

# Semibatch Styrene Suspension Polymerization Processes

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**ABSTRACT:** Emulsion and suspension polymerization processes have widely been studied for more than 40 years. Although both polymerization processes are performed in heterogeneous media, each one presents its own typical characteristics, such as the particle size distribution, molecular weight distribution, polymer particle nucleation rate, and polymerization rate. In this study, semibatch styrene suspension polymerizations were carried out with feed compositions typical of emulsion processes. The initial reactor charge resembled the recipe of standard styrene suspension polymerizations, and the emulsion polymerization constituents were added during the batch. The influence of the moment at which the emulsion feed was started on the course of the polymerization and the effects of the feed on

the polymer properties were analyzed. The polymer particle morphology and the average molecular weights changed very significantly with the emulsion feed time, and the changes could lead to the production of broad molecular weight distributions. Core-shell polymer particles could also be obtained, with the core being formed of polymer particles originating from the suspension polymerization process and the shell being formed of polymer particles originating from the emulsion polymerization. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3021–3038, 2003

**Key words:** core-shell polymers; molecular weight distribution/molar mass distribution; polystyrene; emulsion polymerization

## INTRODUCTION

The final end-use properties of polymer resins depend on a large number of variables, such as the particle size distribution, the polymer composition, and especially the shape of the molecular weight distribution (MWD).<sup>1</sup> For some special applications, bimodal or broad MWD polymer resins may be required because low-molecular-weight polymer chains improve the flow properties, whereas high-molecular-weight polymer chains simultaneously improve the mechanical properties.<sup>2,3</sup>

According to Nele and Pinto,<sup>2</sup> a large number of techniques are available for the production of broad MWD polymer resins. However, all of them rely on a common principle: mixing different polymer materials at the molecular level. This goal may be achieved by the modification of the concentrations of chain-transfer agents,<sup>4,5</sup> the modification of reactor operation conditions,<sup>6</sup> and polymerization with mixtures of different catalysts.<sup>7</sup> Broad MWDs can also be produced

through the blending of different polymer resins during the final processing stage. However, in this case, the final performance of the polymer material may be affected by the much less efficient mixing of the polymer chains. Therefore, there are incentives for producing polymer materials with broad MWDs at the reaction stage.

Different polymerization processes, such as suspension, emulsion, dispersion, solution, and bulk processes, can be used to produce polymer resins with distinct properties.<sup>8</sup> Each process has its own characteristics, such as the number of phases, the magnitude of the reaction rates, the typical particle size distribution, and the MWD of the polymer particles.<sup>9</sup>

Suspension polymerization processes are characterized by the use of monomers that are insoluble in a continuous phase, generally water, and by the fact that monomer droplets are dispersed in the continuous phase by the combination of strong agitation and the use of suspending agents.<sup>10</sup> The polymerization starts when an oil-soluble initiator is added to the system, and the reactions occur inside the stabilized monomer droplets, which can be considered microreactors, in which the polymerization kinetics is similar to the kinetics of the bulk polymerization system.<sup>9</sup> Polymerizations usually follow a free-radical mechanism, and the average particle size of the final polymer particle lies in the interval of 10.0  $\mu\text{m}$  to 1.0 mm. As the polymer particles contain a very large number of radicals, the molecular weight of the final product is normally much lower than the average molecular

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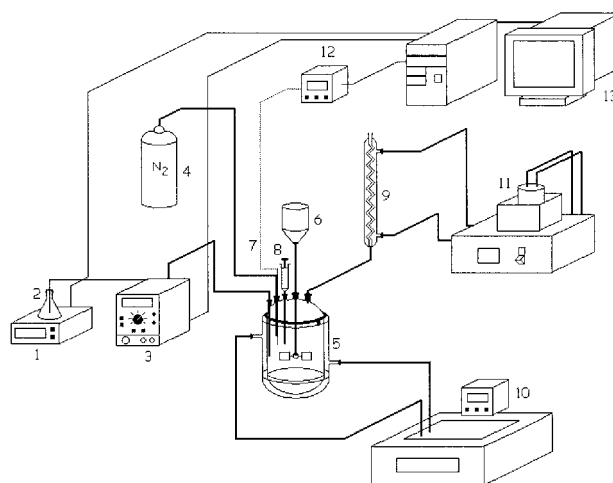
weight of resins prepared with other processes, such as emulsion and dispersion polymerizations.<sup>11</sup>

The main commercial resins produced by suspension polymerization processes are styrene copolymers, such as acrylonitrile-butadiene-styrene resin (ABS) and Styrene-acrylonitrile resin (SAN), and acrylate copolymers. In all cases, polymerizations are carried out in a batch mode. The advantages of this type of polymerization process are the high heat removal capability, the easy separation of the final product, and the low viscosity of the reaction medium. However, one of the main disadvantages is that continuous processes cannot be used because the particles agglomerate and the polymer sticks to reactor internals and reactor walls.<sup>12</sup> The process control challenges involve the design and control of the particle size distribution and the molecular weight averages of the final polymer.<sup>13</sup>

Emulsion polymerization systems are also characterized by the use of a continuous phase, generally water. However, contrary to suspension polymerization systems, the monomer droplets are stabilized by emulsifiers, which also form the main locus of the polymerization. Besides, the initiator is normally soluble in the aqueous phase, so complex mass-transfer steps take place during the course of the reaction.<sup>14</sup>

The mechanism of the styrene batch emulsion polymerization was first established by Harkins.<sup>15</sup> According to the classical mechanism, in the first stage, polymer particle nucleation occurs. This happens when the radicals formed in the aqueous phase either enter a monomer-swollen micelle (micellar nucleation) or precipitate after reaching a critical size (homogeneous nucleation).<sup>16</sup> The size of the monomer droplets is much greater (1.0–10.0  $\mu\text{m}$ ) than the size of the micelles (1.0–10.0 nm), so the main loci of the polymerization are the micelles, whereas the monomer droplets act as raw material reservoirs. The second stage begins when the particle nucleation is finished. The polymerization reactions occur inside the monomer-swollen polymer particles. At this stage, the concentration of the monomer inside these particles is kept constant. When the monomer droplets disappear, the third stage begins. In this last stage, the polymerization continues until the complete depletion of the monomer inside the particles and in the continuous phase. The final product of the polymerization is a latex with a particle size ranging typically from 0.1 to 1.0  $\mu\text{m}$ .<sup>16</sup>

Because of its compartmentalized character, emulsion polymerization systems can present simultaneously high reaction rates and products with high molecular weights, unlike suspension polymerization processes. Moreover, emulsion systems present high heat removal capability, and the final product can eventually be used in the latex form without the need of an additional separation stage.<sup>17</sup> Commercial emulsion products are used mostly as adhesives, paints,



**Figure 1** Schematic representation of the experimental setup: (1) balance (Helmac 1000; São Paulo, Brazil), (2) monomer feed flask, (3) analog pump (Gamma/Gala Prominent 1000SST; Heidelberg, Germany), (4) nitrogen cylinder, (5) 1.0-L jacketed glass reactor (FGG Equipamentos Científicos LTDA; São Paulo, Brazil), (6) mechanical agitator (Fisatom 713-T, São Paulo, Brazil), (7) thermocouple (J kind), (8) syringe for sample collection, (9) condenser for the prevention of monomer loss, (10) thermostatic bath (Haake DC-3) for the reactor jacket (Paramus, NJ), (11) refrigerator bath (Polyscience KR30-A) for the condenser (Niles, IL), (12) chassis (National Instruments SCXI-1000) for signal conditioning (Austin, TX), and (13) microcomputer (233-MHz Pentium MMX) for data acquisition.

and coatings, normally with acrylates monomers. Reactions can be carried out in batch, semibatch, or continuous modes. The process control challenges are related to the design and control of the shape of the MWD, the particle sized distribution, the copolymer composition, and the latex stability of the final products.<sup>18</sup>

Focusing on the production of polymer resins with broad MWDs, one may wonder whether the suspension and emulsion polymerization processes may be combined. Besides the distinct characteristics of the MWDs of suspension and emulsion polymers, the production of emulsion polymer resins with broad MWDs requires the use of large amounts of chain-transfer agents,<sup>5</sup> whereas suspension polymerizations cannot be used for the production of polymer chains with high molecular weights unless very low initiator concentrations are used.

In this work, the semibatch styrene suspension polymerization was studied, with the aim of producing polymer resins with broad MWDs. The initial reactor charge resembled the recipe of standard styrene suspension polymerizations, and the emulsion polymerization constituents were added during the batch. The influence of the moment at which the emulsion feed was started on the course of the polymerization and the effects on the polymer properties were analyzed. Polymer resins obtained with distinct operation con-

TABLE I  
Polymerization Recipes and Operating Conditions

	REAC1	REAC2	REAC3	REAC4	
Constituent (g)					
Styrene <sup>a</sup>	Charged: 30.0 Pumped: 40.0	Charged: 100.0 Pumped: 10.0	Charged: 100.0 Pumped: 10.0	Charged: 100.0 Pumped: 40.0	
Water <sup>b</sup>	500.0	400.0	400.0	400.0	
SLS	3.00	2.50	2.50	2.60	
NaHCO <sub>3</sub>	0.50	0.30	0.30	0.30	
Potassium Persulfate	0.50	0.30	0.30	0.30	
PVA	—	2.00	2.20	2.20	
BPO	—	4.00	4.00	4.00	
Polystyrene seeds	—	—	—	—	
Component					
Temperature (°C)	85.0	85.0	85.0	85.0	
Agitation speed (rpm)	600 ± 15	1050 ± 50	1050 ± 50	1050 ± 50	
Impeller (type)	01	01	01	01	
Feed time (min)	40	40	40	40	
	REAC5	REAC6	REAC7	REAC8	REAC9 <sup>b</sup>
Constituent (g)					
Styrene <sup>a</sup>	Charged (S): 100.0 Charged (E): 30.0 Pumped (E): 45.0	Charged (S): 100.0 Charged (E): 30.0 Pumped (E): 57.0	Charged (S): 100.0 Charged (E): 30.0 Pumped (E): 60.0	Charged: 30.0 Pumped: 40.0	Charged (S): 100.0 Charged (SP): 30.0 Pumped (SP): 57.0
Water <sup>c</sup>	Suspension: 370.0 Emulsion: 115.0	Suspension: 370.0 Emulsion: 115.0	Suspension: 400.0 Emulsion: 112.0	510.0	Suspension: 400.0 Second part: 100.0
SLS	2.50	2.50	2.50	2.50	—
NaHCO <sub>3</sub>	0.30	0.30	0.30	0.30	—
Potassium Persulfate	0.30	0.30	0.30	0.30	—
PVA	3.00	2.00	2.20	3.00	3.00
BPO	4.00	4.00	4.00	—	4.00
Polystyrene seeds	—	—	—	100.0	—
Component					
Temperature (°C)	85.0	85.0	85.0	85.0	85.0
Agitation speed (rpm)	1500 ± 50	1080 ± 50	1100 ± 50	1000 ± 50	1080 ± 50
Impeller (type)	01	02	01	01	01
Feed time (min)	120	120	120	120	120

<sup>a</sup> S refers to suspension polymerization, E refers to the emulsion polymerization, and SP to the second part of the experiment REAC9.

