

# High-Solid-Content Emulsions. V. Applications of Miniemulsions to High Solids and Viscosity Control

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**ABSTRACT:** The use of miniemulsions of styrene and butyl acrylate to make high-solid-content, low-viscosity latices was investigated. Products were obtained with solid concentrations greater than 70 wt % and viscosities as low as 350 mPa s at shear rates of 20 s<sup>-1</sup>. This was possible with monomodal and bimodal latices. In addition, the compartmentalization of the reactive species in the miniemulsion systems was exploited to produce latices with high solid

concentrations, low viscosities, and bimodal molecular weight distributions. This demonstrated a potentially interesting application for this sort of material. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 745–752, 2005

**Key words:** emulsion polymerization; particle size distribution; viscosity; miniemulsions; particle nucleation

## INTRODUCTION

As discussed in previous articles, miniemulsion polymerization has been studied essentially to determine the stabilization before and during the reaction and to elucidate the mechanism of particle formation. The conclusions are not clear and are occasionally conflicting. For instance, certain authors have shown that homogeneous nucleation cannot be avoided,<sup>1</sup> whereas others have claimed that the final particle size distribution (PSD) is a one-to-one copy of the initial droplet size distribution (DSD).<sup>2</sup> In previous articles from this group, it has been shown that homogeneous nucleation cannot be avoided in some systems, but, if the stabilization conditions are maintained under strictly controlled conditions, the stabilization of homogeneously nucleated particles can be avoided, and they can be caused to flocculate onto the larger structures in the reactor.<sup>3,4</sup> This conclusion was drawn for conventional macroemulsions, but there is no reason to suspect that it cannot be applied to miniemulsions. In addition, it has been shown that in a well-stabilized miniemulsion, almost one-to-one copies of the initial DSD are indeed possible.<sup>5</sup>

On the other hand, the DSD and PSD are almost certainly not monodisperse. This property can be undesirable for certain applications; however, for creating high-solid-content systems, a very wide (or bimodal) PSD is an advantage (see ref. 6). Although it is possible to conduct miniemulsion polymerizations that lead to a narrow PSD,<sup>7</sup> most other authors have

shown the opposite. Some in fact have exploited the broadness of the miniemulsion PSD to produce high-solid-content latices with low viscosity.<sup>8–10</sup> For instance, Masa et al.<sup>9</sup> showed that the miniemulsion polymerization of styrene, 2-hexyl acrylate, and methacrylic acid with a 55% solid content had a lower viscosity (0.7 Pa s) than the conventional macroemulsion process with the same composition (4.5 Pa s). Leiza et al.<sup>10</sup> obtained better results in term of the overall solid content and viscosity (65 wt %, 0.44 Pa s) when the solid content of the initial charge and the feed were well adjusted. On the basis of these results, Tang et al.<sup>11</sup> proposed a two-stage semicontinuous process to reach high final solid concentrations with a lower surfactant concentration. In the first stage, a seeded semicontinuous miniemulsion polymerization produced a seed with a medium solid content and a broad PSD, and in the second stage, the solid content was increased by the semicontinuous addition of the monomer with a relatively low emulsifier concentration. The very wide PSD obtained in the first stage allowed them to increase the solid content in the second stage without increasing the viscosity. The best results (61 wt % solid content, 6.1–9.3 Pa s) were obtained when the upper and lower PSD limits were shifted to larger and smaller particle sizes, respectively, during the second stage.

