

Preparation of High Solids Content Poly(*n*-butyl acrylate) Latexes Through Miniemulsion Polymerization

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ABSTRACT: An approach to prepare high solids content latexes (>50 wt %) is presented. The approach is based on a two-stage polymerization where in the first stage low-to-medium solids content seed latexes with a broad particle-size distribution (PSD) were prepared by semicontinuous miniemulsion polymerization. In the second polymerization stage, the solids contents of the latexes prepared in the previous step were increased to 60–70 wt % using relatively low emulsifier concentrations. The approach was used successfully to prepare fluid- and coagulum-free poly(*n*-butyl acrylate) latexes up to solids contents of 61 wt % using an emulsifier (sodium lauryl sulfate) concentration of 0.5 wt % based on a monomer. Nonfluid (pastelike) latexes having solids contents higher than 61 wt % were also prepared using this method. As a result, some guidelines related to the required particle-size distribution to produce fluid latexes of higher solids contents are also presented. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1797–1809, 1997

INTRODUCTION

High solids content latexes (>45–50 wt %) are typically prepared in industrial practice. These are used for coatings and adhesives and in many latex and formulated products. These latexes offer some advantages for most of the commercial applications in which they are employed: low shipping costs (less water is shipped) and little or no need to remove water. One of the major difficulties encountered in the preparation of these latexes is the increase in viscosity once a certain value of the particle volume fraction is achieved. It is well known that this increase in the viscosity is due to the effect of particle–particle interactions and the formation of complex flow units which become very important when the volume fraction of the

dispersed phase approaches the maximum packing concentration.¹

For monodisperse rigid spheres, the value of the maximum packing fraction has been frequently reported to be 0.7405 in volume.^{2–4} Emulsions having a higher volume fraction of the dispersed phase should break down or invert due to the unbalanced forces that take place between the droplet surfaces.² However, stable emulsions having higher volume fractions of the dispersed phase can be imagined and are known under certain conditions: (a) when polydisperse emulsions are prepared; in this case, the small droplets or particles can fit between the voids of the large ones and the maximum packing can be enhanced; (b) under the influence of a centrifugal field, the emulsion can be compressed considerably and particles or droplets can deform in the contact areas moving from spheres to polyhedral configurations, increasing the packing concentration; and (c) even in the absence of the preceding conditions, it has been reported by some authors^{3,5–8} that emulsions having a higher volume fraction than 0.7405 can be prepared; their success is at-

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tributed to the deformation of the droplets into polyhedral structures of particular types. In the latter case, the selection of the surfactant system is a key parameter in being able to surpass the critical volume fraction.

Another parameter that should be taken into account when the viscosity/concentration relationship of a colloidal dispersion is investigated is the effective hydrodynamic volume fraction of the dispersed phase. This may result from electrostatic repulsion, adsorbed emulsifier, adsorbed polymer, and swelling of polymer particles and may significantly reduce the maximum volume fraction at which the viscosity tends to infinity. Krieger⁹ calculated theoretically, for a colloidal dispersion of monodisperse spheres, the maximum volume fraction of particles at which the system will still flow to be about 0.62. However, as has been pointed out above, for polydisperse systems, this value is greater since the maximum packing concentration would be greater. Therefore, by producing latexes with a broad particle-size distribution (PSD), the likelihood for these latexes to achieve higher solids contents should be enhanced.

Miniemulsion polymerization seems to be a good approach to produce latexes having a broad PSD because of its mechanistic differences with conventional emulsion polymerization. Ugelstad et al.,¹⁰ in their early work on the miniemulsion polymerization of styrene, showed that nucleation of polymer particles can take place in submicron droplets if the surface area of the droplets is increased in such a way that they can effectively compete for the capture of free radicals. Several research groups have investigated both mechanistic aspects and applications of miniemulsion polymerization processes. Delgado and El-Aasser,¹¹ in their review of miniemulsion polymerization, concluded that the main differences between miniemulsion and conventional emulsion polymerization are due to the different nucleation mechanisms and the influence of the cosurfactant on the concentration of the monomer in the different phases.

Since nucleation takes place in monomer droplets^{12,13} and the free-radical capture efficiency of the droplets is lower than that of micelles or even polymer particles,¹⁴⁻¹⁷ the nucleation period in a miniemulsion polymerization is longer and this leads to a much broader PSD than in conventional emulsion polymerization processes.

Recently, Miller et al.¹⁸ showed that the addition of a small amount of polymer to the oil phase

of a miniemulsion prior to homogenization causes a significant increase in the radical capture efficiency by the droplets, resulting in an increase in the number of polymer particles formed and in the polymerization rates obtained. On the other hand, Tang et al.¹⁹ showed that monomer droplet nucleation occurred during the seeded semicontinuous polymerization of *n*-butyl acrylate (feeding the monomer as a miniemulsion) and that this nucleation decreased by increasing the seed concentration and by decreasing the miniemulsion feed rate. In these experiments, they obtained latexes with a very broad PSD (S_n/D_n ratios ranging from 0.40 to 0.56). It should be pointed out that some limited coagulation resulting in a population of large particles was also observed in these experiments. The solids content of these latexes was around 25 wt %.

Taking advantage of this unique particle nucleation mechanism, López de Arbina et al.^{20,21} were able to produce coagulum-free high solids content latexes (up to 60 wt %) in the miniemulsion terpolymerization of styrene, 2-ethylhexyl acrylate, and methacrylic acid carried out in bottle polymerizations and in batch and semicontinuous stirred tank reactors. In addition, they measured the stability of these latexes and compared them with those prepared by conventional emulsion polymerization. They found that the viscosity of the latexes produced by the miniemulsion approach was lower and that the maximum solids contents achievable (coagulum-free) by the conventional emulsion process was lower than that obtained by the miniemulsion process. Unzué and Asua²² studied the effect of the operation variables on the feasibility of producing latexes of 65 wt % solids content by semicontinuous miniemulsion terpolymerization of *n*-butyl acrylate, methyl methacrylate, and vinyl acetate. In addition, they studied the effect of the solids content, initiator concentration, feed flow rate, and amount of cosurfactant on the kinetics of that high solids content polymerization. In all these works, different types and combinations of emulsifiers (anionic and nonionic) were employed, but in all cases, the emulsifier concentration was higher than 1 wt % (based on the monomer), and in some cases, it was as high as 5 wt %. Also, no information regarding the PSDs of the resulting latexes was reported.