<sup>b</sup> Second part indicates the amount added in the second part of the experiment.

<sup>c</sup> The terms suspension and emulsion indicate the amount of the component used in each polymerization system, respectively.

ditions were analyzed and compared. The experimental results (the monomer conversions, average molecular weights, MWDs, particle morphologies, particle sizes, and particle size distributions) showed that the final product characteristics changed significantly, depending on the instant of addition of the constituents of the emulsion polymerization system and on the constituents added to the system. In particular, it was found that semibatch suspension polymerizations could be used for the production of polymer resins with broad and bimodal MWDs and polymer particles with a core-shell morphology.

## EXPERIMENTAL

### Chemicals

For the suspension polymerization system, benzoyl peroxide (BPO) was used as an oil-soluble initiator,

and poly(vinyl alcohol) (PVA) was used as a suspending agent. Both products were supplied by Vetec Química Fina (Rio de Janeiro, Brazil). BPO was 25% moisture. PVA had an 85% degree of hydrolysis and a weight-average molecular weight ( $M_w$ ) of 78,000 Da. For the emulsion system, sodium lauryl sulfate (SLS), supplied by Rhodia do Brasil S/A (São Paulo, Brazil), with less than 1% impurities, was used as an emulsifier. Potassium peroxidisulfate ( $K_2S_2O_8$ ), supplied by Merck do Brasil (São Paulo, Brazil), with less than 1% impurities, was used as a water-soluble initiator. Sodium bicarbonate ( $NaHCO_3$ ), supplied by Isofar Indústrias (Rio de Janeiro, Brazil), also with less than 1% impurities, was used as a buffer.

Styrene supplied by Nitriflex Resinas S/A (Rio de Janeiro, Brazil), with 20 ppm hydroquinone as an inhibitor, was used as a monomer. Distilled water was used as the continuous phase and as the heat-ex-

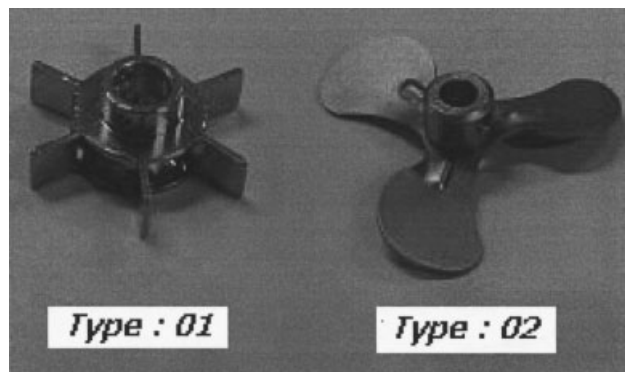


Figure 2 Types of impellers.

change fluid for the reactor jacket. Hydroquinone, supplied by Vetec Química Fina, with less than 1% impurities, was used for reaction termination. Nitrogen, supplied by AGA S/A (Rio de Janeiro, Brazil), with less than 0.01% impurities, was used to maintain the inert atmosphere during the polymerizations reactions. Tetrahydrofuran (THF), with less than 0.1% impurities, was used for gel permeation chromatography, and ethylene glycol was used for refrigeration. Both were supplied by Vetec Química Fina.

All chemicals were used as received, without further purification.

### Reaction system

The experimental setup used to carry out the polymerization reactions is presented in Figure 1. The apparatus was similar to the one described by Santos et al.<sup>19</sup> The data acquisition system was similar to the one described by Neitzel and Lenzi<sup>20</sup> and used the student version of LabView.<sup>21</sup>

### Product characterization

The particle morphology analysis was performed with an Olympus SHZ10 stereomicroscope (Somerset, NJ) with dried samples withdrawn from the reactor along the experimental run. The polymer samples were dried in recirculation ovens at 45°C. The monomer conversions were obtained through gravimetric analysis by the drying of polymer samples in a recirculation oven at 45°C until a constant weight was obtained. The particle size analysis of the obtained latices was performed with laser light scattering equipment (Malvern autosizer; Southborough, MA). For suspen-

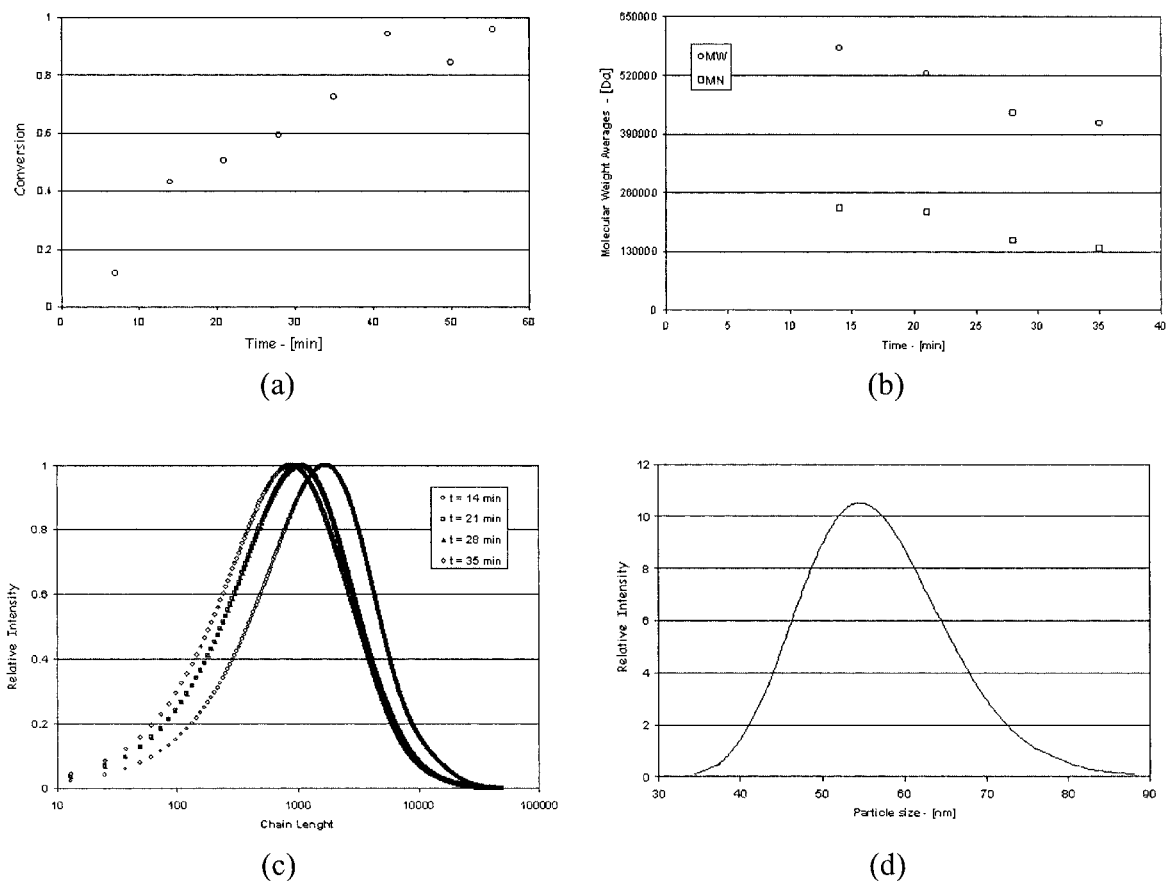
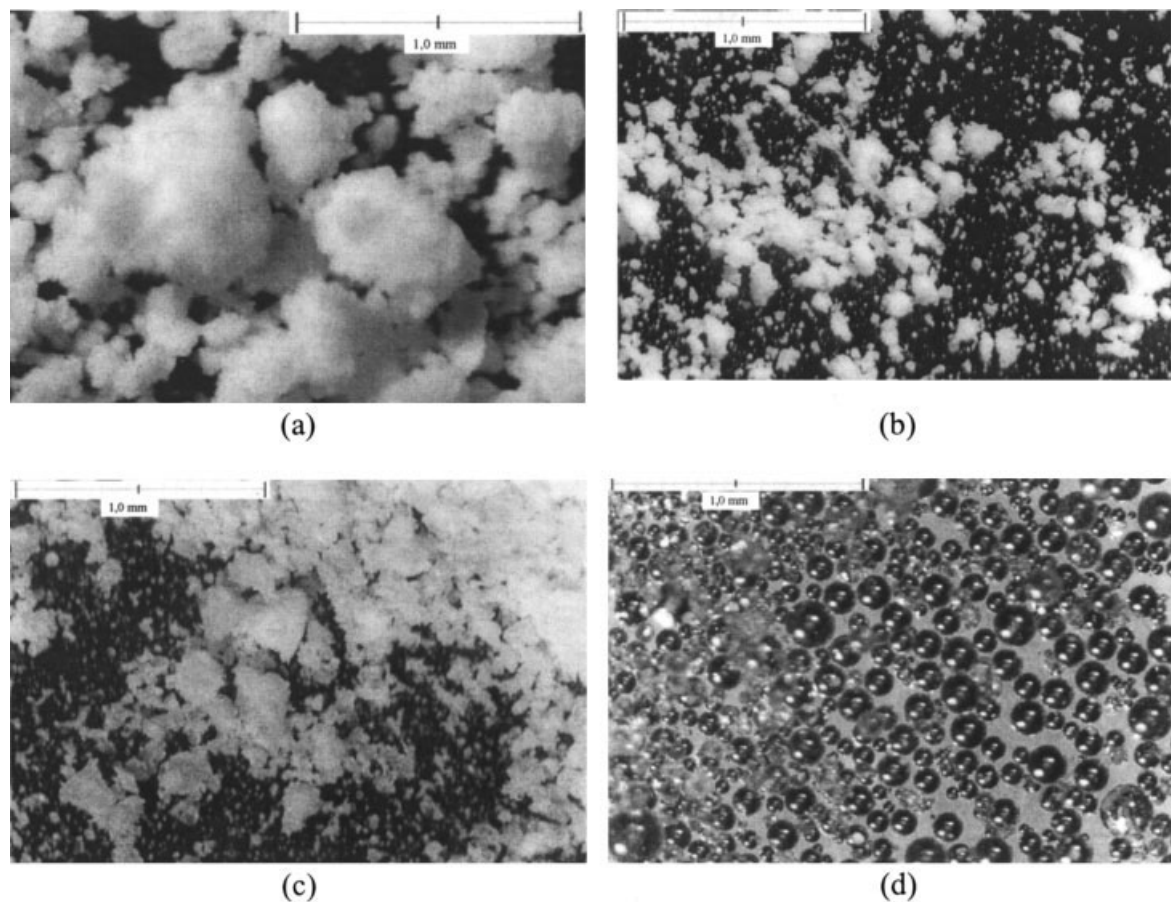


