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Particle Nucleation in High Solids Miniemulsion Polymerization

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ABSTRACT: The nucleation mechanisms in high solids content semicontinuous miniemulsion polymerization was investigated using as case study a silicone−acrylic system. Batch polymerization of the miniemulsion used as initial charge of the reactor was studied. Semicontinuous processes using both miniemulsion feeding and neat monomer feeding were considered. Strategies to maximize the extent of droplet nucleation and to minimize the formation of polymer particles by homogeneous nucleation were discussed.

Introduction

Droplet nucleation is the distinctive feature of miniemulsion polymerization[1] that allows incorporating hydrophobic compounds into polymer particles because mass transfer through the aqueous phase is avoided. This has led to the development of a wide range of useful polymer materials only accessible through this technique. Some examples of these polymer materials are (i) dispersed polymers with well-defined microstructure obtained by controlled radical polymerization,[2−4] (ii) waterborne linear polyethylene produced by means of catalytic polymerization,[5−7] (iii) easy incorporation of hydrophobic monomers,[8] (iv) polymer−polymer hybrid latexes,[9,10] and (v) and polymer−inorganic waterborne dispersions.[11,12] Miniemulsion polymerization has been reviewed recently.[13−17]

The successful synthesis of many of these materials requires an efficient nucleation of the monomer droplets. This can be illustrated by considering the synthesis of polymer−polymer hybrid dispersions. In this process, a preformed polymer is dissolved in a monomer mixture containing a costabilizer (low molecular weight highly water-insoluble compound) and dispersed in an aqueous solution of surfactants to obtain a miniemulsion. The challenge is to transform most of the droplets into polymer−polymer composite particles, maintaining the same polymer/polymer ratio in all particles. This requires a fast nucleation of all the droplets to avoid monomer mass transfer from droplets to growing particles and to minimize secondary nucleation, particle−particle coagulation, and particle−droplet coagulation. Droplet nucleation has been controversial. Early literature supported the idea that only a fraction of monomer droplets was nucleated because of a low efficiency for radical capture attributed to the monomer droplets.[1,18,19,20] More recent results show that nucleation of most of the droplets can be achieved in low solids content batch miniemulsion polymerization.[21,22]

However, high solids content is required for commercial applications. In addition, because free radical polymerization is a highly exothermic process, heat removal is critical for large-scale operations, and semicontinuous reactors are used to control the heat generation rate. Droplet nucleation in high solids semicontinuous miniemulsion polymerization has not been investigated, although one may anticipate that these conditions are far from the ideal ones required for the nucleation of most of the droplets.

The main objective of this work was to study the nucleation mechanisms in high solids content semicontinuous miniemulsion polymerization using as a case study a silicone−acrylic system. High solids batch processes were also considered because frequently the semicontinuous processes start with the batch polymerization of the initial charge of the reactor.

Experimental Section

Materials. Technical grade monomers, methyl methacrylate (MMA) and butyl acrylate (BA), supplied by Quimidroga, and acrylic acid (AA, Aldrich) were used without purification. Polydimethylsiloxane divinyl terminated (PDMS, Aldrich) (Scheme 1.1) was used as polymer, hexadecane (HD, Aldrich) and stearyl acrylate (SA, Aldrich) were used as costabilizers, and Dowfax 2A1 (alkyldiphenyl oxide disulfonate, Dow Chemicals) and Disponil A3065 (mixture of ethylene oxide alcohols, Cognis) were used as surfactants. Potassium persulfate (KPS, Panreac), ammonium persulfate (APS, Panreac), sodium metabisulfite (SBS, Aldrich), *tert*-butyl hydroperoxide (TBHP, Panreac), ascorbic acid (AsAc, Panreac), and azobis(isobutyronitrile) (AIBN, Fluka) were used as initiators. Distilled water was used throughout the work.

Miniemulsification. The organic phase was prepared by dissolving the resin and the costabilizer (when used) in the monomer mixture, and the aqueous phase was formed by dissolving the surfactant in water. Both phases were mixed for 10 min using a magnetic stirrer at 1000 rpm. The coarse emulsion was sonified in a Branson Sonifier 450 at 480 W/L for 20 min and then homogenized in a two-valve Manton-Gaulin high-pressure homogenizer (LAB 60.10) at different number of cycles and under different pressures (41−4 MPa in the first and second valve for 4 cycles when 3 and 12 wt % of PDMS were used and 55−5 MPa for 14 cycles when 25 wt % of PDMS was used). Table 1 summarizes the formulations of the miniemulsions used. The code describing the miniemulsions is as follows: M refers to miniemulsion, the first number refers to the PDMS concentration, and the second letter and number refer to the costabilizer (SA; stearyl acrylate when used) and its concentration.

