in the film, which would evidently increase the water uptake. If we add a salt ($Na_2SO_4$) to the neutralized form of latex TR36, we can see from this same figure that the water uptake is of the same order of magnitude as that observed for TR26, thus lending credence to the formation of hydrophilic zones in the films made with APS. In addition, the serum of TR26 contains more hydrosoluble material than does that of TR36. Because this material will not evaporate with the water during film formation, it is left behind on the surface of the particles, thus enhancing the hydrophilicity of the films. However, it must be said that we do not have a real way of determining the significance of this contribution. Regardless, it is clear that films produced from multimodal emulsions using the process suggested in this study have more favorable water uptake characteristics than those of films made using classic emulsion polymerization methods.

## CONCLUSIONS

We have presented a method that allows us to combine two concentrated seeds, and to polymerize them together to obtain latices with viscosities between 300 and 1000 mPa s$^{-1}$ at shear rates of 20 s$^{-1}$ and with solids contents of 73% (>70% polymer). The key to these high solids contents and low viscosities is a well-controlled, reproducible PSD. This is obtained by replacing the water-soluble initiator, commonly used in emulsion po-

lymerization, by an oil-soluble initiator that is present in only one of the seeds. This allows us to eliminate most of the problems caused by homogeneous nucleation, given that there are no radicals in the aqueous phase. In addition, because we are able to specifically target only one of the particle populations, we can concentrate only that portion of the emulsion, which gives us excellent control over the final PSD.

It was found that the lowest viscosities were obtained from a bimodal latex, with 15% (v/v) small particles (110 nm) and 85% (v/v) large particles (900 nm). This size ratio and proportion of small and large particles agrees well with the data presented in Part I.[1] No particular advantage was found using trimodal latices, although this point could certainly be explored further for PSDs other than those used here. It was also found that trimodal latices were slightly more sensitive (in terms of variations of the viscosity) to changes in the PSD than were bimodal latices.

Residual monomer is removed using HPO as a water-soluble initiator (necessary given that the monomers MMA and AA are water soluble). HPO is (here) activated by continuous addition of AscA. When we add a persulfate initiator to finish the reaction at reaction temperature, the decomposition is so rapid that it provokes local nucleation that leads to the formation of large amounts of floc. The use of an activated initiator system offers the advantage of being able to disperse the initiator throughout the reactor before provoking its decomposition and the formation of free radicals, thereby significantly reducing the amount of floc formed during the reaction. The replacement of APS by DEAB also allows us to significantly reduce the water uptake of films formed from both neutralized and unneutralized latices.

A certain number of the problems exposed in Part III[3] that were motivating factors for the research presented here are closely associated with the hydrosolubility of the MMA and AA included in the recipes. This process has the advantage of being useful for emulsions with both hydrophobic and hydrophilic monomers. Because we can nicely control the PSD for emulsions made with hydrophilic monomers, it is reasonable to expect that we should obtain results at least as good with hydrophobic compounds.

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