Figure 3 Evolution of (a) the monomer conversion, (b) the molecular weight averages, (c) the MWD, and (d) the particle size distribution of the polymer product of REAC1.



**Figure 4** Morphology of the final products of (a) REAC2 (50 $\times$ ), (b) REAC3 (70 $\times$ ), (c) REAC4 (70 $\times$ ), and (d) a standard suspension polymerization.

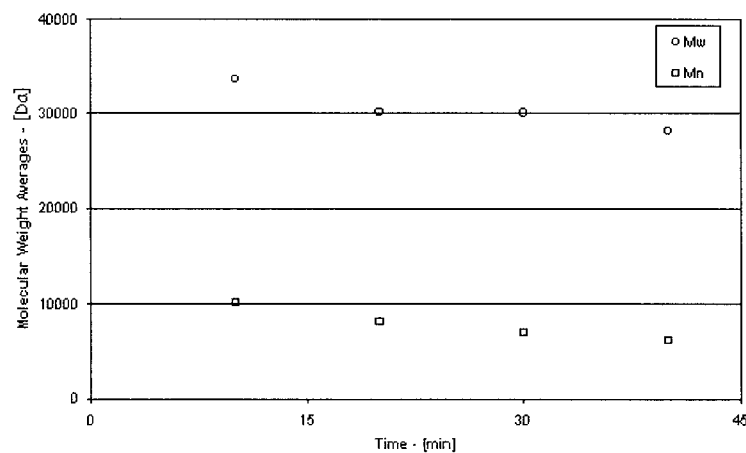
sion polymer particles, the particle size analysis was performed by the measuring and counting of at least 300 particles photographed with the optical microscope. Finally, the molecular weight averages and MWDs were obtained with gel permeation chromatography. The system was composed of three linear columns (Phenomenex®, Torrance, CA) with gel porosities ranging from  $10^3$  to  $10^6$  Å. The calibration was done with polystyrene standards (Phenomenex) with molecular weights ranging from  $10^4$  to  $2.0 \times 10^6$ . THF was used as a mobile phase, and the analyses were carried out at 40°C. A refractive-index detector (SFD RI-2000F; Schambeck, Germany) and a pumping system (Konik; Miami, FL) were connected to a 233-MHz Pentium MMX microcomputer (Konik) for data acquisition and data handling.

#### Experimental procedure

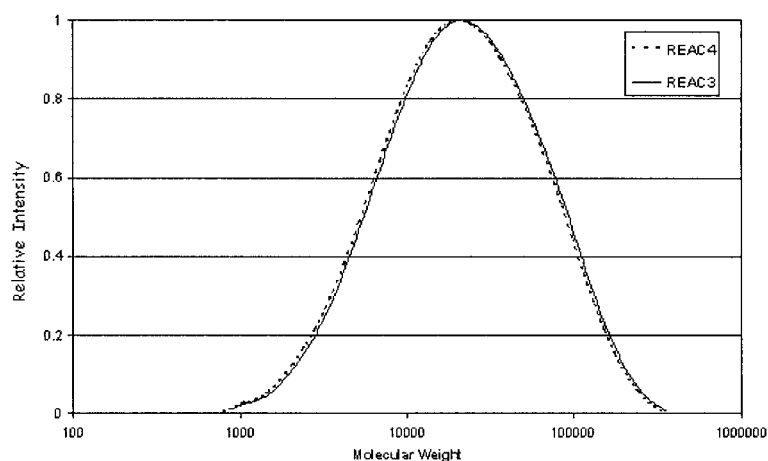
The experimental runs were divided into six groups, depending on the moment at which the emulsion feed was started during the course of the polymerization. The constituents of the emulsion polymerization system were the monomer (styrene), the

emulsifier (SLS), the continuous phase (water), the water-soluble initiator ( $K_2S_2O_8$ ), and the buffer ( $NaHCO_3$ ). The constituents of the suspension polymerization system were the monomer (styrene), the suspending agent (PVA), the continuous phase (water), and the oil-soluble initiator (BPO). In all the experimental runs, the solid constituents were dissolved either in the continuous phase or in the oil phase before being added to the reaction system.

Classical styrene emulsion polymerization runs (REAC1) formed the first group of experiments. Semi-batch reactions were performed to avoid thermal runaway and to allow a fair comparison with other experiments. Before the initial reactor charge, the reaction vessel was purged with nitrogen for 15 min and heated to the desired reaction temperature (85°C). After this, the emulsifier solution was added, followed by the buffer solution, the monomer, and the rest of the water required to complete the polymerization recipe. Afterward, the monomer feed line was connected to the reactor, and the water-soluble initiator was added, starting the reaction. Nitrogen was continuously fed into the reactor during the reaction. Samples of 5.0 mL were withdrawn along the reaction



(a)



(b)

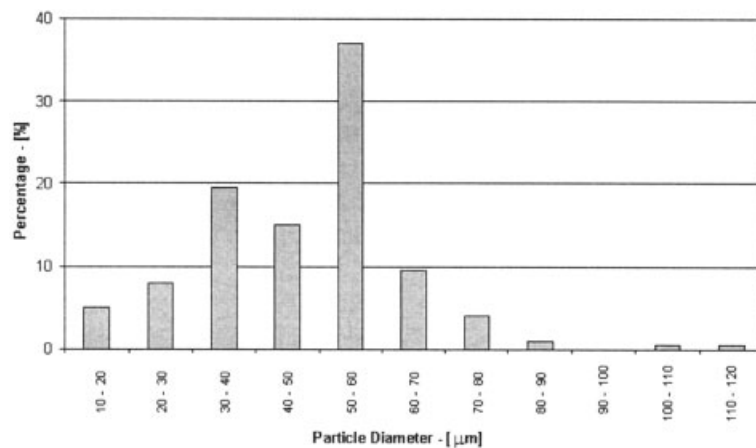
**Figure 5** Evolution of the molecular weight averages of REAC2 and (b) a comparison of the MWDs of the final products of REAC3 and REAC4.

course with a 10.0-mL glass syringe. Samples were added to a previously weighed flask containing 2.0 mg of a hydroquinone solution (2.0 g/L) for reaction termination. The reaction temperature was set to 85°C, and the agitation speed was set to 600 rpm. The recipe of REAC1 is presented in Table I.

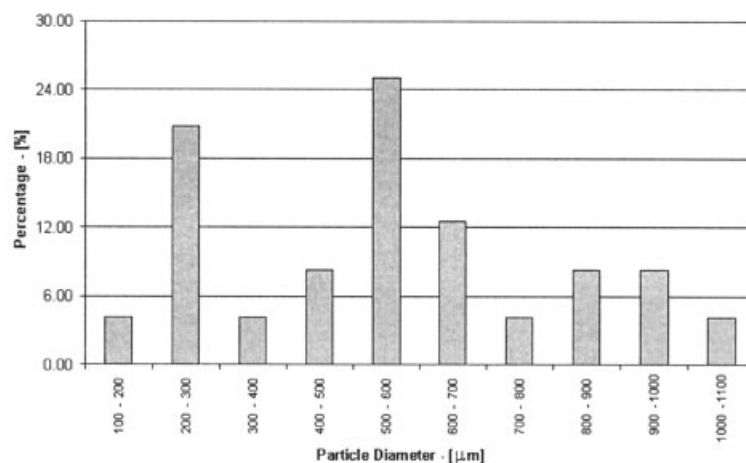
The second group of runs was composed of semi-batch styrene suspension polymerizations with the feed of the emulsion constituents since the start of the polymerization (REAC2 to REAC4). The recipes of the experiments are presented in Table I. After the preparation of the reactor, the PVA solution was added, followed by the addition of the emulsifier solution and the buffer solution. The desired amount of BPO was dissolved in styrene, and the oil solution was added. After this, the pumping system was connected to the reaction vessel, and the required amount of the water-soluble initiator was added, starting the reaction. The

samples were withdrawn along the reaction, as explained before.