Polymerization Processes. Batch polymerizations were carried out in a 1 L glass reactor equipped with reflux condenser, stirrer, sampling device, and nitrogen inlet. Reaction temperature (70 °C) was set constant by controlling the temperature of the fluid in the jacket by means of a thermostatic bath and a heat exchanger. The miniemulsion was added to the reactor and kept under stirring and nitrogen atmosphere (12−15 mL/min). When the reaction temperature was reached, the aqueous initiator (KPS) solution was injected. The polymerizations carried out using this strategy are designated as B.

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Table 1. Miniemulsion Formulations Based on 100 g of Monomer

	stability	MMA/BA/AA (49/50/1) (g)	PDMS (g)	SA (g)	Dowfax2A1 (g)	H_2O (g)	d_d (nm)
M0SA4	+	100		4	1.8	86	75
M3SA4	++	100	3	4	1.8	86	94
M12	++	100	12		1.8	95	115
M25	+++	100	25		1.8	110	177

Semicontinuous polymerizations were carried out in the same reactor setup as the batch polymerizations. Two different feeding strategies were explored. In the first one, 33 wt % of the miniemulsion (50 wt % organic phase, including acrylic monomers and PDMS) was used as initial charge, and it was allowed to polymerize in batch for 1 h. Then, the rest of the miniemulsion and the aqueous initiator solutions were fed for 4 h. The experiments carried out using this strategy were designed as SM. Alternatively, a preformed seed was used as initial charge (experiments SSM). In the second strategy, the polymerizations were performed by charging in the reactor a 10 wt % organic phase miniemulsion containing 30 wt % of the PDMS (based on monomers) and polymerizing it for 2 h in batch. Then the remaining mixture of the monomer (MMA/BA/AA (49/50/1)), the initiator system, and the surfactant solution were fed for 3 h. The final products reached 50 wt % solids content, and the final PDMS concentration was 3 wt % with respect to the total monomer. All the reactions were carried out at 70 °C. These experiments were designated as SNM.

In both batch and semicontinuous processes, samples were withdrawn at regular intervals, and the polymerization was short-stopped with hydroquinone. The conversion was determined gravimetrically. The conversion was calculated with respect to the monomer; namely, the PDMS content was not taken into account.

Analytical Techniques. *Droplet, Particle Size, and Particle Size Distribution.* Miniemulsion droplets (d_d) and latex particles (d_p) *z*-average diameters were measured by dynamic light scattering using a Zetasizer Nano Z (Malvern Instruments). Miniemulsion was diluted in distilled water (no differences were observed when distilled water or distilled water saturated with MMA was used), and the droplet size was measured within 10 min of its preparation. Particle size distribution (PSD) was measured by a disc centrifuge photosedimentometer (BI-DCP, Brookhaven). The density of the particles needed for this measurement was estimated as a weighted average taking into account the monomer conversion. The BI-DCP determines particle size by monitoring the sedimentation of the particles in a liquid under a centrifugal force in a spinning disc.

Surface and Interfacial Tensions. The surface tension was measured with a KSV Sigma 70 tensiometer equipped with a DuNouy ring, and the interfacial tension was measured using a OCA Dataphysic tensiometer by the pendant drop method.

Miniemulsion Stability. The stability of the miniemulsions was measured at 30 °C in a TURBISCAN LAb^{expert}. The miniemulsion was placed in a cylindrical glass cell which was completely scanned by a light source. The backscattered light, which depends on the droplet mean diameter and on the volume fraction, provided fast measurement of the miniemulsion stability. Figure 1 presents the time evolution of the backscattering profiles of miniemulsions M0SA4, M3SA4, M12, and M25. It is observed that M0SA4 started degrading in less than 1 h. The decrease in backscattering intensity was due to droplet coalescence and likely creaming, as the appearance of a monomer layer at the top of the cell was evident. The stability of the miniemulsions strongly improved with the amount of PDMS, and M25 was stable for at least 5 h. In order to summarize the stability data, the following code was used: (+) stable enough to perform batch polymerizations, (++) stable enough to perform semicontinuous polymerizations, and (+++) very stable.