These are interesting results, but they are much lower than the 70–75% solid concentrations obtained in studies by Schneider and coworkers<sup>3,4</sup> on macroemulsions. In their work, the authors prepared bimodal PSDs containing approximately 80 vol % large particles; the ratio of the diameters of the large particles to the small particles was approximately 6–8. In this work, we propose the synthesis of high-solid-

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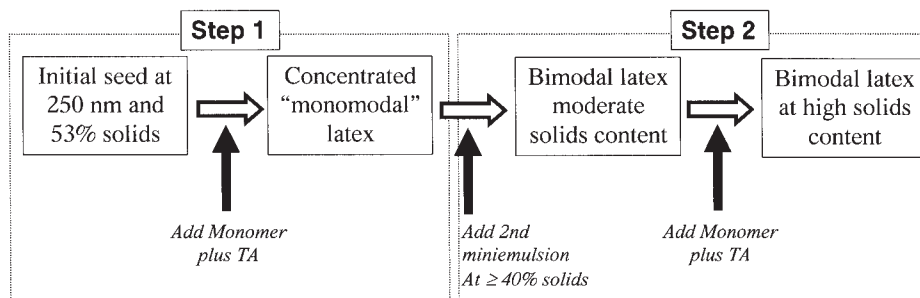


Figure 1 Process flow sheet for the production of high-solid-content miniemulsions.

content latices with different PSDs with miniemulsions. This process is necessarily a two-step, semibatch polymerization. In the first step, we create an initial seed of large particles, and in the second step, we adjust the solid content and viscosity of the product by adding a second seed of smaller particles and by polymerizing the two populations together.

## EXPERIMENTAL

Styrene, butyl methacrylate (BMA), ammonium persulfate (APS), sodium dodecyl sulfate (SDS), Triton X-405 (70% in an aqueous solution), and stearyl methacrylate (SMA) were obtained from Acros Organics (Noisy LeGrand, France) and used as received. The initial dispersions of the miniemulsions were homogenized by sonification (with an ultrasonifier at a 90% amplitude) for 4 min, and the reactor and polymerization conditions were described in general terms by

Ouzineb et al.<sup>5</sup> They were stabilized with Triton 405-X, and SMA was used as a polymerizable costabilizer. During the semicontinuous mode, the monomer was added at a constant rate under gravity flow, and the aqueous surfactant solution was injected with a programmable syringe pump. All the reactions were run at a constant jacket temperature of 70°C.

The average particle sizes were measured with fixed-angle quasi-elastic light scattering (QELS; 90° on a Malvern lo-C) (Villeurbanne, France), and in certain cases, full PSDs were approximated with variable-angle QELS (Malvern 4800). All the values reported here are averages of 10 measurements per sample. The conversions were measured by gravimetry. The glass-transition temperatures ( $T_g$ 's) were determined with a Setaram DSC 131 (Calvire, France). The viscosity of the latices was measured with a Rheometric Scientific RFS III viscometer (Champs sur Marne, France) at room temperature.

TABLE I  
Recipe for Runs SCM1 and SCM2 (70°C)

	Step 1		Step 2	
	Initial charge	Feed	Second seed	Feed
Run 1: High-solids BMA homopolymer				
BMA	$d_m = 264$ nm		$d_m = 130$ nm	
Miniemulsion	221.9 g		25.3 g	
Neat	—	190.8 g		57.8 g
Triton	14.7 g		1.8 g	
SMA	12.0 g		1.6 g	
APS	0.266 g		—	
Water	187.6 g		38.0 g	
Run 2: High-solid blend of styrene and BMA				
Styrene	$d_p = 275$ nm			
Miniemulsion	114.0 g			
Neat		640.0 g		40 g
BMA			$d_m = 154$ nm	
Miniemulsion			84.6 g	
Triton		4.2 g	2.1 g	0.5 g
SDS			0.31 g	
SMA				1.8 g
APS	0.65 g			
Water	386.0 g		74.8 g	

**TABLE II**  
Results of Run 1

	Solid content (mass %)	Viscosity (mPa a shear rate of at 20 s <sup>-1</sup> )
End step 1	63	600
Intermediate step 2	63	120
End step 2	70	70