The third group of reaction runs included experiments in which the constituents of the emulsion system were added to the reactor 2 h after the beginning of the suspension polymerization reaction. After the reaction start-up, as explained before, the reaction began only with the constituents of the suspension polymerization system. After 2 h of reaction, the constituents of the emulsion polymerization system were added to the reactor as described before: first the emulsifier solution, followed by the buffer solution, the monomer, the water-soluble initiator solution, and the connection of the pumping system. The samples were withdrawn as explained before. The recipes are presented in Table I. Some of the operation conditions were purposely changed, as explained later, to modify the particle size distri-



(a)



(b)

**Figure 6** Particle size distribution of the polymer particles of (a) REAC5 and (b) REAC6 at  $t = 120$  min.

bution. Figure 2 shows the types of impellers used in each experiment.

The fourth group of reaction runs was characterized by the fact that the emulsion constituents were added to the reactor 4 h after the beginning of the suspension polymerization (REAC7). The experimental procedure was similar to the one described previously. The recipes are shown in Table I.

The fifth group of experiments included seeded emulsion polymerizations with dried suspension polymer particles as seeds (REAC8). These experiments simulated the addition of the emulsion constituents after the completion of the suspension polymerization. The experimental procedure was similar to the ones described previously, except that the suspension polymerization period was replaced by the addition of the polymer seeds. The recipes are shown in Table I.

The sixth group of runs included semibatch suspension polymerizations, which were similar to the experiments included in group IV, except that the emulsi-

fier, the water-soluble initiator, and the buffer were not added to the reactor (REAC9). The recipes are shown in Table I.

Although not presented as a separate group, styrene batch suspension polymerization reactions were also performed and used as benchmarks for comparison. Experimental results for classical suspension polymerizations could be obtained from the experimental runs performed in the third and fourth groups, with experimental data collected during the first part of the reaction runs.

## RESULTS AND DISCUSSIONS

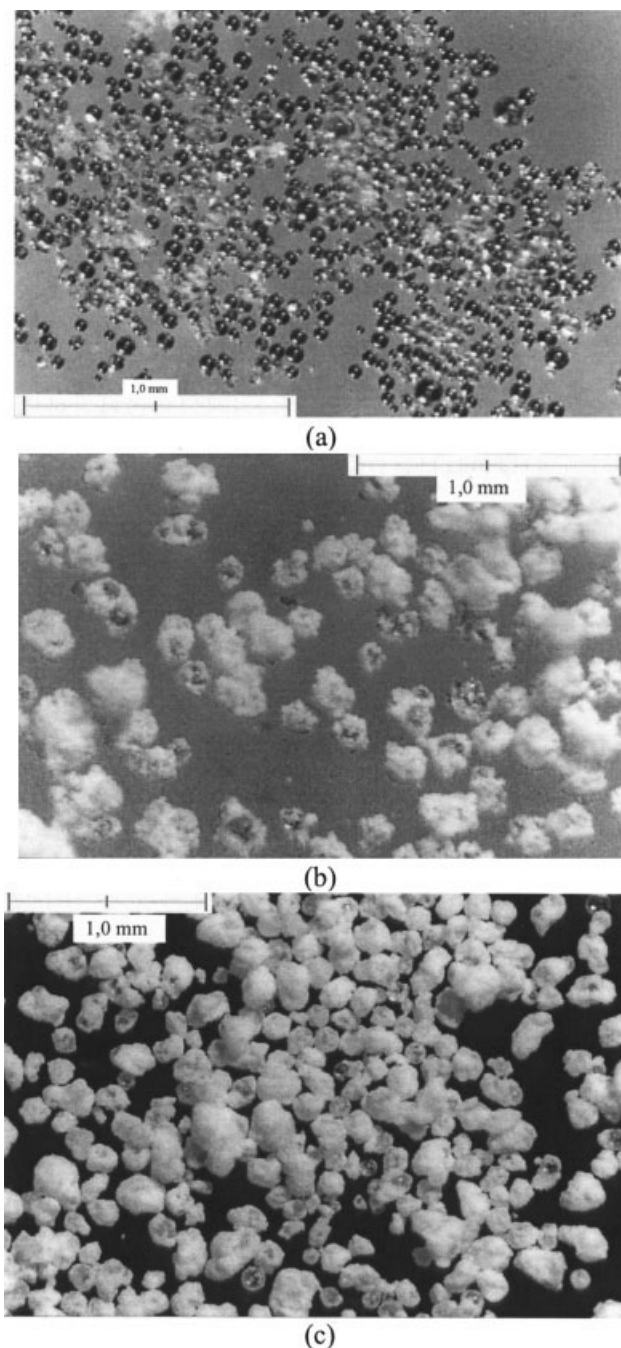
Reactions in group I constitute a benchmark for emulsion polymerizations. Reactions in groups II–V allow the analysis of the effect of the feed policy on the final product properties. Reactions in group VI allow the evaluation of the emulsion feed constituents on the polymerization course and the final polymer proper-

ties. As explained before, the first part of the reactions in groups III and IV constitutes a benchmark for suspension polymerizations.

Figure 3(a) presents the typical evolution of the monomer conversion along the reaction course in the experiments of group I. Complete conversion is attained in less than 1 h, and the monomer conversion increases almost linearly during the course of the reaction. This indicates that the reaction rates are not controlled by feed rates and that the particle concentration is essentially constant throughout the batch. Therefore, the monomer reactions are carried out under flooded conditions. Figure 3(b) shows the evolution of  $M_w$  and the number-average molecular weight ( $M_n$ ) of the polymer samples, whereas Figure 3(c) illustrates the evolution of the MWDs. High average molecular weights can be obtained throughout the reaction course. The continuous drift toward smaller average molecular weights is probably due to the accumulation of chain-transfer impurities not removed from the monomer feed, as observed at the plant site. However, as the final  $M_w$  is around 400,000 Da and the final polydispersity is around 3, the results are regarded as very good for the purposes of this study. Figure 3(d) presents a typical particle size distribution of the final product of REAC1. The mean particle size is within the range of 50–60 nm (in the particular case analyzed, it is equal to  $54 \pm 2$  nm). Moreover, the particle size distribution is unimodal and narrow, indicating the existence of a single stage of particle nucleation. The final concentration of the polymer particles is around  $1.50 \times 10^{18}$  particles per liter ( $1.41 \times 10^{18}$  particles per liter in the particular case analyzed), and the shelf life of the final latex is longer than 5 months, which illustrates the stability of the final emulsion product.

Figure 4(a) shows a typical photograph of the final polymer powder obtained in reactions included in group II, in which the constituents of both suspension and emulsion polymerization systems are mixed since the beginning of the run. The final particles, in these cases, have the shapes of flakes, with very heterogeneous size distributions in the range of micrometers and very irregular surfaces. As Figure 4(d) indicates that suspension polymer particles obtained under similar conditions are much more uniform and have the classical shape of pearls, it may be concluded that suspension particles are not stabilized in the presence of the emulsion constituents. This fact indicates that some kind of interaction between both polymerization processes exists.

The conversion profiles obtained for reaction runs in group II are similar to the one presented in Figure 3(a) for the emulsion polymerizations, indicating that the monomer conversion is controlled somehow by the much faster emulsion polymerization process. Probably, as long as micelles are present, the sus-

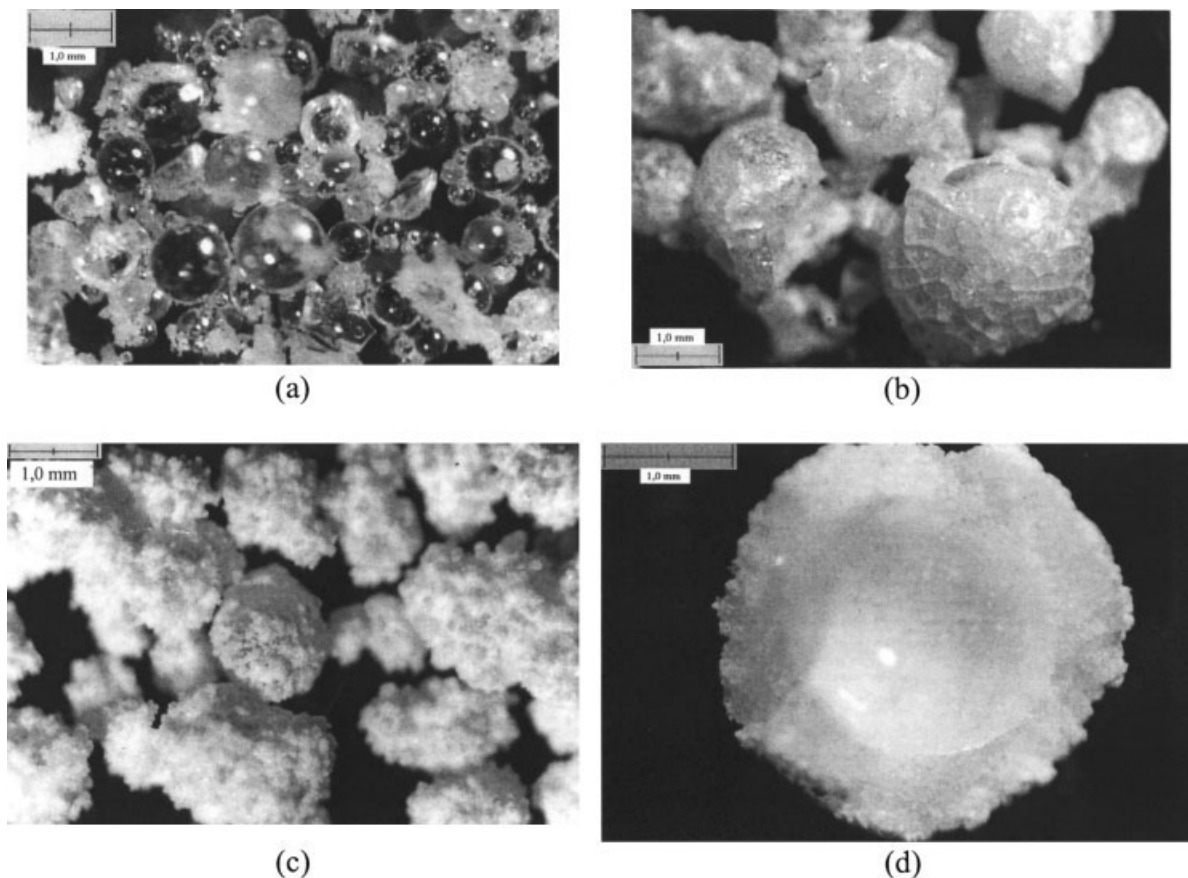


**Figure 7** Morphology of the polymer particles of REAC5 at (a)  $t = 120$  min, (b)  $t = 215$  min, and (c)  $t = 320$  min.

pending monomer droplets work simultaneously as raw material reservoirs and polymerization loci. However, as suspended droplets contain the oil-soluble initiator, they become sticky and also act as agglomeration centers. The flocculent structure shown in Figure 4(a) suggests that the agglomeration of emulsion particles around fine polymer pearls originates from the suspension polymerization process.