On the other hand, Ruckenstein and Kim,^{5,8} following the method developed by Lissant and Mayham^{3,6} to prepare highly concentrated emulsions (higher than 74% by volume), carried out gel-like emulsion polymerizations of styrene and

styrene/methacrylic acid in small centrifuge tubes using an oil-soluble initiator (AIBN) with sodium dodecylsulfate as an emulsifier. The effects of the initiator and emulsifier concentrations, volume fraction of the dispersed phase, temperature, and ionic strength of the aqueous solution were studied. They showed that both the polymerization rate and molecular weight were higher than in bulk polymerizations carried out under the same conditions. However, they reported that some amount of polymer was formed under bulk conditions because some droplets agglomerated and formed a separate phase. The lower the emulsifier-to-monomer ratio, the larger the amount of polymer formed under bulk conditions. In addition, they could not reach 100% conversion during the experiments and, hence, the final solids contents of the latexes produced were somewhat lower than the initial volume fraction of the monomer dispersed in the tubes. Neither the final solids content of the latexes nor their viscosity were reported. In addition, it does not seem straightforward to scale up these batch gel-like emulsion polymerizations to stirred tank reactors because of the large amount of heat that they can release and the difficulties in achieving a sufficient mixing to homogenize the emulsion.

In the present work, a new approach to prepare high solids contents latexes based on miniemulsion polymerization and using a lower level of emulsifier than in other works is presented. The approach requires two polymerization stages. In the first stage, and following the procedure described by Tang et al.,¹⁹ medium solids content latexes having a broad PSD are prepared by seeded semicontinuous miniemulsion polymerization. Thereafter, in the second stage, the solids content of these broad PSD latexes are increased by using seeded conventional emulsion polymerization carried out under batch and semibatch conditions with the total emulsifier concentration not exceeding 0.5 wt % based on the monomer.

Table I Recipe Used for the Preparation of the P(BA) Seed Latex Used in the First-stage Experiments; Temperature = 75°C

| Ingredient | Weight (g) |
|--|------------|
| <i>n</i> -Butyl acrylate | 375 |
| Aerosol MA (Cyanamid) | 5.36 |
| NaHCO ₃ | 1.27 |
| DDI water | 1104 |
| K ₂ S ₂ O ₈ | 1.24 |

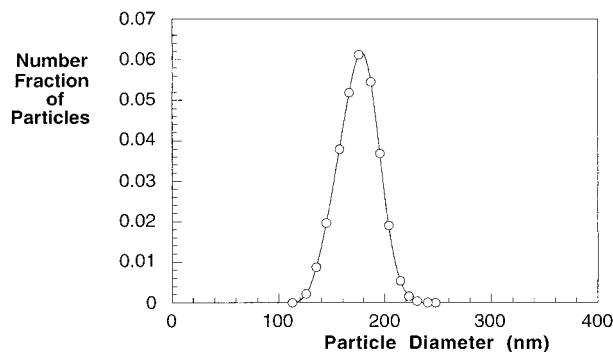


Figure 1 Number PSD of the P(BA) seed measured by capillary hydrodynamic fractionation (CHDF).

This approach is applied to the homopolymerization of *n*-butyl acrylate.

EXPERIMENTAL

N-Butyl acrylate was used either as received (technical grade, containing 10–55 ppm of hydroquinone monomethyl ether [Aldrich]), cleaned using inhibitor removal columns (Aldrich), or distilled. Sodium lauryl sulfate (SLS), ammonium persulfate [(NH₄)₂S₂O₈], potassium persulfate (K₂S₂O₈), sodium bicarbonate (NaHCO₃), and hexadecane (HD) were used as received. Distilled and deionized water (DDI) was used throughout the work.

In the first stage, seeded semicontinuous miniemulsion polymerizations were carried out. The poly(*n*-butyl acrylate) [P(BA)] seed latex was prepared using the recipe given by Maxwell et al.²³ as shown in Table I. The emulsion was allowed to polymerize batchwise for 15 h at 75°C. The particle size obtained in the polymerization was measured by capillary hydrodynamic fractionation (CHDF 1100, Matec Instruments) and the distribution is plotted in Figure 1. The values of the measured particle diameter averages are as follows: $D_v = 163.4$ nm, $D_n = 161.0$ nm, $D_w = 167.2$ nm, and PDI = 1.03. As can be seen, the PSD can be considered monodisperse.

The semicontinuous seeded miniemulsion polymerizations of the first stage were carried out at 60°C in a $\frac{1}{2}$ L jacketed reactor equipped with a reflux condenser, a stainless-steel turbine stirrer (six blade, $d = 5.2$ cm, $h = 1.0$ cm; 300 rpm), a feed inlet tube, a nitrogen inlet tube, and a sampling tube. The pump used for the addition of the miniemulsion was a piston pump (Milton-Roy). The miniemulsion used as the feed mixture dur-

ing these experiments was prepared as follows: SLS was dissolved in water, and hexadecane, in BA. These two solutions were mixed using a magnetic stirrer for approximately 15 min. Then, this mixture was sonified (Branson sonifier; conditions: duty cycle = 50, output control = 7 and pulsed) for 2 min with mixing provided by a stir bar to initially break up the monomer droplets forming an emulsion. Then, a Microfluidizer-110 (Microfluidics Corp.) was used to create the sub-micron monomer droplets. This was operated at 80 psi inlet pressure and about 3000 psi outlet pressure with 10 passes of the mixture.

In all the second-stage experiments, BA was cleaned using inhibitor removal columns. Experiments were carried out in the same $\frac{1}{2}$ L reactor but two different configurations were used for the semibatch runs. When the monomer was added neat, it was fed to the reactor using the piston pump and a second pump (syringe pump, Harvard) was used for the initiator and emulsifier solutions. If the monomer was added as an emulsion, the piston pump was used for the monomer emulsion and the initiator was added via the syringe pump. The emulsion was prepared by dissolving the emulsifier in water and then adding the monomer to the solution. The mixture was mixed for 20 min using a magnetic bar. Thereafter, the emulsion was loaded in the addition reservoir where agitation was applied using a propeller (three blade, $d = 5.0$ cm; 300 rpm) which was maintained during the whole addition period.

The final solids contents and conversions of the latex samples withdrawn from the reactor during the experiments were measured by gravimetry, and the PSDs, by CHDF. In addition, the apparent viscosity of the latexes was measured using a Brookfield viscometer at room temperature (temperature was measured for each latex analyzed, and in all the cases, the temperature was within 23–24°C) in a 250 mL beaker.