## RESULTS AND DISCUSSION

The approach taken to the generation of high-solid-content, low-viscosity seeds is shown in Figure 1. The process is generally divided into two overall steps, each with two substeps. In step 1, a seed is created with a moderately concentrated miniemulsion. Because it is important to maintain a balance between the large and small populations in terms of the volume fraction and average diameter of each, it is important to adjust the number of particles in this initial seed (see refs. 3 and 4). This is done preferably by the adjustment of the recipe of the initial miniemulsion to obtain the desired number of seed particles (as large as possible) or by the adjustment of the number of particles by dilution. The second part of step 1 consists of concentrating the initial seed to approximately 60% polymer by volume (or mass because the polymers considered here had specific gravities between 1.05 and 1.15). Step 2 begins with the addition of a well-defined second seed, and the two populations are grown in parallel in the second part of this step. Once again, the size and number of the particles added in

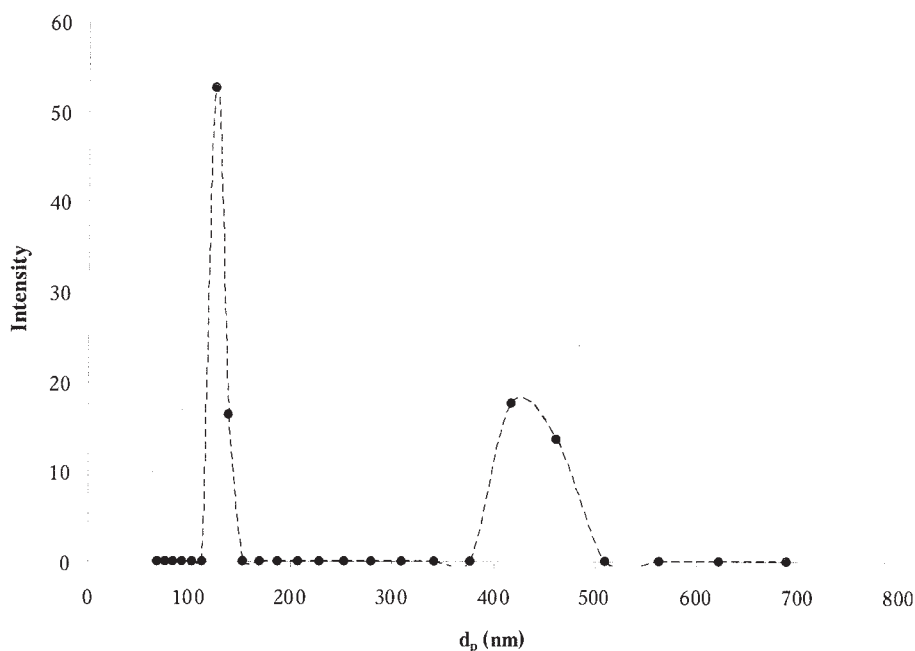
**TABLE III**  
Recipe Used for the Batch Miniemulsion Polymerization  
of the Seed Used in Run 2

Recipe				
Styrene (wt %/total)	SMA (wt %/styrene)	SDS (×cmc)	Triton (×cmc)	APS (wt %/total)
39	0.50	0.15	4.5	0.13
Characterization of dispersions				
$d_m$ , nm	PI <sub>initial</sub>	$d_{p, final}$ , nm	PI <sub>final</sub>	$N_{m, f}/N_{p, f}$
265	0.16	275	0.06	1.2

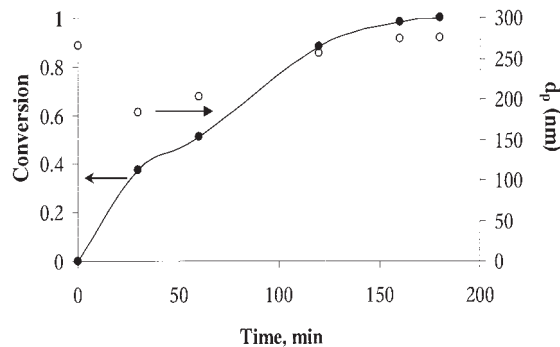
cmc, critical micelle concentration; PI, polydispersity index; PI<sub>final</sub>, final PI; PI<sub>initial</sub>, initial PI.

the second seed should be properly adjusted to provide the most favorable conditions possible for low viscosity at the end of the polymerization. In addition, it is preferable to have a relatively concentrated second seed to avoid dilution of the intermediate latex, which would lead to a relatively long concentration phase in step 2. We illustrate this principle with a number of examples, the recipes of which are given in Table I.