A typical evolution of average molecular weights for reactions in group II is presented in Figure 5(a).





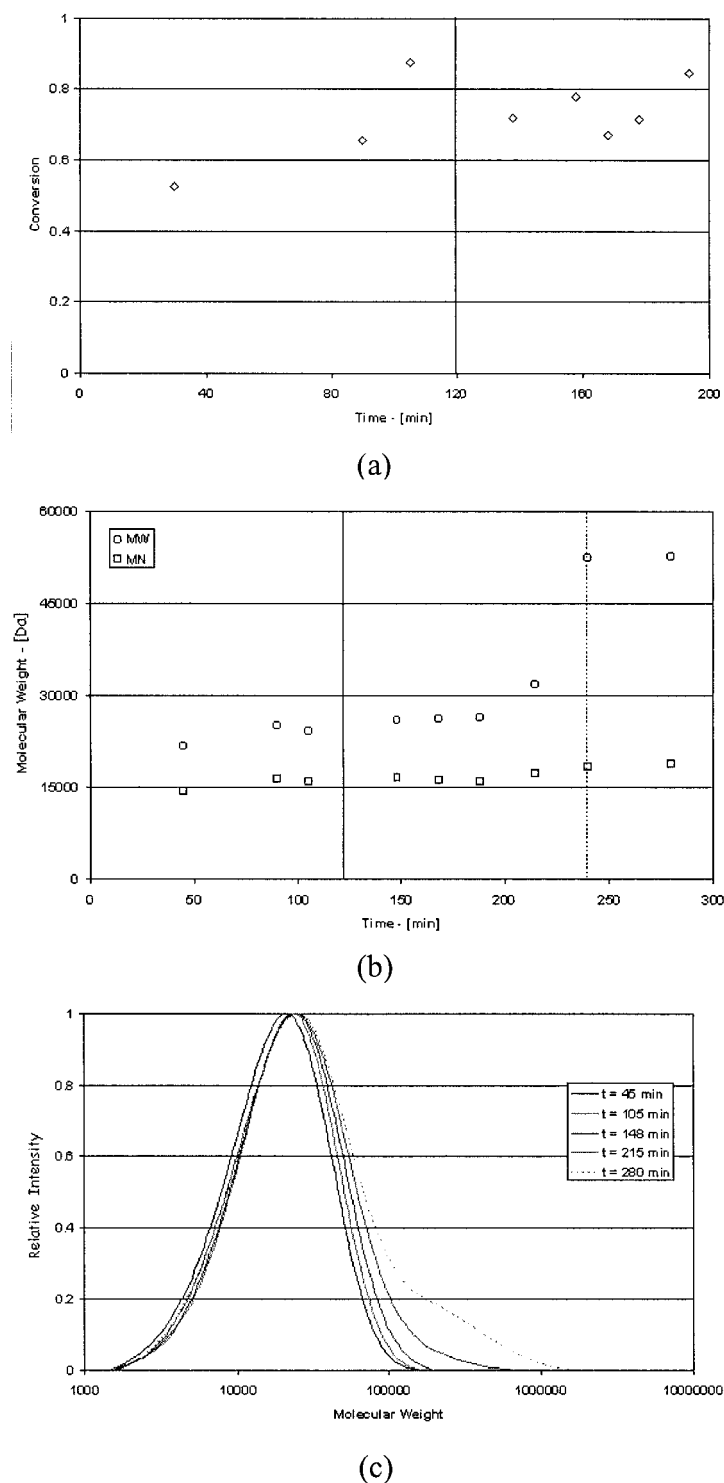
**Figure 8** Morphology of the polymer particles of REAC6 at (a)  $t = 120$  min, (b)  $t = 180$  min, (c)  $t = 260$  min, and (d)  $t = 260$  min.

The polydispersity index (PI) of the final product is around 5 (4.6 in the particular case analyzed), much higher than the PI of the products obtained through classical emulsion and suspension polymerization processes. This fact seems to confirm the existence of a considerable degree of mixture between both polymerization processes. Moreover, the much lower average molecular weights show that the compartmentalization character is considerably reduced under such operation conditions. This is probably because the emulsion polymer particles are caught by the sticky monomer droplets during the polymerization course, and this also leads to a consistent reduction of the average molecular weights along the run.

Despite the apparent reduction of the compartmentalized character of the classical emulsion process, the MWDs of the final products of reaction runs in group II are much broader as desired. This is probably because there is a strong interaction between both polymerization systems. As the emulsion system leads to very high polymerization rates, initial micellar nucleation is expected to occur. As the number of emulsion polymer particles increases, coalescence with the sticking monomer droplets takes place, and some sort of equilibrium between the rates of particle nucleation

and particle coalescence is achieved. This may explain why reaction rates are high and average molecular weights are low. The collected emulsion particles provide polymer radicals that continue to grow inside the unstable suspension polymer particles. The collection of emulsion particles modifies the suspension polymer particle morphology, and the pearls cannot be formed any more. It must be emphasized that the collection of emulsion polymer particles is very efficient, as the light scattering equipment could not detect the presence of polymer particles in the supernatant of the final product. This result was also confirmed by an independent gravimetric analysis, which indicated the presence of less than 0.3% polymer in the supernatant.

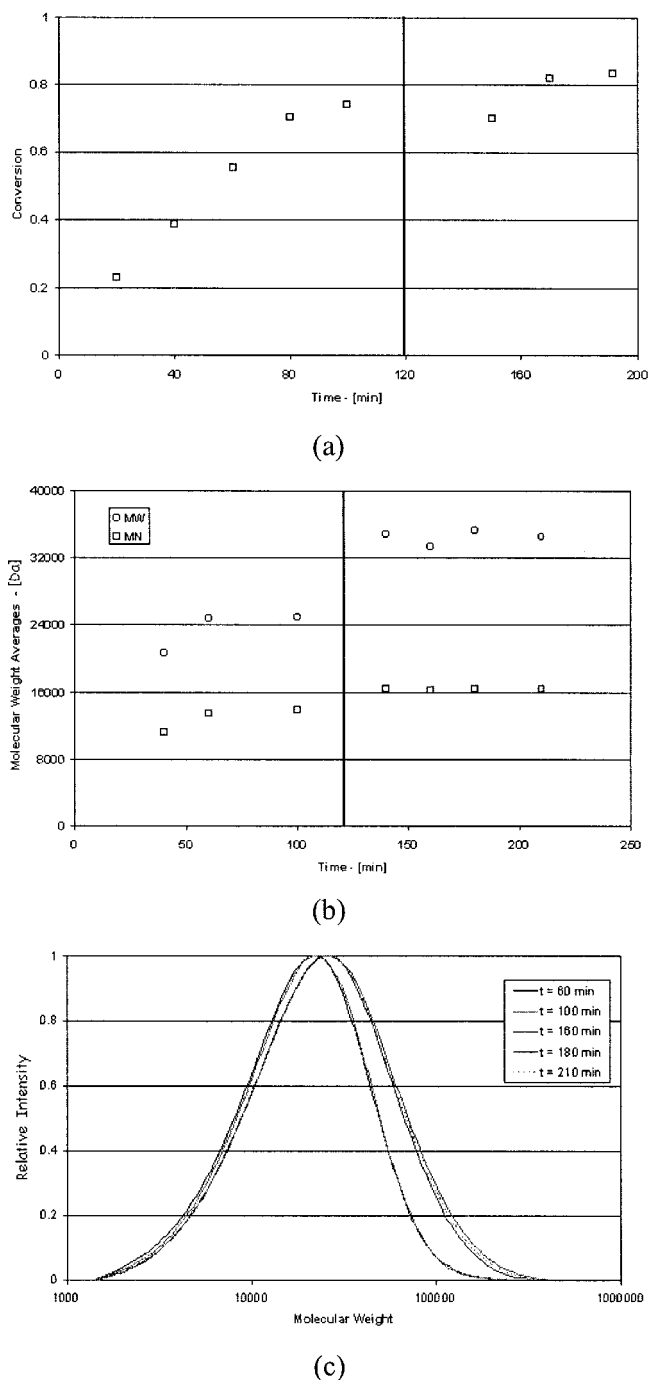
Figures 4(b) and 5(b) show very interesting characteristics of reaction runs in group II. Figure 5(b) shows that the sensitivity of the molecular structure of the final polymer powder to small changes in the operation conditions is very low. However, a comparison of Figure 4(a–c) illustrates that the morphology of the final product of the final polymer particles is extremely sensitive to small changes in the operating conditions. In particular, differences observed between Figure 4(a) and Figure 4(b), in which the only significant change introduced is a light increase in the



**Figure 9** Evolution of (a) the monomer conversion, (b) the molecular weight averages, and (c) the MWD of the polymer product of REAC5.

concentration of the suspending agent, is a strong indication of this high sensitivity to small process perturbations. We believe that this is due to a number of different facts. First, coalescence occurs at random and in an uncontrollable manner under the conditions analyzed. Second, because of the random coalescence

of polymer particles and because of heterogeneous mixing conditions (as always happens in stirred vessels), particle size distributions are expected to be broad. Finally, it is quite possible that particle coalescence continues after sampling and during particle drying. However, the most important feature of Fig-



**Figure 10** Evolution of (a) the monomer conversion, (b) the molecular weight averages, and (c) the MWD of the polymer product of REAC6.

ure 4 is that it shows that the final polymer material is not constituted of individual pearls when both suspension and emulsion processes are initiated simultaneously, as in classical suspension processes [see Fig. 4(d)], and when the emulsion process is initiated later, as discussed later.