RESULTS AND DISCUSSION

First Stage: Preparation of Broad PSD Seed Latexes

Following the procedure proposed by Tang et al.,¹⁹ seeded semicontinuous miniemulsion polymerizations were carried at 60°C using the recipe presented in Table II. Several experiments were carried out varying the emulsifier (SLS) concentration in the initial charge, the quality of the monomer (technical grade, cleaned, and distilled)

Table II Recipe Used for the Seeded Semicontinuous Miniemulsion Homopolymerizations of BA at 60°C

| Ingredients | Quantity |
|---|--------------------------------|
| Reactor initial charge | |
| Seed P(BA) (24.4 wt % solids) | 20 g |
| SLS | 0, 4, and 21.7 mM ^a |
| DDI Water | 60 g |
| NaHCO ₃ | 0.34 g |
| (NH ₄) ₂ S ₂ O ₈ | 6.6 mM ^b |
| Feed mixture | |
| <i>n</i> -Butyl acrylate | 100 g |
| DDI Water | 150 g |
| SLS | 8 mM ^c |
| Hexadecane | 27 mM ^c |

^a Based on the aqueous phase of the initial charge.

^b Based on the total amount of water in the recipe.

^c Based on the aqueous phase of the feed mixture.

and the miniemulsion (stored for 12 h or fresh), and the flow rate of the feed mixture (0.4 or 0.23 g/min with respect to the monomer). The main conclusion drawn from these experiments was that even though the monomer and miniemulsion quality and the flow rate of the feed mixture did not have a significant effect on the final PSD obtained the emulsifier concentration in the initial charge did play an important role. Only when the SLS concentration in the initial charge was lower than the CMC (6–8 mM) was there a continuous droplet nucleation during the addition period of the miniemulsion, creating a broad PSD (bimodal), where particles ranging from 50 to 400/500 nm were produced as was reported by Tang et al.¹⁹ In contrast, when [SLS] > CMC, nucleation in monomer droplets was almost negligible compared to micellar nucleation, and as a result, the final PSD showed a bimodal PSD where the new population of particles, generated from micelles, was significantly important in terms of number. In addition, the final PSD was considerably narrower than in the cases where [SLS] < CMC.

Figure 2 shows the final PSDs of the latexes produced in the experiments carried out under the conditions described in Table III. In addition, the volume-average particle size and a measure of the polydispersity of the PSD (S_n/D_n) are shown in Table IV. More detailed information on these experiments can be found elsewhere.²⁴

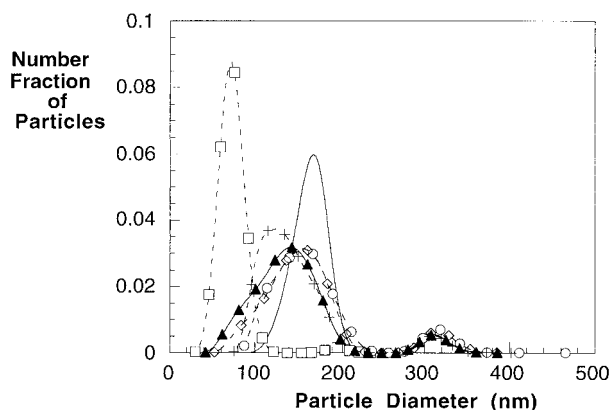


Figure 2 Number PSDs (CHDF) of the final latexes obtained in the first-stage polymerization of BA carried out under conditions shown in Table III: (—) seed; (\square) run J7; (\circ) run J12; (\diamond) run J13; (\blacktriangle) run J16; ($+$) run J18.

These latexes (with the exception of J7) were used as seed latexes in the second-stage polymerizations with the goal of increasing the solids contents up to values close to 70 wt %, taking advantage of the broadness of the PSD to limit the increase in the viscosity during the polymerization process as has been frequently reported in the literature.

Second Stage: High Solids Content Latexes

An increase in the solids content of the latexes prepared in the previous stage can be accomplished by using different monomer addition policies and different emulsification processes. The additional monomer needed to increase the solids content can be incorporated into the latex batchwise or it can be added in a semicontinuous fashion. Furthermore, the monomer can be added neat or as an emulsion or a miniemulsion.

Table IV Volume-average Particle Size and Polydispersity (S_n/D_n) of the Final Latexes of the First Stage of Seeded Emulsion Polymerization of BA Measured by Means of CHDF

| Run | D_v (nm) | S_n/D_n^a |
|-----|------------|-------------|
| J7 | 82 | 0.22 |
| J12 | 196 | 0.34 |
| J13 | 190 | 0.37 |
| J16 | 177 | 0.40 |
| J18 | 175 | 0.37 |

^a S_n = standard deviation; D_n = number-average diameter.

Batch Polymerizations

In the present work, the usefulness of the broad PSD seed prepared in the first-stage series of experiments by means of seeded semicontinuous miniemulsion polymerization was first checked by increasing the solids content in batch experiments. These experiments were carried out at 60°C and using as seed the latex produced in run J13 ($D_v = 190$ nm, solids content = 24.4 wt %). The recipe used in these experiments is shown in Table V and a summary of the results obtained is given in Table VI.

In run JH-1 (45 wt % solids content), where the lowest SLS concentration was used, some coagulum was observed at the end of the polymerization (<1 wt %). A further experiment at the same solids content was carried out, JH-2, with a doubled concentration of SLS. In this experiment, no coagulum was observed at the end of the process and the latex viscosity and the average volume particle diameter were almost identical to that obtained for run JH-1. In runs JH-3 and JH-4 (55 and 65 wt % expected final solids, respectively), no coagulum was observed even though the emulsifier concentration based on monomer

Table III Experimental Conditions of the Seeded Semicontinuous Miniemulsion Polymerizations of BA Carried Out at 60°C

| Run | [SLS] (mM) | Monomer | Miniemulsion | Flow Rate ^a (g/min) |
|-----|------------|-----------------|-----------------|--------------------------------|
| J7 | 21.7 | Technical grade | Stored for 12 h | 0.4 |
| J12 | 0 | Cleaned | Fresh | 0.4 |
| J13 | 4 | Cleaned | Fresh | 0.4 |
| J16 | 0 | Distilled | Fresh | 0.4 |
| J18 | 4 | Distilled | Fresh | 0.23 |

^a Based on the monomer.