The results of the first example, run 1, are for the homopolymerization of BMA, and they are summarized in Table II and Figure 2. The results show that the production of a bimodal latex based on well-controlled miniemulsions allows us to achieve the objectives of a high solid concentration and a low viscosity. Although the ratio of the diameters of the two populations is closer to 4 than to the supposedly optimal value of 6–7, the bimodality of the product clearly



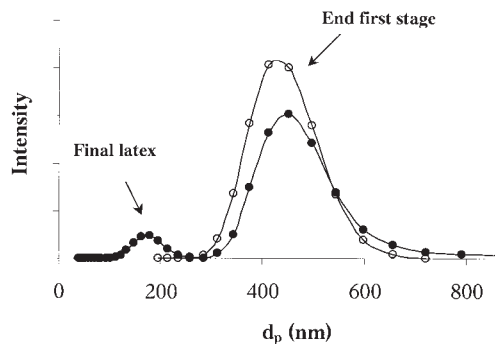
**Figure 2** PSD for the final latex in run 1.



**Figure 3** Time evolution of (●) the conversion and (○) the dry particle size obtained for the batch miniemulsion polymerization of styrene at 70°C (Table III). The data point for the particle size at time zero corresponds to the estimate of the initial droplet size.

leads to a lower viscosity. We return to this notion later.

Run 2 is based on the same principle, but with some slight modifications. In this case, the first population of large particles began with a seed of polystyrene (PS) particles. The recipe for this seed is given in Table III. As shown in Figure 3, this recipe led to the successful production of a latex with a final particle diameter ( $d_{p,final}$ ) of 275 nm for a 40 wt % solid concentration. The ratio of the initial number of droplets to the final number of particles ( $N_{m,i}/N_{p,f}$ ) was close to one. Unfortunately, the recipe was poorly adjusted in terms of giving us the right number of particles, and it was necessary to significantly dilute it. The product obtained after dilution was used as seed latex in step 2 and was concentrated as shown in Table I. Styrene monomer was added under starved conditions (i.e., at a constant instantaneous conversion of ca. 90%, which corresponds to a monomer concentration below what would saturate particles made by conventional emulsion polymerization). Under these conditions, the seed particles now behave as a regular macroemulsion. This last point is true of all miniemulsions once the critical saturation concentration of the monomer (i.e., the point at which the monomer droplets disappear in a conventional system) is passed. The reason for run-



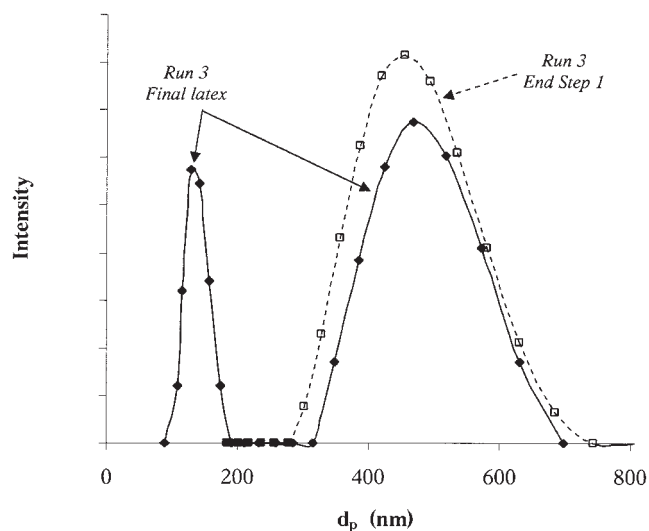
**Figure 4** PSDs of the latex produced in run 2 at the end of the first step and of the final latex (measured with the non-negative least squares (NNLS) mode on the Malvern 4800).

ning the reaction under these conditions was to avoid secondary nucleation and to ensure that the particles grew near the maximum polymerization rate.