Results and Discussion

Batch Polymerizations. Figure 2 shows the conversion evolution for batch polymerizations with different PDMS

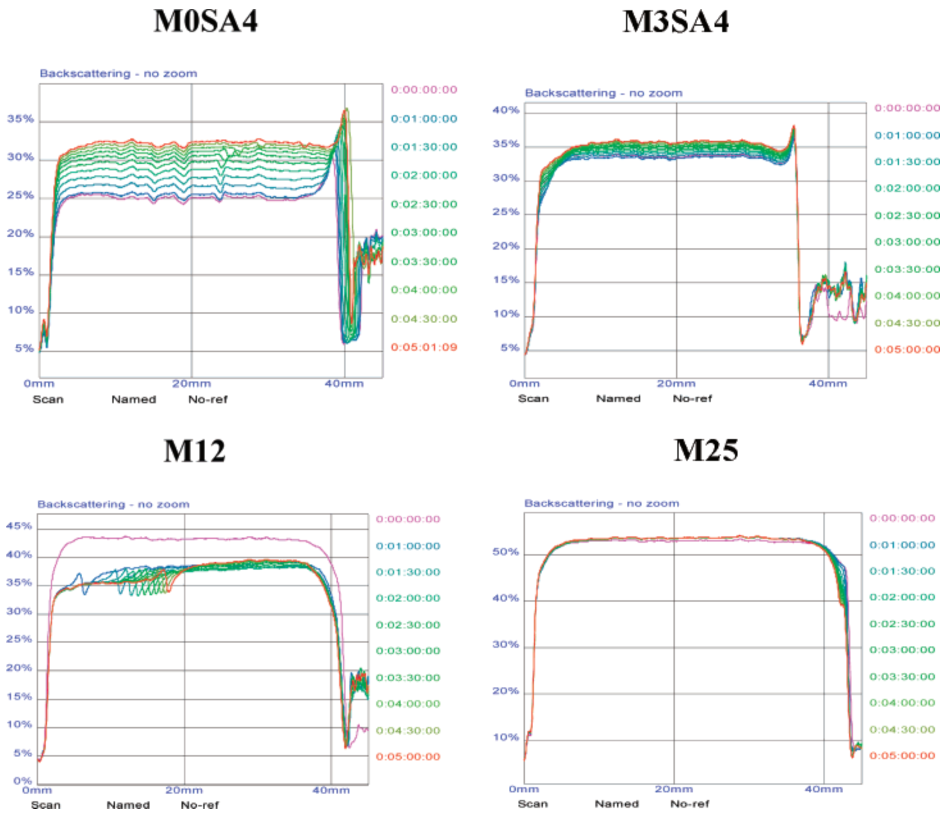


Figure 1. Stability of the miniemulsions.

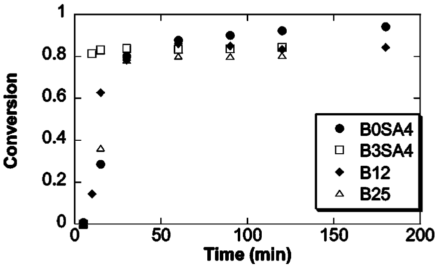


Figure 2. Evolution of monomer conversion in batch miniemulsion polymerizations carried out with varying concentrations of PDMS.