Table V Recipe Used in the Second-stage Batch Experiments Carried Out at 60°C

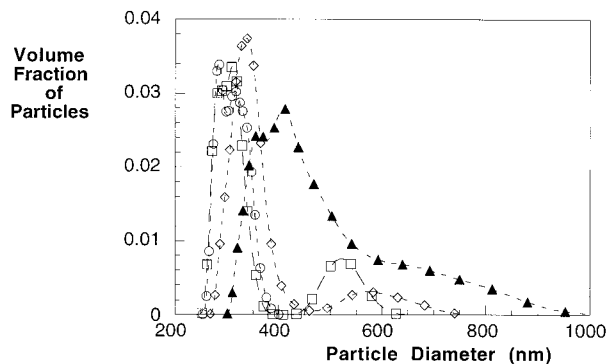
| Ingredient | Amount (g) |
|---|---|
| P(BA) seed (J13) | 50 |
| SLS | 4 mM ^a (JH-1) and 8 mM ^a (all others) |
| (NH ₄) ₂ S ₂ O ₈ | 3 mM ^a |
| NaHCO ₃ | 3 mM ^a |
| DDI water | 100 |
| BA | Function of the solids content ^b |

^a Based on aqueous phase.

^b 100.9 g (JH-1 and JH-2), 155.6 g (JH-3), and 243.7 (JH-4).

decreased compared to that of run JH-2. However, in run JH-3, where the turbine was used as the impeller, a film was formed on the reactor wall due to poor mixing during the experiment. The stagnant region close to the wall, observed during the last portion of the experiment, and the increase in the final latex viscosity confirmed this point. For experiment JH-4, a different impeller was chosen (Jiffy type, recommended for viscous liquids, having two sets of two-bladed impellers separated by two vertical arms which can closely approach the sides of a reactor; $d = 6.5$ cm, $h = 6.0$ cm; Cole-Parmer) to enhance mixing during the experiment. This was achieved, but due to the high monomer concentration in the reactor and, hence, in the polymer particles, a thermal runaway occurred, leading to reaction temperatures around 80–85°C. As expected, polymerizations aiming to produce latexes with solids contents higher than 55 wt % could not be accomplished by running batch processes. The final solids content of run JH-4 was 58 wt % due to the loss of some monomer during the runaway and, in addition, the latex viscosity was higher than in the previous runs.

Figure 3 shows the final volume PSDs obtained

**Figure 3** Volume PSDs (CHDF) of the final P(BA) latexes in the batch process: (□) JH-1; (○) JH-2; (◇) JH-3; (▲) JH-4.

for these experiments. It can be seen that the experiments carried out at 45 wt % solids have almost the same distribution except for a peak at large particle sizes (400–600 nm) that showed up in experiment JH-1 (where the lower SLS concentration was used). This result, together with the coagulum encountered in the latex (JH-1), suggests that the SLS concentration was at a critical level for providing stability to the latex. At the higher solids contents (JH-3 and JH-4), no coagulum was observed even though the SLS concentration based on the monomer was lower than in experiment JH-2. However, it is important to note that in these experiments (JH-3 and JH-4) the PSD was very broad (spanning 550 and 700 nm, respectively) and that this broadness was due mainly to agglomeration or limited coagulation and growth of the seed particles.

In addition to these experiments, a further polymerization was carried out to check the usefulness and importance of the broad PSD seed used to obtain fluid latexes of high solids content. For this purpose, run JH-3 was repeated but using a monodisperse seed (the one prepared for the seeded experiments of the first stage [$D_v = 163.4$

Table VI Summary of Data and Results for the High Solids Content Experiments Carried Out Under Batch Conditions Using as Seed the P(BA) Latex Prepared in Run J13 ($D_v = 190$ nm)

| Run | Expected % Solids | Measured % Solids | [SLS] ^a | Impeller | Viscosity (cp) | D_v (nm) |
|------|-------------------|-------------------|--------------------|----------------------------|----------------|------------|
| JH-1 | 45 | 44 | 0.15/4 mM | Turbine | 24–30 | 305 |
| JH-2 | 45 | 43 | 0.31/8 mM | Turbine | 26–30 | 304 |
| JH-3 | 55 | 53 | 0.2/8 mM | Turbine (film on the wall) | 74–78 | 332 |
| JH-4 | 65 | 58 | 0.132/8 mM | Jiffy | 272–335 | 398 |

^a Wt % based on the monomer. Also based on aqueous phase.

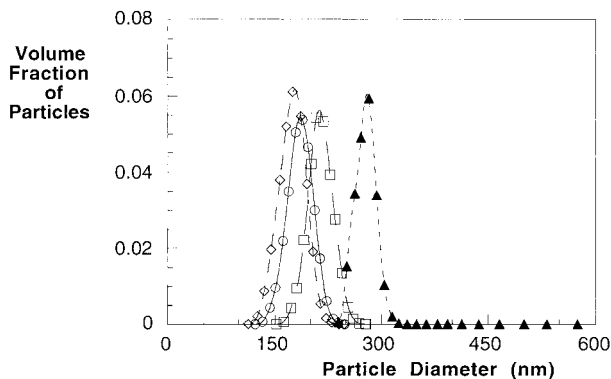


Figure 4 Evolution of the volume PSD measured by CHDF during the control experiment as a function of conversion: (\diamond) seed; (\circ) 0.042; (\square) 0.114; (\blacktriangle) 0.360.

nm, PDI = 1.03]) instead of the broad PSD latex (J13). Table VII shows the results obtained in both experiments. In addition, Figure 4 presents the evolution of the PSD during the control run up to the point at which a considerable change in the PSD took place at about 36% conversion. Figure 5 shows the PSD of the latex obtained at the end of the experiment. It seems evident that these two experiments evolved in different ways. Some coagulum (2.5 wt %) and a larger particle size was obtained in the experiment where the monodisperse seed was employed. Note that the average particle size of the polydisperse seed was larger than that of the monodisperse one.

Both experiments resulted in bimodal distributions but with different breadths. While run JH-3 had a breadth of particle sizes ranging from 260 to 760 nm, in the experiment where the monodisperse seed was used (control), the breadth was as narrow as 300 nm with no small particles below 400 nm. It can be concluded from these batch experiments that using a broad PSD seed is important for obtaining high solids content latexes without coagulum formation. PSD plays a role in latex stability and rheology and, consequently, in achieving fluid latexes of high solids content. As

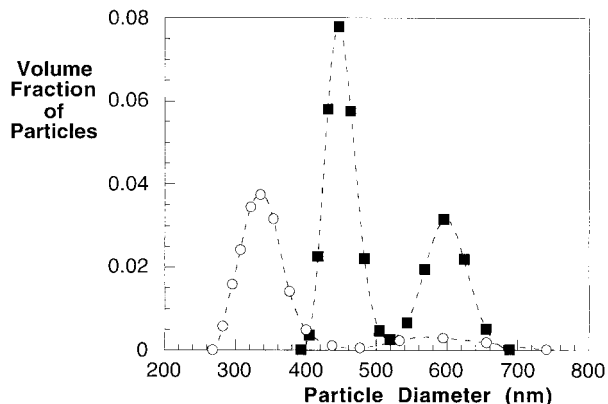


Figure 5 Comparison of the final volume PSDs (CHDF) for experiment JH-3 and control experiment: (\circ) JH-3; (\blacksquare) control.

shown, a PSD having a minimum breadth of 500 nm seems to be necessary to ensure a coagulum-free latex of 55 wt % solids.