The number of PS particles per unit of volume of miniemulsion remained constant throughout step 1. At the end of this step, the latex contained 63 wt % solids, and the particle diameter ( $d_p$ ) increased to 430 nm (after the dilution of the original seed particles, the semibatch process began at a solid concentration of 15 wt %). Once the solid content was 63 wt %, the styrene feed was interrupted for 30 min to obtain the complete conversion of the residual monomer. A sample was withdrawn to measure the viscosity and PSD at this stage of the reaction (i.e., a latex at a 63 wt % solid concentration with a monomodal PSD). Step 2 was begun with the addition of 151 g of a BMA miniemulsion [56% solids, droplet diameter ( $d_m$ ) = 152 nm], which was added over the course of a few minutes, following which styrene was once again added for 40 min. This last addition of the monomer increased the solid concentration and was used to investigate its effect on how the BMA miniemulsion behaved. The final latex was obtained after a finishing period (batch). Light scattering measurements of the final latex (Fig. 4) show a bimodal PSD; the larger population is clearly that of PS, and the smaller population corresponds to the BMA miniemulsion. The results of

**TABLE IV**  
Analyses of Run 2

	$d_p$ (nm)	$T_{g1}$ (°C)	$T_{g2}$ (°C)	Polymer content (wt %)	Viscosity (mPa s at a shear rate of 20 s <sup>-1</sup> )
End step 1	430.1	—	—	62	679
End step 2	—	34.2	100.2	63	60
Supernatant after the centrifugation of latex from end Step 2	174.1	32.1	—	—	—



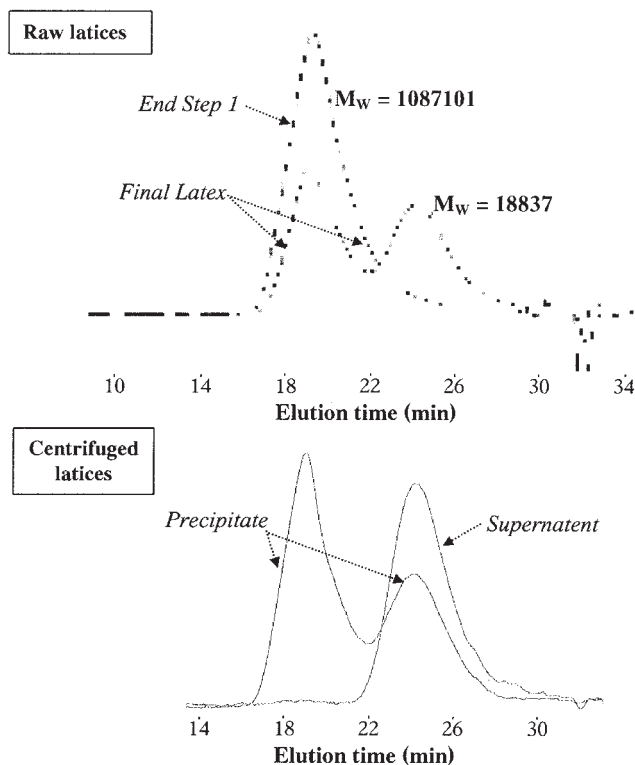
**Figure 5** PSDs of the latex produced in run 3 at the end of the first step and of the final latex (measured with the NNLS mode on the Malvern 4800).

the viscosity measurements are shown in Table IV. Although we did not increase the solid content to the same level as that in run 1, it is clear that the simultaneous proper adjustment of the PSD (the ratio of the diameter of large particles to small particles was ca. 3.5) and the solid content allowed us to significantly reduce the viscosity of the final latex. In fact, in the example, the solid contents at the end of steps 1 and 2 are very similar, but the viscosity of the bimodal latex is an order of magnitude lower.