contents. All processes showed fast polymerization rate. Notice that the miniemulsions containing 0 and 3 wt % of PDMS also contained 4 wt % SA because otherwise they were not stable. Table 2 presents the number of droplets and particles, per liter of latex, calculated from the diameters measured by light scattering. This table also includes the ratio between the area that could be covered by the surfactant (A_E) and the total surface area of the monomer droplets (A_d). In order to calculate A_E, the parking area of Dowfax 2A1 on a MMA/BA/AA (49/50/1) latex was determined by adsorption measurements (174 Å^2/molecule), and it was assumed that it was the same for the monomer droplets. Table 2 shows that the total surface area formed by the droplets (A_d) was larger than the area that could be covered by the surfactant (A_E). At this point, it could be stated that the assumption that the parking area of the surfactant on droplets and particles is the same could be erroneous. In fact, Erdem et al.[23] reported larger parking areas on monomer droplets as compared to those on the corresponding polymer. Therefore, the surface tension of the miniemulsion M25 (which had the smallest surface area and in consequence the higher free surfactant concentration) was measured, giving a value higher (30.8 mN/m) than the surface tension at the cmc of the surfactant (28.8 mN/m). Table 2 also presents the droplet−water interfacial tensions for these systems. It can be seen that the PDMS content had no effect on the interfacial tensions, likely because the PDMS was located in the core of the droplets, whose surface was enriched with the more hydrophilic monomers. Therefore, no effect of the PDMS on the emulsifier adsorption was expected, and it could be concluded that no micelles were present in the reactor during the polymerization. Table 2 also includes the ratio between the number of particles and the initial number of droplets (N_p/N_d). It is worth pointing out the uncertainties associated with this ratio because an average diameter of the droplets/particles was first estimated from the dynamic light scattering measurements and the third power of this value was used to calculate N_p and N_d. Nevertheless, the values of N_p/N_d showed valuable trends. The reaction carried out without PDMS (B0SA4) presented the lowest N_p/N_d ratio, probably because the miniemulsion was not stable enough during the polymerization process. Most of the droplets were nucleated in runs B3SA4 and B12. The slightly higher fraction of nucleated droplets found in run B12 could be attributed to the higher stability of this miniemulsion, but the difference represents less than a 2% variation in the measurement of the droplet and particle sizes. A substantial secondary nucleation was observed in run B25. Because there were no micelles in the system, the particles were produced by homogeneous nucleation.

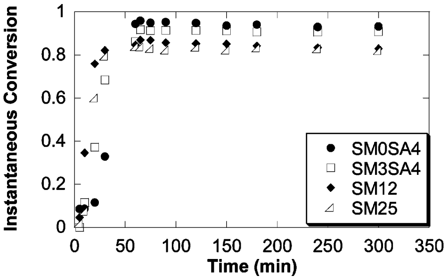


Figure 3. Effect of PDMS content on the kinetics of semicontinuous polymerizations with miniemulsion feeding.

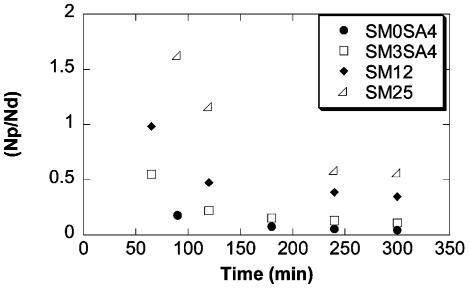


Figure 4. Effect of PDMS content on N_p/N_d along the semicontinuous polymerization with miniemulsion feeding.

These results show that in batch miniemulsion polymerization the number of particles is determined by the interplay between droplet nucleation and homogeneous nucleation. Droplet nucleation is strongly affected by miniemulsion stability; i.e., the droplets should survive for a period of time long enough to allow radical entry. In this series of experiments the rate of radical entry per monomer droplet was minimum for run B0SA4 because the number of droplets was maximum. Therefore, the poor droplet stability and the high number of droplets were likely the reason for the low N_p/N_d ratio of run B0SA4. On the other hand, for a given formulation in terms of monomers, initiators and surfactants, the probability of formation of new particles by homogeneous nucleation increases as the number of particles/droplets in the system decreases.[24] The reason is that the oligoradicals in the aqueous phase can grow to the critical size for precipitation before being captured by the particles/droplets. This is what happened in run B25, whereas the number of droplets/particles in run B3SA4 and B12 was high enough to minimize the occurrence of homogeneous nucleation.

Semicontinuous Polymerizations. *Miniemulsion Feeding.* The formulation used in the semicontinuous polymerizations with miniemulsion feeding is given in Table 3. Figure 3 presents the kinetics of the polymerizations carried out using miniemulsions with varying concentrations of PDMS (M0SA4, M3SA4, M12, and M25). A 0.5 wt % of APS/SBS was used as initiator during the semicontinuous operation. Figure 3 shows that the higher the PDMS content the lower the monomer conversion. This was due to the formation of inactive radicals upon propagation with the vinyl groups of the PDMS.[25] Figure 4

Table 2. Different Batch Polymerizations Data

system	droplet−water interfacial tension (mN/m)	d_d (nm)	d_p (nm)	N_d (droplets/L latex)	N_p (part/L latex)	N_p/N_d	A_E/A_d
B0SA4	3.3	75	112	2×10^{18}	5.8×10^{17}	0.3	0.4
B3SA4	3.38	94	114	1.1×10^{18}	9×10^{17}	0.8	0.5
B12	3.06	115	117	6.4×10^{17}	6×10^{17}	0.9	0.5
B25	3.03	177	137	1.8×10^{17}	4×10^{17}	2.2	0.7

Table 3. Formulation of Semicontinuous Polymerizations with Miniemulsion Feeding

	initial charge	feed 1	feed 2	feed 3
miniemulsion/seed	200 g	400 g		
APS	0.75 wt %[a]			
water	13 g			
oxidant			0.25−0.5 wt %[a]	
reductant				0.25−0.5 wt %[a]

[a] Weight percent with respect to the monomer.