Semibatch Polymerizations

To reach higher solids contents and to avoid thermal runaways due to the high monomer concentrations (such as in the batch experiment JH-4), semibatch processes were chosen. Among others, these processes offer two advantages: (i) better temperature control and (ii) the possibility of modifying the PSD.

Several experiments were carried out varying the emulsifier concentration and its partition between the initial charge and the feed mixture, the monomer addition (neat or as emulsion), the temperature, the impeller type, and the initiator concentration. The recipe used in these experiments is based on that of the batch processes presented in Table V. Seed, initiator, buffer, and water concentrations were the same as given in this recipe (otherwise, changes are specified), but the temperature, monomer concentration (expected solids content), monomer addition type (neat or

Table VII Comparative Results of Two High Solids Content (55 Wt %) Experiments Carried Out with Different Seeds Using Batch Polymerization at 60°C

| Run | Seed | Measured % Solids | Coagulum | D_v (nm) | Viscosity (cp) |
|---------|--|-------------------|----------|------------|----------------|
| JH-3 | Broad (J13) $D_v = 190$ nm, $S_n/D_n = 0.37$ | 53 | None | 332 | 74–78 |
| Control | Monodisperse $D_v = 163$ nm, $S_n/D_n = 0.11$ | 52 | 2.5 wt % | 470 | 30–31 |

Table VIII Summary of the Experimental Conditions and Some Results for the High Solids Content Experiments Carried Out in Semicontinuous Processes

| Run/ <i>T</i> (°C) | Expected Solids (Wt %) | Measured Solids (Wt %) | [SLS] ^a | Impeller Type | Viscosity (cp) | <i>D_v</i> (nm) | Monomer Feed Rate (g/min) |
|-----------------------|------------------------------|------------------------------|---------------------------|-------------------------|--------------------------------------|---------------------------|--|
| JH-5/60 | 70 | 49 | 0.104/8 mM | Jiffy | 3.28–3.44 × 10 ⁵ paste | 393 | Neat <i>F_M</i> = 1 ^b |
| JH-6/60 | 65 | 60 | 0.405/23.1 mM | Jiffy | 3710–5800 | 317/531 ^c | Neat <i>F_M</i> = 1 ^b |
| JH-7/60 | 65 | 60 | 0.405/4.3 mM ^d | Jiffy | 7690–8000 | 442 ^c | Neat <i>F_M</i> = 1 |
| JH-8/60 | 65 | Xfr = 0.69 53 | 0.405/4.3 mM | Turbine + four blade | Paste | Xfr = 0.69 358 | Neat <i>F_M</i> = 0.522 |
| JH-9/70 | 65 | 64 | 0.5/6.6 mM | Jiffy | 13,000 | 378 | Emulsion <i>F_M</i> = 0.511 |
| JH-13/70 ^e | 65 | 61 | 0.5/25 mM | Anchor | 6100–9300 | 372 | Emulsion <i>F_M</i> = 0.523 |
| JH-14/70 | 65 | 54 | 0.5/32.5 mM | Jiffy | 134,000 paste | 254 | Neat <i>F_M</i> = 0.541 |

^a Wt % of SLS based on monomer. Concentration of SLS based on water in the initial charge.

^b The whole amount of initiator and SLS are initially charged in the reactor.

^c Light scattering (NICOMP).

^d 80% (SLS + buffer + I₂) solution was added in 23 min (monomer addition time = 220 min).

^e Initiator concentration in the recipe is 10 times higher in this run.

Xfr = fractional conversion.

emulsion), emulsifier concentration and its partition, and impeller type were modified.

A summary of these experimental conditions and some relevant results of the semibatch, high solids content experiments are presented in Table VIII. Experiments were carried out as follows. The seed plus a solution of a fraction of the emulsifier and buffer (except in experiments JH-5 and JH-6 where the entire amount of water, emulsifier, and buffer in the recipe were initially charged into the reactor) and a fraction of the monomer were initially loaded into the reactor and allowed to reach the reaction temperature. Once this was achieved, a solution (approximately 5 mL) of a fraction of the initiator in the recipe (except in runs JH-5 and JH-6 where the whole amount of the initiator was initially charged into the reactor) was injected into the reactor. The reaction mixture was then allowed to polymerize for 15 min before the addition of the monomer (neat or as emulsion) and initiator plus buffer solution streams were begun. The flow rate of the monomer implemented in each experiment is shown in Table VIII. The addition of the initiator plus buffer solution was always completed in the time required for the addition of the monomer stream (except in run JH-7 as stated in the footnote to Table VIII). It is worth noting that when the monomer was added neat and not the entire amount of emulsifier was loaded initially into the reactor (as in runs JH-5 and JH-6) the remaining emulsifier was added with the initiator and buffer stream (runs JH-7, JH-8, and JH-14).

In the first experiment of this series (JH-5, 70 wt % expected final solids content), all the ingredients were initially charged into the reactor except the monomer (only 22% was initially loaded into the reactor) and a solution of the initiator (approximately 5 mL). The flow rate of the monomer was 1 g/min. The concentration of SLS was kept at the same level (based on the aqueous phase) as in experiments JH-3 and JH-4 carried out in batch, but, of course, it was lower based on the monomer since this concentration was increased. This polymerization could not be completed because of the high viscosity achieved during the experiment, i.e., a significant amount of unreacted monomer was still present in the latex. The final solids content was only 49 wt % and the latex appearance was pastelike.

A new experiment was carried out (JH-6) with the only difference being that the SLS concentration was higher (0.405 wt % based on monomer and 23.1 mM based on the aqueous phase) and the final expected solids was 65 wt % (41 wt % of the monomer was initially charged into the reactor). In this case, the latex produced was fluid and the solids content higher (60 wt %), but again the polymerization was not completed.