In addition to the control of the viscosity, this example also illustrates interesting possibilities for the use of miniemulsions in high-solid-content systems: the exploitation of the compartmentalization of the monomer to obtain latices with properties different from what are attainable in a conventional macroemulsion. This refers to the tendency of monomers to remain inside the polymerizing miniemulsion particles as long as the monomer concentration remains above the saturation concentration typical of interval II of conventional macroemulsion polymerization (for a more in-depth discussion of this phenomenon, see refs. 5 and 12). In this particular example, the second population of particles was introduced in the form of an unpolymerized miniemulsion of BMA, but the feed to this step was styrene monomer. The final latex from run 2 was centrifuged, and a differential scanning calorimetry analysis was performed on the supernatant phase (the larger particles were concentrated in the bottom of the tube, and the smaller ones were in the upper, or supernatant, phase) and the original latex. As expected, the supernatant phase contained small particles of BMA. However, only one  $T_{gr}$ , that of poly(butyl methacrylate) (PBMA), was observed for this phase. This tells us that none of the styrene fed

during step 2 was consumed by the BMA particles. This was also confirmed by an analysis of the average particle size of the large population, which increased by an amount that corresponded to the amount of styrene fed during this step. This type of behavior cannot be observed in a conventional macroemulsion and leads us to believe that it is possible to create high-solid-content, low-viscosity latices with different properties in different particle populations. To explain this observation, we point out that the conversion of BMA in the second miniemulsion was approximately 30% (based on the results of BMA homopolymerization under similar conditions<sup>13</sup>). This means that it is below the saturation condition, and the shift in mass-transfer conditions provoked by the miniemulsion stabilization system (i.e., that prevents Ostwald ripening) has created a situation in which the styrene added to the reactor will not be absorbed (at least at detectable levels) by the miniemulsion and so can only enter the macroemulsion particles already present.

As a further example of the type of process, another experiment (run 3) was performed to make a bimodal molecular weight distribution (MWD) at a moderately high solid concentration. Run 3 was identical to run 2, with the exception of the addition of 2% (w/w) *n*-dodecyl mercaptan to the BMA miniemulsion before its addition in step 2 ( $d_m = 150$  nm). If no mass transfer



**Figure 6** MWDs of the latex from run 3. The top figure shows the latex at the end of step 1 and the uncentrifuged final latex. The bottom figure shows the supernatant and the precipitate phase.

TABLE V  
Recipe for Runs 4 and 5

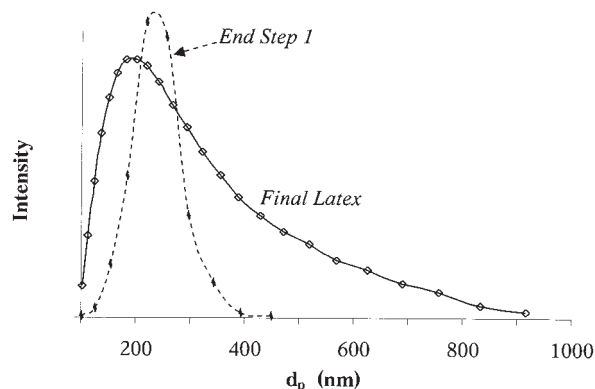
	Step 1		Step 2	
	Initial charge	Feed	Second seed	Feed
Run 4				
PS seed particles (42% solids)	99 g of PS			
BMA				
Miniemulsion			48.5 g	
Neat		56 g		350 g
Triton		3 g	1.7 g	5 g
SDS			0.3 g	
SMA			1.1 g	
APS	0.3 g			
Water	137 g		47.5 g	
Dodecyl mercaptan			0.98 g	
Run 5				
PBMA seed	413 g of PBMA			
BMA				
Miniemulsion				
Neat		600 g		
Triton	5 g	5 g		
SDS				
SMA				
APS	1.02 g			
Water	367 g			
Dodecyl mercaptan				

of the chain-transfer agent (CTA) occurred between the BMA and PS particles, then the final latex should have a bimodal MWD. In the event that CTA was transferred, the MWD would be trimodal. In this last case, the PS particles would contain the high-molecular-weight component from the first miniemulsion and a second lower molecular weight component created during the latex concentration step in the presence of CTA, in addition to the peak attributable to PBMA particles.