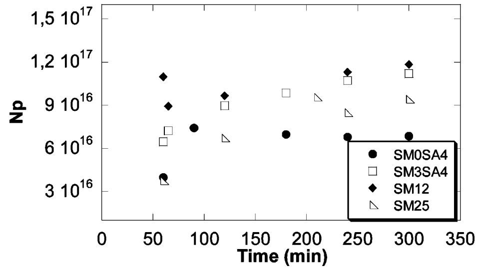


Figure 5. Effect of the PDMS content on the evolution of the number of particles in the semicontinuous polymerizations using miniemulsion feed.

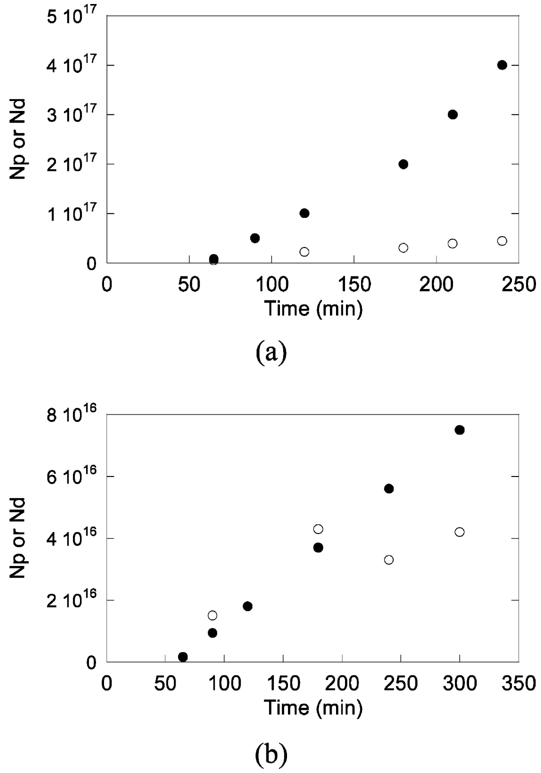


Figure 6. Comparison of the evolution of the number of new particles (○) and number of feed droplets (●) for (a) run SM3SA4 and (b) run SM25.

presents the evolution of the ratio between the polymer particles in the reactor and the monomer droplets fed up to the moment in which the sample was withdrawn from the reactor. It is important to point out that in this calculation it was considered that during the semicontinuous process the disperse phase was formed solely by polymer particles. Figure 4 shows some interesting features. On one part, N_p/N_d continuously decreased for all systems, which means that only a fraction of the entering droplets was nucleated, even though in the experiments containing PDMS N_p continuously increased during polymerization (Figure 5). In addition to those which were nucleated, droplets could disappear by both Ostwald ripening and coagulation.[26] Increasing PDMS concentration yielded more stable droplets because Ostwald ripening was less acute, and their colloidal stability increased as they were larger and hence they had more surfactant at the surface. The smaller number of particles (Figure 6) also favored the radical capture by the entering droplets.

Figure 7 presents the evolution of the weight particle size distribution (PSD) as measured by BI-DCP. In the discussion of this figure it is worth to have in mind that the droplet sizes of the miniemulsions fed (as measured by QELS) were $d_{\mathrm{M0SA4}} = 75$ nm, $d_{\mathrm{M3SA4}} = 94$ nm, $d_{\mathrm{M12}} = 115$ nm, and $d_{\mathrm{M25}} = 177$ nm. Figure 7a shows that during run SM0SA4 the PSD broadened and that both ends of the PSD moved toward higher sizes. The increase in size of the small particle size end of PSD indicates that no significant nucleation or homogeneous nucleation yielding small particles occurred. This agrees with Figure 6 which shows that N_p was roughly constant for most of this reaction. The lack of droplet nucleation was probably due to the poor stability of the miniemulsion droplets. Likely, the PSD became broader because the volumetric growth of large particles was faster than that of the smaller particles.