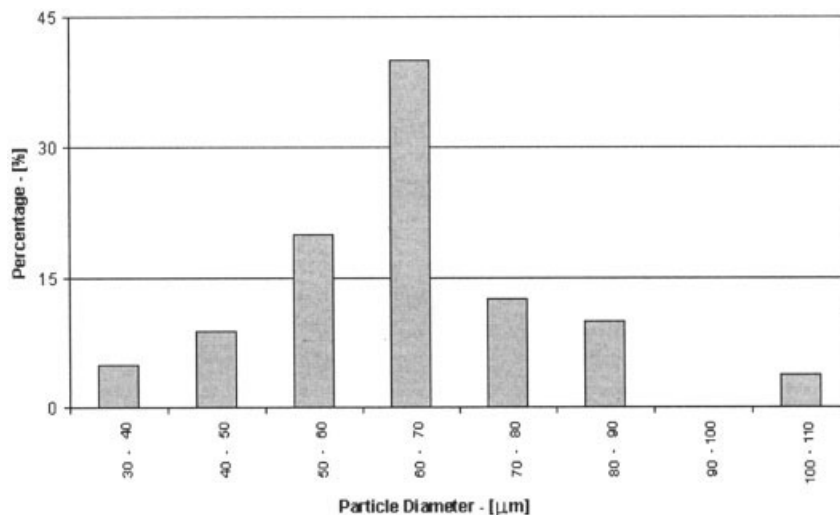
It is particularly interesting to observe that the final product of REAC4 was a thick and stable uniform suspension of polymer particles in water and that the

presence of a supernatant could not be detected. This fact was confirmed by the gravimetric analysis of a hypothetical supernatant, which revealed a solid content around 22.0%, equal to the nominal solid content of the suspension. Independent light scattering analysis indicated that the mean particle size was equal to  $13.3 \pm 6.8 \mu\text{m}$ . Although this large average particle size was out of the confidence range of the equipment used, it indicated that the particles of the final product were much bigger than the ones formed by a classical emulsion polymerization process, suggesting once more the significant degree of interaction between both polymerization processes.

It is important to note that such big particles were not expected to form a stable suspension, as obtained experimentally. This result may be explained in terms of the classical results of the percolation theory.<sup>9</sup> Based on the principles of the percolation theory, it may be assumed that if the particles present very irregular shapes and are not too heavy, a microporous three-dimensional network may be formed by polymer particles being placed in layers. In this case, the suspension is not stable in the classical sense, as particles in fact are not suspended, but the solid phase cannot be separated through decantation either, unless the suspension is submitted to a strong force field. It was even more interesting that the final polymer product formed films after drying in recirculation ovens, like emulsion polymer samples.

Figures 6–8 show the morphology of the polymer particles obtained when the feeding of the emulsion constituents is started 2 h after the beginning of the suspension polymerization. The main difference between the reaction conditions of REAC5 and REAC6 is the type of impeller used for agitation. The typical particle size distribution of polymer particles of REAC5 immediately before the addition of the constituents of the emulsion polymerization system is shown in Figure 6(a). The mean particle size is around  $50 \mu\text{m}$ . However, the typical particle size distribution of polymer particles of REAC6 can be visualized in Figure 6(b). The polymer particles of REAC6 have a mean diameter of about  $550 \mu\text{m}$ . Besides the fact that the mean particle size of REAC6 is almost 10 times greater, it can be noted that the distribution of REAC6 is much broader, indicating that the impeller type 02 is less efficient than the impeller type 01 at keeping the suspension dispersed.

Figures 7 and 8 show that, as soon as the constituents of the emulsion polymerization system are added, the polymer particles formed by the suspension polymerization process start to be covered by the emulsion polymer particles, originating a core-shell-like structure. The covering of suspension particles is so efficient that, regardless of the average particle size, it is almost impossible to identify the original polymer particles at the end of the batch. This fact was also



**Figure 11** Particle size distribution of the polymer particles of REAC7 at  $t = 240$  min.

supported by an independent gravimetric analysis of the supernatant of REAC5, which indicated the presence of less than 0.4% polymer, and by a light scattering analysis of the aqueous phase, which could not detect the presence of polymer particles. Similar results were obtained for REAC6, although the solids content of the supernatant was higher in this case, 1.5%, probably because of the smaller collection efficiency of the larger particles due to the smaller overall particle surface. The core-shell structure of the final polymer particle can be visualized unequivocally in Figure 8(d). Figure 8(d) shows that the central core is formed by the polymer particle formed by the suspension polymerization system, whereas the shell is formed by the emulsion polymer particles collected by the core during the reaction.

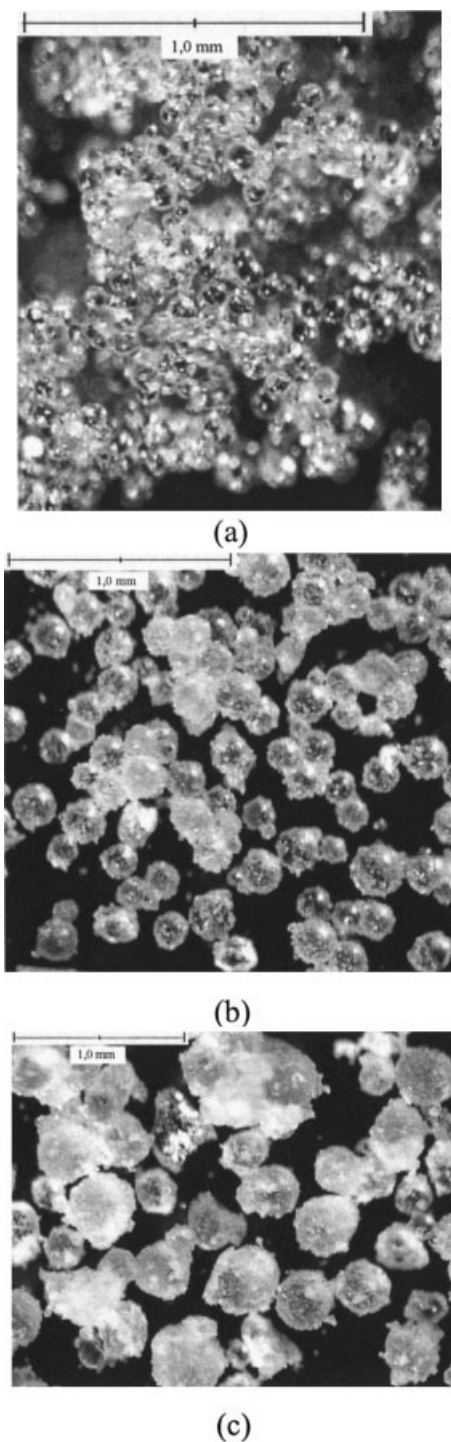
Figures 9 and 10 show results related to the polymerization kinetics. Figure 9(a) presents the typical evolution of the monomer conversion for REAC5. The vertical line indicates the moment at which the components of the emulsion polymerization system are added to the reaction vessel. Comparing Figure 3(a) to Figure 9(a), we can observe that the reaction rates of the suspension polymerization process are much slower than the reaction rates observed for the emulsion polymerization and that the addition of the emulsion constituents does not lead to an increase in the rate of monomer consumption. This also indicates the existence of significant interactions between both polymerization processes. Similar results are shown in Figure 10(a) for REAC6. In this case, however, as the collection of emulsion polymer particles is less efficient, the rates of monomer consumption are slightly higher after the addition of the emulsion constituents.

The evolution of the average molecular weights and MWDs for both REAC5 and REAC6 are shown in Figures 9(b,c) and 10(b,c), respectively. The influence

of the constituents of the emulsion polymerization system is very clear. An increase in the average molecular weights and the PIs and a shift of the MWDs toward larger molecular weights can be observed as soon as the addition of the emulsion constituents is started. Despite the reduction of the compartmentalized nature of the emulsion polymerization system, broad MWD polymer samples are obtained. As the capture of emulsion particles due to coalescence is very efficient, only a small amount of the polymer is produced in the compartmentalized way. For this reason, the final MWD is broad but not bimodal.

Figure 11 shows the particle size distribution of suspension polymer particles after 4 h of reaction for REAC7, immediately before the addition of the constituents of the emulsion polymerization system. The mean particle size is around  $66 \mu\text{m}$ . Figure 12(a) shows the polymer pearls immediately before the addition of the constituents of the emulsion polymerization system. The evolution of the particle morphology can be visualized in Figure 12(a-c). As observed previously, polymer particles become covered by the emulsion polymer particles after the initiation of the feed of the emulsion constituents. It must be emphasized that the core-shell structure is gradually formed and that, after a given instant, significant changes in the particle morphology are not observed any more.

Comparing the morphological properties of the final product of REAC7 with the morphological properties of the final product of REAC5, we can observe that the polymer particles of REAC5 present a higher degree of coverage. This is probably due to the lower monomer conversion in REAC5 when the emulsion feed is started, showing the great influence of this variable on the course of the reaction course. This is confirmed by a gravimetric analysis of the supernatant of REAC7, which indicates a solid content of 1.5%,



**Figure 12** Morphology of the polymer particles of REAC7 at (a)  $t = 240$  min, (b)  $t = 280$  min, and (c)  $t = 520$  min.