Figure 6 shows the final PSDs of both experiments (JH-5 and JH-6). Unfortunately, samples were not taken during the polymerizations and the differences in the final latex appearance cannot be explained. However, it can be speculated as to why one of the experiments resulted in a paste, and the other, in a fluid latex. Looking at

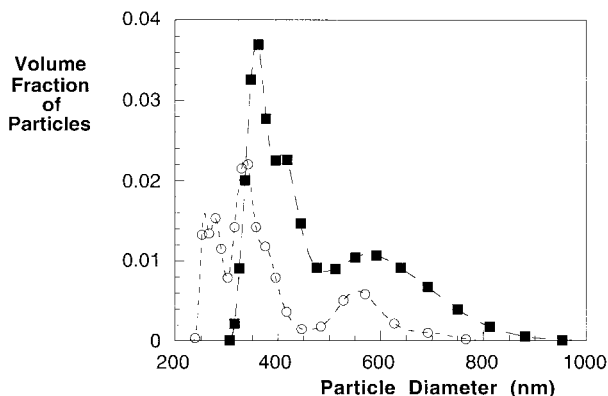


Figure 6 Final volume PSDs (CHDF) of P(BA) latexes for experiments JH-5 and JH-6: (■) JH-5; (○) JH-6.

the final PSDs, both latexes have a very broad PSD, even broader than the seed (see Fig. 2, run J13), and the average particle sizes achieved are also larger than expected if only growth of the seed particles would have taken place (the expected particle diameters were 280 nm for JH-5 and 260 nm for JH-6). This suggests that some agglomeration took place during both experiments. However, it is clear from the final PSDs that in experiment JH-6 there is a population of particles below 300 nm that allowed a better arrangement of particles and, hence, the lower viscosity (as can be seen in Table VIII) achieved in the latex. In addition, this lower viscosity allowed a higher solids content to be realized in experiment JH-6. Consequently, it can be postulated that the population of polymer particles below 300 nm was formed as a result of a nucleation process during the experiment since the SLS concentration was far above the CMC in the initial charge of experiment JH-6 (and not in experiment JH-5). To check this point, new experiments were carried out where samples were withdrawn during the reaction and the particle size was analyzed.

Run JH-7, as shown in Table VIII, was designed to be similar to experiment JH-6 with the sole difference being the distribution of the SLS between the initial charge (9% or 4.3 mM based on the water initially charged in the reactor) and the feed mixture. By mistake, however, 80% of the SLS, initiator, and buffer solution was fed to the reactor in 23 min (much faster than planned since the target addition time was 220 min), which meant that, again, the SLS concentration was well above the CMC in the early stages of the polymerization. As a result, experiments JH-6

and JH-7 were rather similar with samples being taken throughout the polymerization in JH-7. Figure 7 presents the evolution of the PSD during the experiment, showing that nucleation, growth, and some agglomeration took place during the polymerization. This led to a very broad multimodal distribution of polymer particles and, consequently, to a fluid latex of relatively low viscosity (7690–8000 cp). As in the previous experiments, the polymerization could not be completed, with a final solids content of 60 wt % being attained. Ruckenstein and Kim⁵ observed the same incomplete polymerization when they polymerized highly concentrated emulsions of styrene using an oil-soluble initiator such as AIBN. They demonstrated that due to the high concentration of monomer some amount of monomer droplets coalesced and that some polymerization proceeded in a bulk phase at a much slower polymerization rate. However, in the present work, the incomplete polymerization seems to be a consequence of the viscosity and water-soluble nature of the

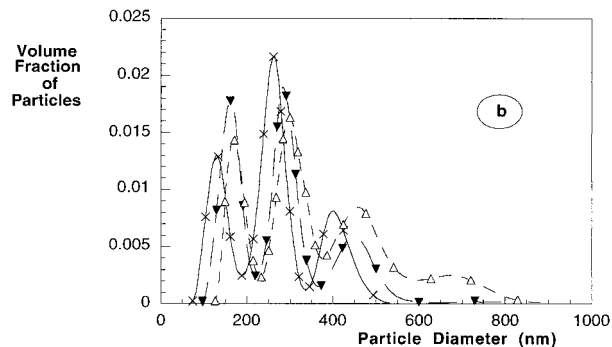
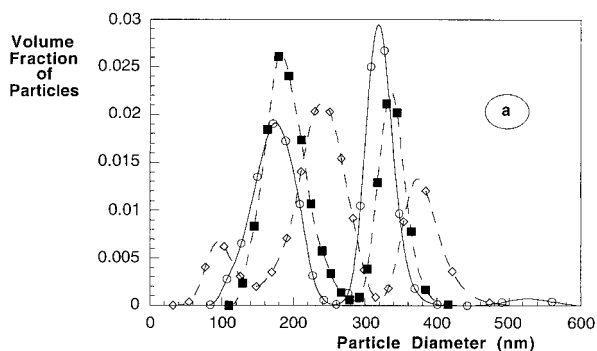


Figure 7 Evolution of the volume PSD (CHDF) during experiment JH-7 as a function of the fractional conversion: (a) (○) seed; (■) 0.151; (◇) 0.205. (b) (×) 0.303; (▼) 0.503; (△) 0.615.

initiator which probably causes a lack of radicals in all the polymerization loci (perhaps due to a poor mixing) and, hence, a decrease in the polymerization rate. Thus, to complete the polymerization, extremely long times would be required.

To overcome the problem of incomplete polymerization, the impeller was changed and a combination of the turbine (bottom part) and a pitch blade (4 blade, $d = 5$ cm, $h = 0.8$ cm) impeller (upper part) was used in experiment JH-8 (300 rpm). In addition, the flow rate of the monomer was reduced to 0.522 g/min. The SLS concentration was kept the same (0.405 wt % based on the monomer), but in this case, the concentration was 4.3 mM (below the CMC) in the initial charge and the remainder was fed together with the initiator and buffer at a constant flow rate over 373 min.

Because of the lower flow rate of the monomer, the instantaneous conversion was higher (see Fig. 8) than that attained in the previous experiment. The impeller combination did not work better than the Jiffy type and a monomer pool was formed on the top of the mixture showing that there was insufficient mixing in the reactor. The final latex was a paste of high viscosity. Figure 9 presents the evolution of the PSD during the experiment. The final distribution (at 70% conversion) did not reveal any polymer particles below 300 nm, which indicates that new particles were not formed, although the final PSD is broader than the original seed. As a result of this distribution, the viscosities achieved during the process were extremely high.