The evolution of the PSD during run SM3SA4 (Figure 7b) shows that a substantial number of particles were formed during the process. (The position of the small particle size end of the PSD stayed at about 100 nm for the whole process.) In this case, a fraction of the entering miniemulsion droplets could be nucleated because they were stable enough to survive in the reactor for long enough to capture a radical. Some broadening of the PSD was observed in this run because the large particles present in the reactor from the beginning of the process grew due to the monomer that diffused from the entering miniemulsion droplets and from coagulation with miniemulsion droplets.

Run SM12 (Figure 7c) showed the narrowest PSD of this series of experiments, suggesting that a substantial fraction of the entering droplets was nucleated. The evolution of the PSD in run SM25 was interesting because it shows a continuous nucleation of relatively small particles (110 nm). These particles were substantially smaller than the entering monomer droplets. Two explanations for these results can be offered. First, these small particles resulted from nucleation of droplets that stayed in the reactor for some time before being nucleated, and hence they lost a substantial fraction of the monomer to the polymer particles. Second, the small particles resulted from homogeneous nucleation. The latter would agree with the results obtained in batch that showed that for miniemulsion M25 a large fraction of particles were formed by homogeneous nucleation. The reason was that the droplet size was large, the rate of capture of radicals by droplets was lower, and the oligoradicals growing in the aqueous phase could reach the critical length for formation of a new particle.

An attempt to modify the PSD was made by reducing the size of the polymer particles present in the reactor just before starting the miniemulsion feed. This was achieved by using a seed with a particle size smaller than that obtained by polymerization of the miniemulsion used as initial charge ($dp_{\mathrm{SM3SA4}} = 123$ nm). This seeded semicontinuous miniemulsion was referred as SSM. The particle sizes of the seed was $dp_{\mathrm{SSM3SA4}} = 93$ nm. The droplet size of the miniemulsion fed was 90 nm. Figure 8 shows that the use of a smaller seed allowed to slightly reduce the broadness of the PSD by lowering the size of the larger polymer particles.

As nucleation is strongly affected by the initiator type, in an attempt to maximize the percentage of nucleated droplets, different initiator systems were used: (1) APS/SBS. This water-

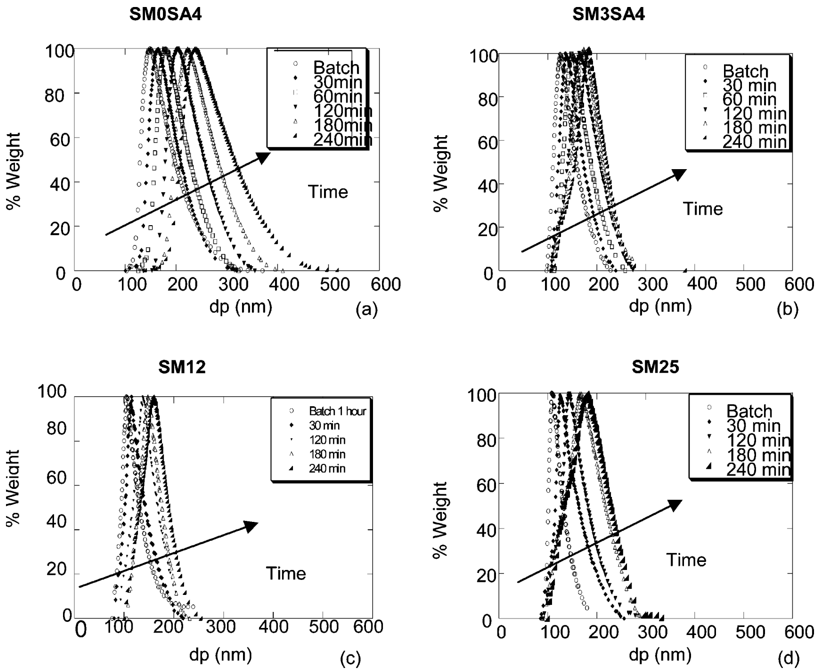


Figure 7. Effect of the PDMS content on the particle size distribution in the semicontinuous polymerizations using miniemulsion feed: (a) SM0SA4, (b) SM3SA4, (c) SM12, and (d) SM25.