At the end of the first step, the ratio of the number of droplets in the initial styrene miniemulsion to the number of particles was 1.01, with an average  $d_p$  value of 460 nm. At this point, the viscosity was 690 mPa s at a shear rate of  $20 \text{ s}^{-1}$  and a solid concentration of 62 wt %. The final latex contained the bimodal PSD shown in Figure 5, and the viscosity was 56 mPa s (same shear) for a solid concentration of 63% (w/w). The latex was centrifuged, and the supernatant phase contained only small particles with a diameter of 147 nm (very close to  $d_m$  of the original BMA miniemulsion); the precipitate contained a bimodal distribution with small particles of  $d_p = 149$  nm and large particles of  $d_p = 468$  nm.

An analysis of the MWD is shown in Figure 6. As expected, the polymer at the end of the first stage had a monomodal PSD. The same figure also shows that the polymer at the end of the reaction had a bimodal PSD with a peak clearly corresponding to that of the PS homopolymer and a lower molecular weight corresponding to that of the smaller particles. As in run 2, the final latex was centrifuged, and the MWD of the

supernatant and precipitate are shown at the bottom of Figure 6. The MWD of the particles remaining in the supernatant phase clearly corresponds to the low molecular weight peak seen at the end of step 2. The precipitate shows a bimodal MWD (i.e., no transfer of CTA), with the high molecular weight peak corresponding to that of PS from step 1 and the low molecular weight peak corresponding to that of PBMA (small particles were likely trapped in the precipitate phase). There is no evidence of a third peak that would have resulted from a copolymer of styrene and BMA or from the diffusion of the dodecyl mercaptan to the styrene phase. The properties of PS particles at step 1 are maintained until the end of the reaction, and the addition of the BMA miniemulsion allowed us to create a latex with two bimodal distributions: one in particle size and one in MWD. Interestingly enough, the BMA droplets were not destabilized by the presence in the reactor of PS particles polymerizing and the addition of the styrene monomer at the same time. The balance between the Laplace and osmotic pressure was maintained throughout the second stage, and so the majority of the droplets added to the second population were nucleated, and no monomer or transfer-agent desorption occurred. The PBMA particles did not adsorb styrene monomer because in the miniemulsion, the concentration of the monomer in the droplets was twice the saturation value obtained in a classical emulsion. When the reaction began in step 2, this concentration remained above the satura-



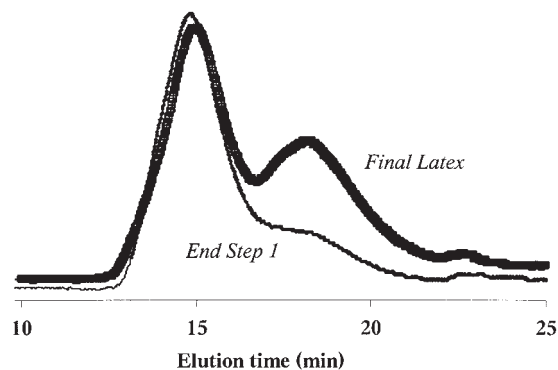
**Figure 7** PSDs of the latex obtained at the end of step 1 and of the final latex for run 4 (measured with the NNLS mode on the Malvern 4800).

tion until 60% conversion, and there was no driving force for mass transfer.

Two similar experiments were then run with dry seeds (previous produced, with essentially no residual monomer). The recipes are shown in Table V. Run 4 was intended to demonstrate that one could achieve high solid concentrations, low viscosities, and bimodal MWDs with this approach and, along with run 5, to show that it is not always necessary to have a bimodal PSD; in some cases, a wide PSD is enough to control the viscosity.