A new experiment was carried out (JH-9) with several other changes being made in the experi-

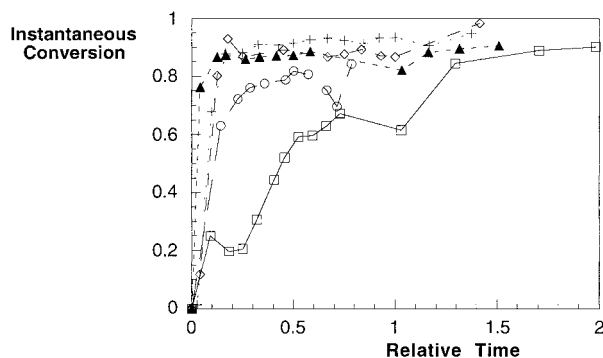


Figure 8 Evolution of the instantaneous conversion measured by gravimetry in the semibatch experiments carried out at 65 wt % solids content. (Relative time = run time/final monomer addition time.) (\square) JH-7; (\circ) JH-8; (\diamond) JH-9; (\blacktriangle) JH-10; (+) JH-13.

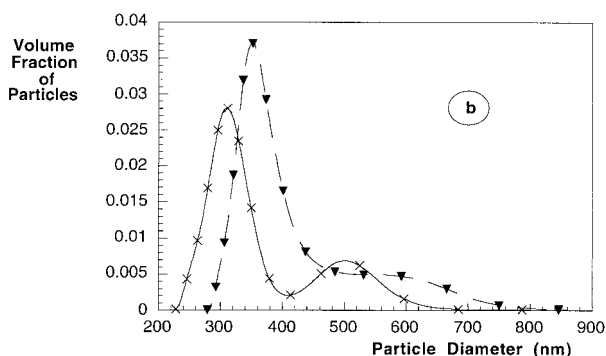
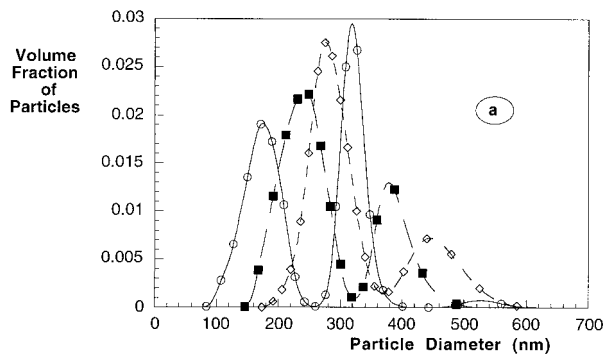


Figure 9 Evolution of the volume PSD (CHDF) during experiment JH-8 as a function of the fractional conversion: (a) (\circ) seed; (\blacksquare) 0.163; (\diamond) 0.324. (b) (\times) 0.453; (\blacktriangledown) 0.696.

mental conditions: (a) the SLS total concentration was increased to 0.5 wt % based on the monomer and the concentration in the initial charge was set to 6.6 mM (9% of the total amount); (b) the Jiffy impeller was used; (c) the reaction temperature was increased to 70°C; and (d) the monomer was fed to the reactor as an emulsion at a flow rate of 0.511 g/min (20% of the total amount in the recipe was initially charged into the reactor with the remainder added as an emulsion). In this case, the polymerization was almost completed and the final solids content was 64 wt %. However, the latex viscosity was high (approximately 13,000 cp) and pastelike, although it could be poured.

Figure 10 shows the evolution of the PSD as a function of conversion during the experiment. At the highest conversion at which the PSD is available, the distribution is bimodal and broad but, again, the population of particles below 300 nm is absent. As in the previous experiments where

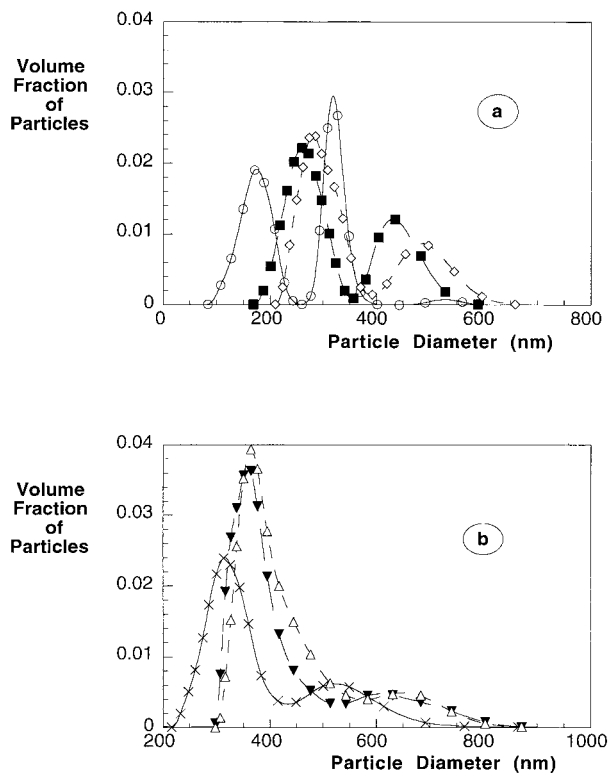


Figure 10 Evolution of the volume PSD (CHDF) during experiment JH-9 as a function of the fractional conversion: (a) (○) seed; (■) 0.245; (◇) 0.347. (b) (×) 0.497; (▼) 0.633; (△) 0.821.

this phenomenon occurred (JH-5 and JH-8), the viscosity of the latex was high. It should be pointed out that during this experiment no monomer pool was formed in the reactor, which indicates that the preemulsion addition helped the mixing in the reactor, which, in turn, helped to complete the polymerization.

In experiment JH-13, run JH-9 was repeated with three changes in order to produce a latex of the expected solids content but with a lower viscosity. For this purpose and to promote nucleation of new particles, the SLS (0.5 wt % based on the monomer) was distributed in the following way: 40% of the total amount of SLS was included in the initial charge (25 mM based on the initial aqueous phase) and the remainder (60%) was added in a preemulsion with the monomer. The second change was that an anchor ($d = 7.5$ cm, $h = 8.0$ cm; 300 rpm) impeller (Mettler-Toledo) was used instead of the Jiffy impeller. In addition to these changes, the total initiator concentration was increased 10 times in this experiment. The result was that a fluid latex of lower viscosity was produced during the reaction but the solids con-

tent achieved was a little bit lower (61 wt %) than expected (65 wt %).