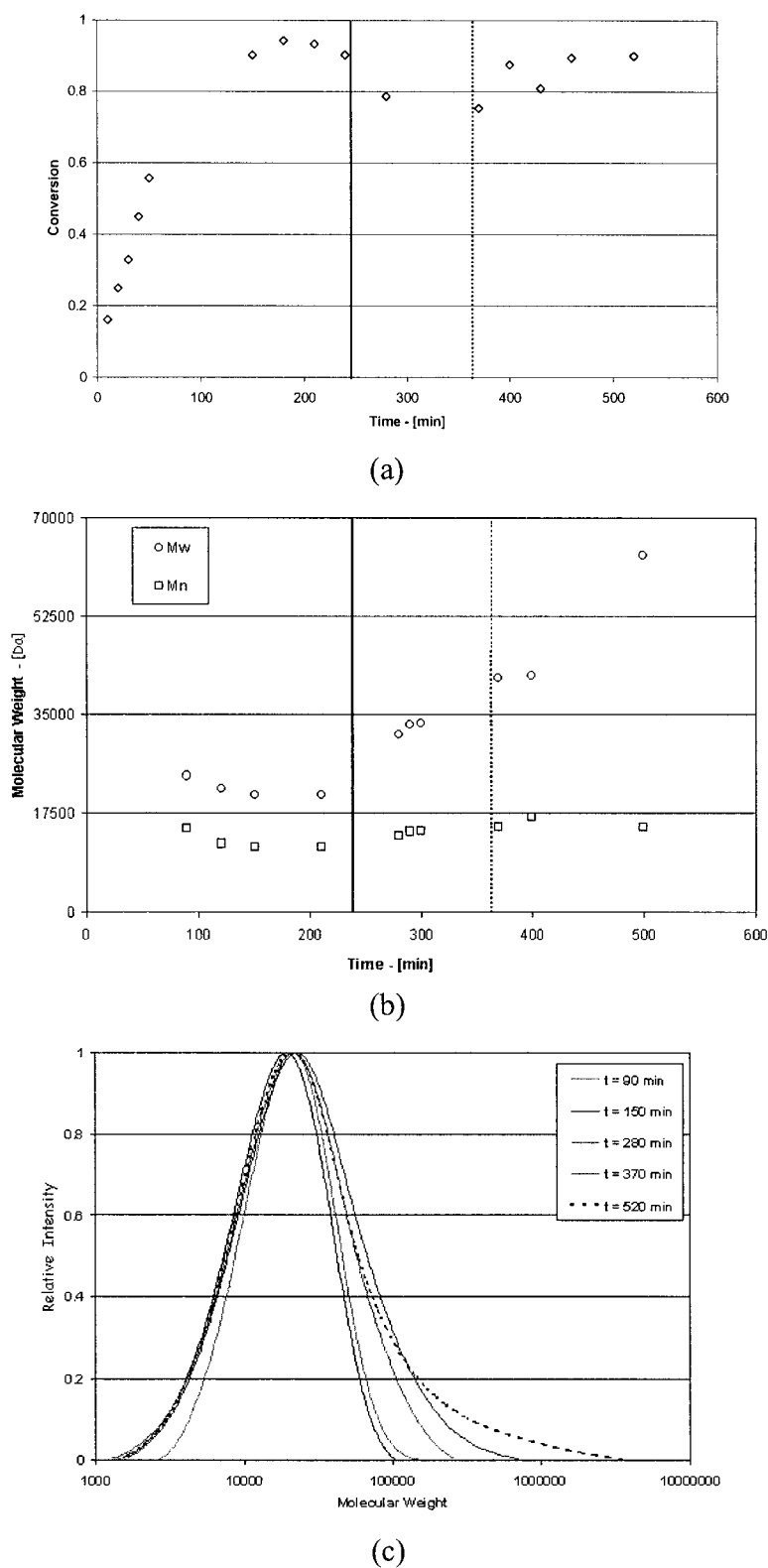
which is larger than the value observed in REAC5 for a similar suspension particle size. Besides that, the light scattering analysis of the supernatant of REAC7 indicates the presence of two distinct peaks: the first with a mean around  $185.0 \pm 43.0$  nm and the second with a mean around  $475.0 \pm 59.0$  nm. Although these results cannot be overemphasized, given the very low solid content of the supernatant, this is an indication

that the emulsion particles can grow before coalescence, also indicating that the rate of coalescence is slower in REAC7 than in REAC5. This can probably be justified by the higher conversion of the hard polymer pearls of REAC7 present in the reactor at the moment at which the emulsion feed is started.

The evolution of the monomer conversions in REAC7 can be visualized in Figure 13(a). The solid vertical line indicates the moment at which the constituents of the emulsion polymerization system are added to the reactor, and the dashed vertical line indicates the moment at which the monomer feed is cut off. As observed in the previous experimental runs, the addition of the constituents of the emulsion polymerization system does not increase the monomer conversion rates. Contrary to that, and similarly to the previous experiments, the addition of the emulsion constituents retards the rate of monomer consumption. Figure 13(b) shows the evolution of the average molecular weights. The presence of the emulsion polymerization system increases the averages and the PI. The evolution of the MWDs is presented in Figure 13(c). A broad MWD is obtained because the tail of high-molecular-weight chains increases significantly, undoubtedly showing the influence of the emulsion polymerization system. If Figures 13 and 9 are compared, it can be observed that the influence of the emulsion feed is much more significant in REAC7 than in REAC5. This is a strong indication that the interaction between suspension and emulsion polymer particles depends on the state of the polymer particles, which can be controlled by the moment at which the emulsion feed is started.

When seeded styrene emulsion polymerizations are performed, with dry polystyrene pearls produced by a classical suspension process as seeds, one may obtain the results presented in Figures 14 and 15. It can be observed in Figure 14 that the core-shell structure is once more obtained for the final polymer particle. Moreover, the evolution of the average molecular weights, presented in Figure 15, shows once more that significant interactions exist among suspension and emulsion polymer particles, even when the initial suspension particles are dry. Despite the increase of the averages due to the presence of the emulsion polymerization system, bimodal MWDs are not obtained. This suggests that the emulsion polymer particles that coalesce with the swollen suspension particles lose the compartmentalized character.

It is interesting to observe the results obtained for REAC9, when the water-soluble initiator, the buffer, and the emulsifier are removed from the monomer feed. In this case, the particle morphology of the final product, shown in Figure 16, indicates that the formation of the core-shell structure does not occur. Therefore, the formation of small emulsion polymer parti-



**Figure 13** Evolution of (a) the monomer conversion, (b) the molecular weight averages, and (c) the MWD of the polymer product of REAC7.

cles is of fundamental importance for the development of the core-shell structure. The particle size distribution of the polymer particles of the final prod-

uct of REAC9 is presented in Figure 17. The mean particle size is around  $86 \mu\text{m}$ , but the histogram has a long tail in the region of big particles.

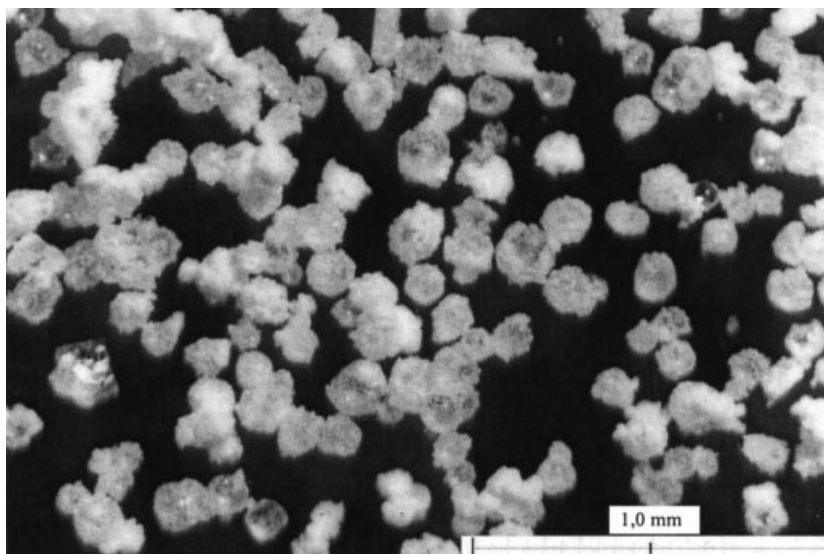
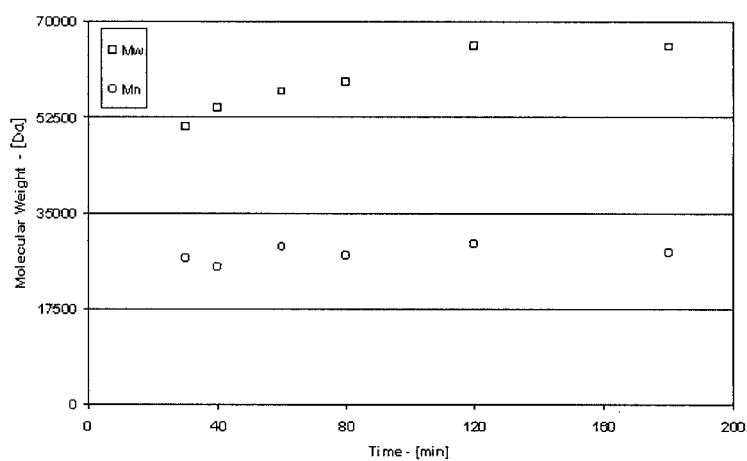
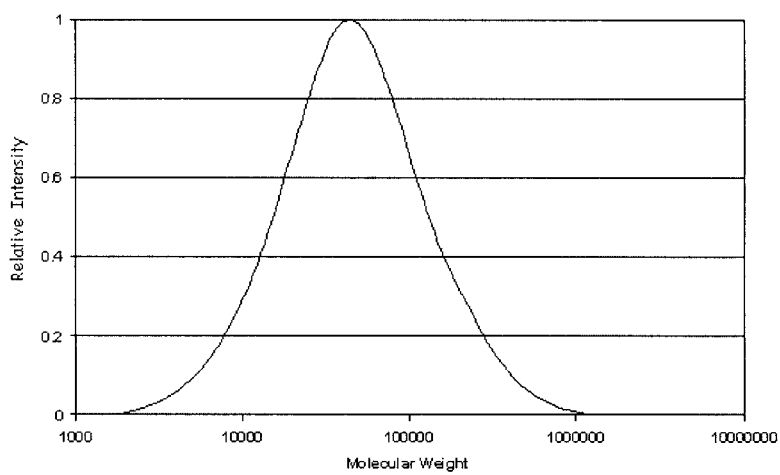


Figure 14 Morphology of the final product of REAC8.