During the first stage of run 4, BMA was added to a PS seed [PS was used simply for convenience; the composition of the seed particles at this point was not important ( $d_p$  of the seed = 215 nm)] at a feed flow rate such that starved conditions were maintained. A monomodal PSD was obtained at the end of step 1 with a  $d_p$  value of 250 nm and a solid concentration of 54%. A BMA miniemulsion was added ( $d_m = 150$  nm), and we continued to add BMA monomer. In this case, the feed in step 2 lasted for approximately 5 h. This means that unlike run 2, both populations were able to absorb the BMA monomer after the first hour (the point at which the conversion in the small particles passed the critical saturation conversion), and we had competitive growth of the two PSDs.

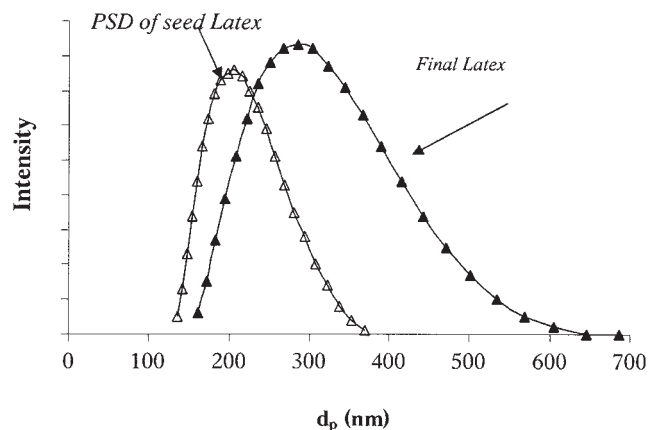
Multiple-angle QELS, gel permeation chromatography, and viscosity measurements were performed on the final latex. The final solid polymer concentration was 70 wt %, with a viscosity of 690 mPa s at a shear rate of  $20 \text{ s}^{-1}$ . The results of the PSD analysis are shown in Figure 7, and the MWD is shown in Figure 8. The final latex showed a broad PSD and a bimodal MWD. A very broad PSD yields the same possibility of obtaining a high-solid-content latex with a low viscosity as the creation of a bimodal latex. In addition, we succeeded in obtaining a bimodal MWD, which would be particularly interesting if we wanted



**Figure 8** MWD results obtained for the final latex and the latex obtained at the end of step 1 for run 4.

to manipulate the properties of the final product (e.g., for adhesives).

In run 5, the formulation of the process was altered and was in fact performed in one prolonged step 1 because no second seed was added. A PBMA seed latex, with the PSD shown in Figure 9, was concentrated with a feed of BMA and Triton. The evolution of the PSD for this shows an increase in the average particle size and a significant broadening. This broadening was enough to allow us to produce a latex with a polymer concentration of 70 wt % with a viscosity of 350 mPa s at a shear rate of  $20 \text{ s}^{-1}$ . Although most of the evolution appears to be by natural particle growth, enough agglomeration seems to have occurred to have generated large enough particles at the high end of the PSD to provide an advantageous rheological effect. Although this latex did not have the exact same PSD as the one in run 4, the tendency of these two experiments seemed to be the production of a very wide PSD with no particles under 100 nm (the ratio of the largest particles to the smallest particles was 5 in run 5 and 9 in run 4).



**Figure 9** Evolution of PSD for run 5.

## CONCLUSIONS

Different means of producing high-solid-content, low-viscosity latices with miniemulsions were proposed in this work. It was relatively straightforward to produce such products with this means of polymerization. Excellent results were found for both bimodal and monomodal products.

No particles much under 100 nm were detected in any of the products, and this seems to lend credence to the idea proposed by Schneider and coworkers<sup>3,4</sup> that the production of very small particles leads to a loss of control of the product viscosity and reproducibility of the process.

In addition to being useful for the production of low-viscosity products, the fact that the monomer is compartmentalized during a good portion of the polymerization process for miniemulsions<sup>5,12</sup> means that we can use them as a very interesting means of manipulating the MWD at high solid concentrations in ways not possible with conventional macroemulsions.

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