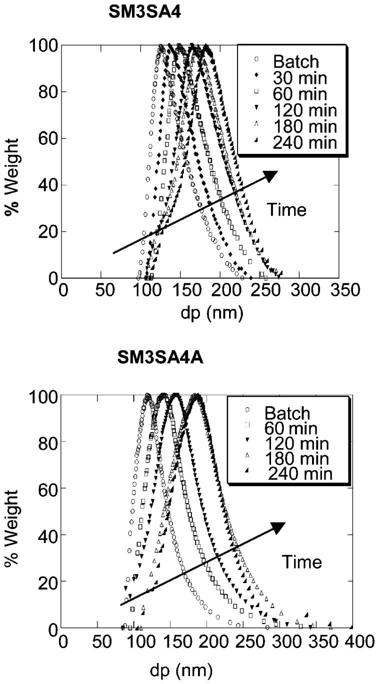


Figure 8. Effect of the seed particle size on the particle size distribution in the semicontinuous polymerizations using miniemulsion feed.

soluble redox system (used in the experiments discussed above) yields water-soluble radicals, which have to react with monomer in the aqueous phase to be able to enter into the organic dispersed phase (droplets and particles). (2) TBHP/AsAc. It is a water-soluble redox system which yields hydrophobic radicals that enter rapidly into the dispersed organic phase (droplets and particles).[27] (3) AIBN. It is an oil-soluble initiator, mainly located in the oil phase. The role of the water-soluble fraction is under debate.[28−30] The goal of using this initiator was to improve droplet nucleation and minimize homogeneous nucleation.

The efficiencies of the two redox systems were compared in the seeded semicontinuous miniemulsion polymerizations [SSM3SA4 (APS/SBS) and SSM3SA4TA (TBHP/AsAc), Table 4], finding no significant differences between them. On the other hand, the water-soluble redox system SM3SA4 (APS/SBS) and the oil-soluble initiator SM3SA4A (AIBN) were compared in semicontinuous miniemulsion polymerizations. The miniemulsions used in these reactions presented similar droplet sizes (Table 4). The addition of AIBN to SM3SA4A formulation did not change the stability of the miniemulsion.

Table 4. Formulations and Droplet Size of the Miniemulsion

	miniemulsion	seed	d_d (nm)	initiator semicontinuous
SSM3SA4	M3SA4	B3SA4[b]	92	0.5 wt % APS/SBS
SSM3SA4TA	M3SA4	B3SA4[b]	90	0.5 wt % TBHP/AsAc
SM3SA4	M3SA4		89	0.5 wt % APS/SBS
SM3SA4A	M3SA4+AIBN[a]		93	

[a] AIBN 0.7 wt % with respect to the monomers. [b] APS as initiator.

Figure 9 shows that homogeneous nucleation was avoided with AIBN, but very large particle sizes were obtained. This suggests extensive monomer diffusion from the entering droplets to the particles already present in the reactor caused by the low polymerization rate obtained with AIBN, which allowed additional time for monomer mass transfer.

The probability of radical entry in monomer droplets decreases with the number of polymer particles present in the system. This means that in a semicontinuous polymerization using miniemulsion feeding the probability of nucleation of the droplets entering into the reactor decreases along the process. On the other hand, the probability of droplet nucleation is expected to increase with the initiator concentration. In an attempt to increase droplet nucleation toward the end of the process, the increasing initiator feed profile shown in Table 5 was used (SSM3SA4V). Figure 10 shows that this strategy led to a narrower PSD, namely that a larger fraction of incoming droplets was nucleated.

The nucleation mechanism in a semicontinuous process with miniemulsion feeding can be summarized as follows: (i) Most