The evolution of the PSD obtained during experiment JH-13 is shown in Figure 11. The final PSD was broad (breadth of about 600 nm) but the population of particles below 300 nm was not as significant as in experiments JH-6 and JH-7 where the lowest viscosities were achieved. It is not clear whether a population of new particles was created during this experiment or that only growth of the original seed particles had occurred. Unfortunately, the first two consecutive samples analyzed by CHDF correspond to a very low conversion (0.3%, the distribution was close to that of the seed) and to almost 30% conversion, where the distribution did not show a new peak of particles and it seemed that the original bimodal distribution shifted to larger sizes with no new particles being generated.

Another experiment, JH-14, was also run at 70°C where the monomer was added neat and the SLS concentration (0.5 wt % based on monomer) in the initial charge was higher than the CMC

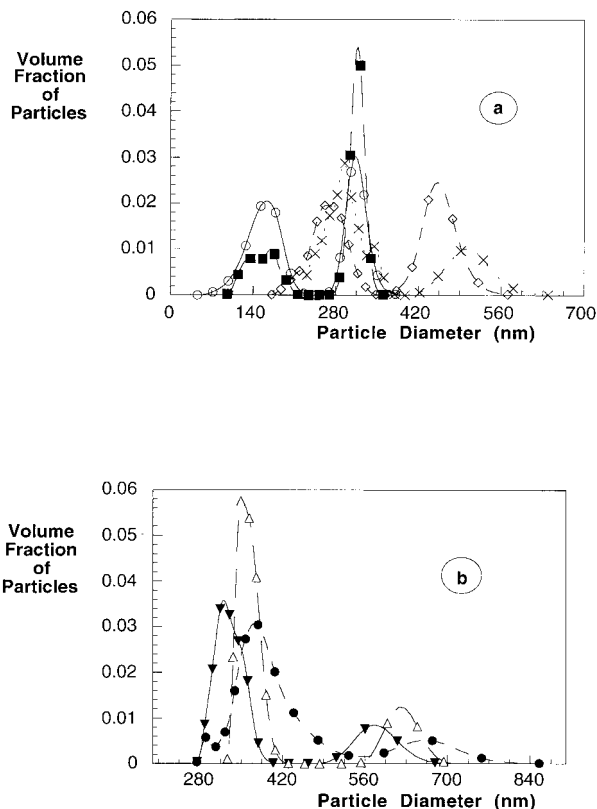


Figure 11 Evolution of the volume PSD (CHDF) during experiment JH-13 as a function of the fractional conversion: (a) (○) seed; (■) 0.003; (◇) 0.292; (ts) 0.415. (b) (▼) 0.610; (△) 0.798; (●) 0.947.

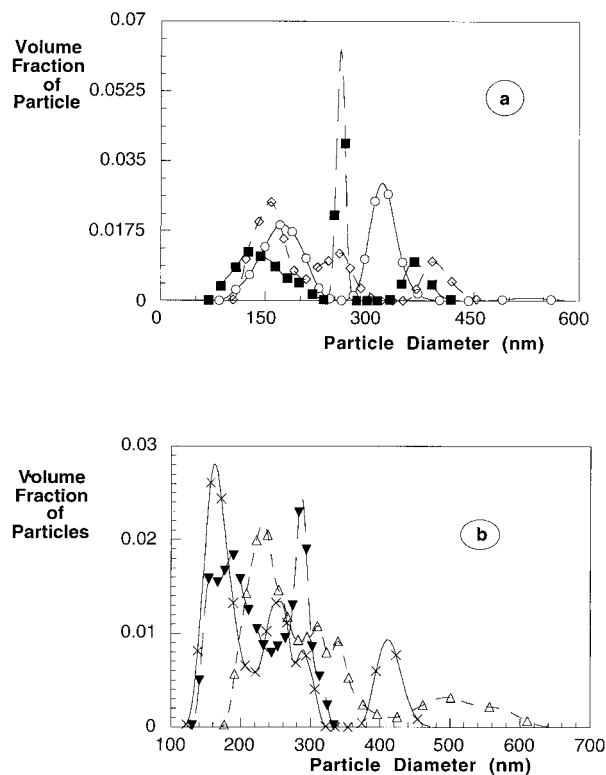


Figure 12 Evolution of the volume PSD (CHDF) during experiment JH-14 as a function of the fractional conversion: (a) (○) seed; (■) 0.258; (◇) 0.346. (b) (×) 0.454; (▼) 0.579; (△) 0.906.

(32.5 mM). In this case, the Jiffy impeller was used and mixing was again insufficient, creating a monomer pool on the top of the reaction mixture. Figure 12 shows the evolution of the PSD for this experiment. Although new particles were formed during the experiment (a population of particles below 300 nm exists in the PSD), there are no particles at sizes larger than 640 nm, i.e., the breadth of the whole PSD is lower than 500 nm. As a result of this PSD, the latex viscosity was very high and the polymerization was not completed.

CONCLUSIONS

Poly(*n*-butyl acrylate) latexes having high solids contents were produced using a new two-stage polymerization approach. In the first stage, a broad PSD seed was prepared by a seeded semicontinuous miniemulsion polymerization. In the second stage, these seed latexes were further polymerized in batch and semibatch processes in order to increase the solids content. It was found that a

seed latex with a broad PSD (breadth of 400 nm) obtained in the first-stage process did not guarantee producing latexes with solids contents higher than 55 wt % in the homopolymerization of BA, even though it was demonstrated that for a latex of 55 wt % solids the use of a broad PSD seed is crucial to produce a coagulum-free latex. However, the theoretical studies that predicted that the solids content of latexes can be enhanced by broadening the PSD, and, hence, decrease the viscosity, were proven through the second series of experiments carried out in batch and semibatch reactions where fluid latexes of high solids content were prepared.

It was also shown that when the breadth of the PSD of the latexes was smaller than 550 nm the viscosity increased significantly and the latexes became nonfluid pastes once the limit of 55 wt % was reached. Nevertheless, latexes with a PSD breadth larger than 550 nm were achieved in experiments where nucleation of new particles, growth of the already broad seed particles prepared in the first stage, and limited agglomeration of particles took place during the process. In this way, the breadth of the PSD was extended in both directions (toward smaller and larger particle sizes) and this distribution allowed an arrangement of the particles at high solids content, reducing the viscosity of the dispersion. Thus, coagulum-free, fluid latexes with solids contents up to 61 wt % were successfully prepared by the proposed approach using a concentration of an emulsifier (sodium lauryl sulfate) of 0.5 wt % based on the monomer and without the addition of any other stabilizing agent (such as acrylic acid) or nonionic surfactants. Nevertheless, some difficulties were found in completing the polymerizations and obtaining even higher solids contents. High viscosities, lack of radicals in the polymerization loci, and insufficient mixing were the main reasons suggested for this phenomenon.

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