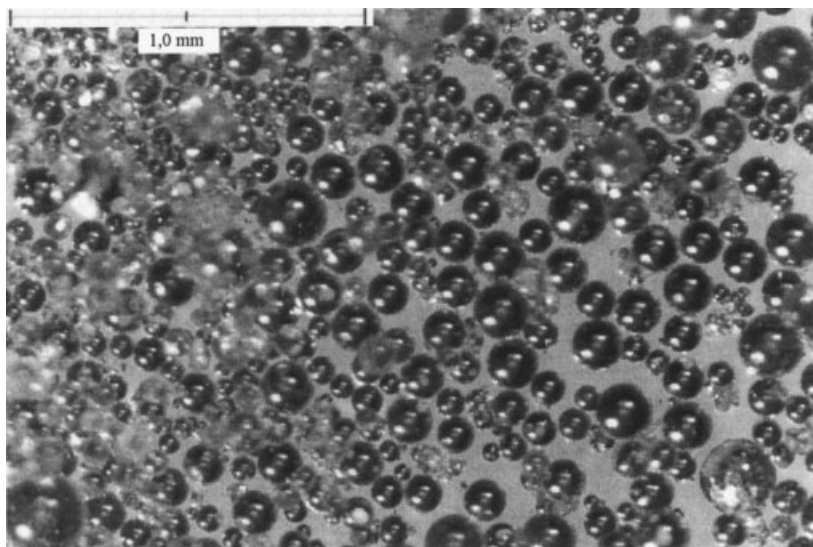


(a)



(b)

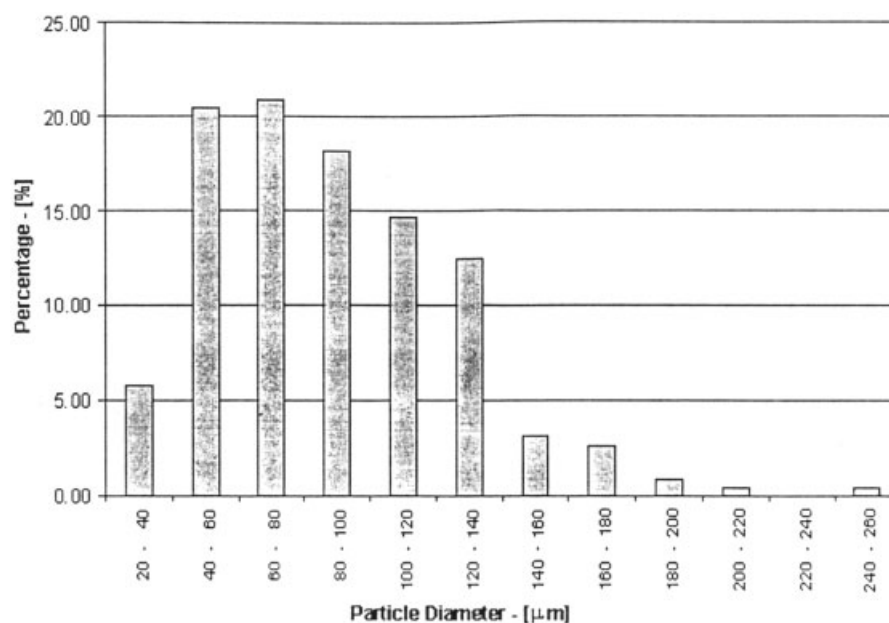
Figure 15 Evolution of (a) the molecular weight averages and (b) the MWD of the polymer product of REAC8.



**Figure 16** Morphology of the final product of REAC9.

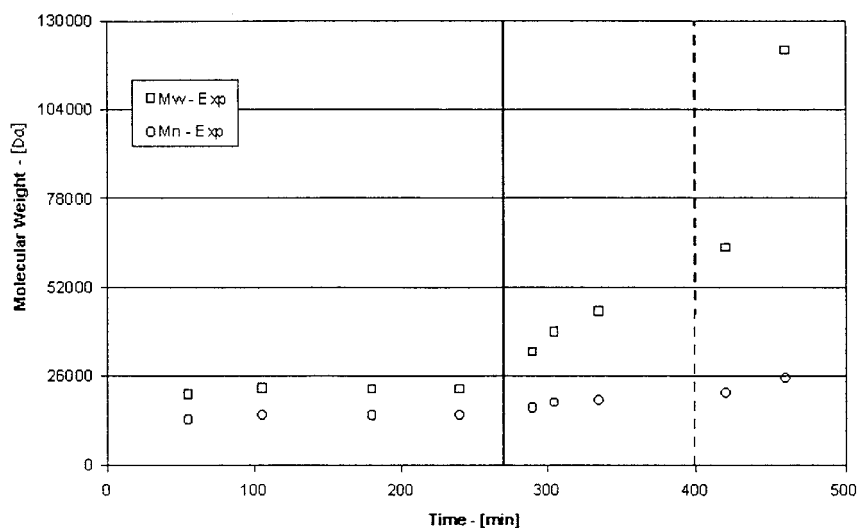
The evolutions of the average molecular weights and MWDs shown in Figure 18 indicate, however, that there is significant degree of interaction between old and new monomer droplets inside the reactor. The solid vertical line indicates the moment at which the addition constituents are added to the reactor, and the dashed vertical line indicates the moment at which the monomer feed is cut off. An increase in the average molecular weights after the addition of the specified amounts of the monomer and water can be observed. Moreover, Figure 18(b) shows the formation of a typical bimodal MWD. The most probable explanation for the obtained results is the variation of the initiator concentrations in the system. When the monomer is

added to the reaction system, the relative concentration of the initiator decreases, so polymer chains of high molecular weight are formed, leading to a high-molecular-weight peak. However, this also implies that old and new monomer particles coalesce and/or exchange mass. This is surprising, given the very high levels of monomer conversion after 4 h of reaction. Given the relatively low reaction temperature, spontaneous thermal polymerization is not expected to play a major role, as observed through independent polymerization experiments. Therefore, during semi-batch suspension polymerization, significant interactions should be expected among suspension/suspension and suspension/emulsion polymer particles.

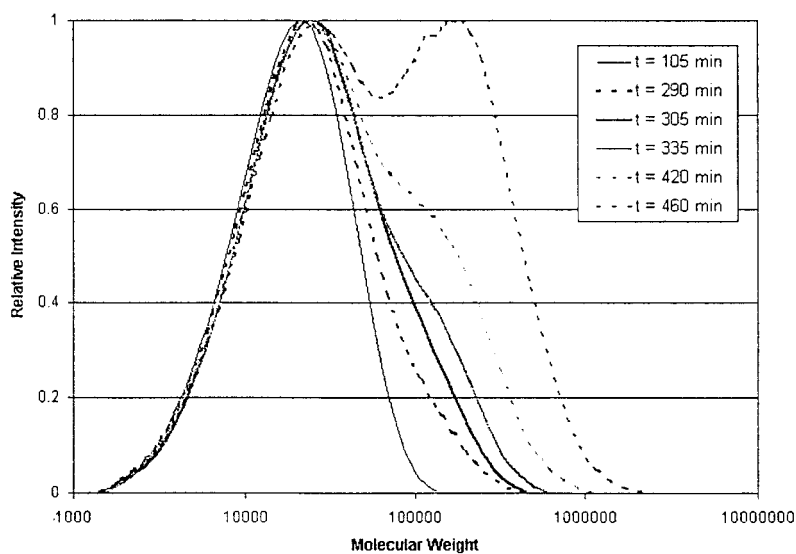


**Figure 17** Particle size distribution of the final product of REAC9.





(a)



(b)

**Figure 18** Evolution of (a) the molecular weight averages and (b) the MWD of the polymer product of REAC9.

## CONCLUSIONS

The semibatch styrene suspension polymerization was studied for feed streams containing chemical constituents normally used to perform emulsion polymerizations. The experimental runs took into account the moment at which the emulsion feed was started and analyzed the effects caused by the emulsion feed on the course of the polymerization. Moreover, the effects of some additional operation conditions, such as the shape of the impeller of the agitator, were also analyzed.

The obtained results show that the polymerization technique studied here allows the formation of core-shell-like polymer particles. The core is formed by polymer particles generated from the suspension po-

lymerization system, whereas the shell is formed by the coalescence of polymer particles from the emulsion polymerization system. It must be emphasized that the rate of coverage seems to depend basically on two variables:

1. The degree of conversion of polymer particles formed by the suspension polymerization process: the lower the initial conversion, the higher the rates of coalescence.
2. The size of the polymer particles formed by the suspension polymerization process: the bigger the particle size, the smaller the total contact area with the emulsion particles and the lower the rates of coalescence.

The experimental results show that the moment at which the emulsion feed is started exerts a great influence not only on the polymer particle morphology but also on the average molecular weights and the MWD. The core-shell structure is formed only when the components of the emulsion polymerization system are fed. When only monomer and water are fed into the reaction vessel, the core-shell structure is not formed, but a bimodal MWD polymer resin can be obtained.

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