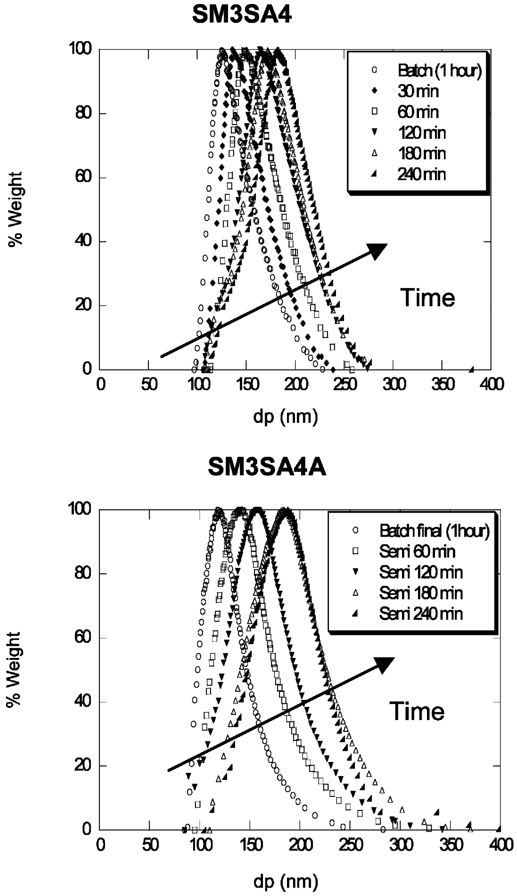
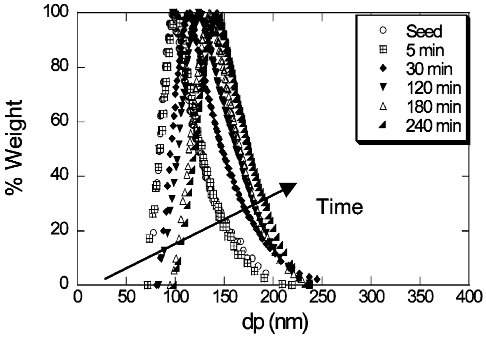


Figure 9. Particle size distributions obtained in semicontinuous polymerization with miniemulsion feeding using a water-soluble redox initiator (APS/SBS, run SM3SA4) and an oil-soluble initiator (AIBN, run SM3SA4A).

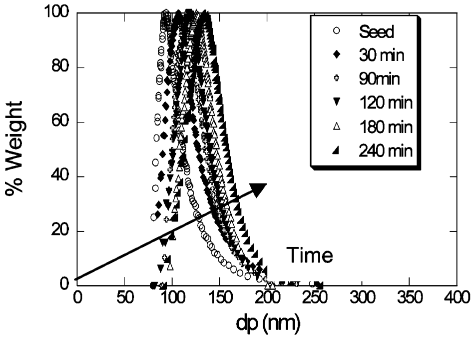
Table 5. Initiator Flow Rate (g/min) Profile in Experiment SSM3SA4V

initiator	1st hour	2nd hour	3rd hour	4th hour
APS	0.05	0.1	0.2	0.4
SBS	0.05	0.1	0.2	0.4

of the droplets of the miniemulsion forming the initial charge of the reactor are nucleated, provided that miniemulsion is stable enough. Particle formation by homogeneous nucleation is likely for large droplets sizes. (ii) During the first stages of the semicontinuous process, a large fraction of the droplets are nucleated because the number of particles in the system is still moderate, and hence the droplets efficiently compete for radicals. (iii) As the process proceeds, the number of particles in the system increases, and it is less likely that droplets entering into the reactor can capture radicals. Therefore, the monomer in the droplets diffuses to the polymer particles and eventually the droplets disappear, or if they are nucleated, they yield relatively small particles because they have lost a substantial part of the monomer.



SSM3SA4 (a)



SSM3SA4V (b)

Figure 10. Effect of the initiator feeding profile on particle size distribution for the semicontinuous polymerization with miniemulsion feeding: (a) constant flow rate (run SSM3SA4) and (b) increasing flow rate (run SSM3SA4V).

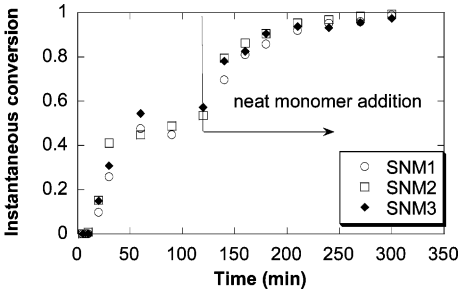


Figure 11. Conversion evolution in the semicontinuous polymerizations using neat monomer feeding.

Neat Monomer Feeding. In this strategy, the goal was to achieve an efficient droplet nucleation of the miniemulsion used as initial charge and then to make the composite particles to grow, avoiding both secondary nucleation and particle coagulation. The initial charge was a miniemulsion containing 30 wt % PDMS. The formulations, in which the concentrations of initiator and surfactant were varied, are summarized in Table 6.

Figure 11 presents the evolution of monomer conversion in experiments SNM1−SNM3. It can be seen that low limiting conversion was encountered in the batch polymerization of the

Table 6. Formulations of Semicontinuous Process with Neat Monomer Feeding

	MMA/BA/AA (g)	PDMS (g)	Dowfax 2A1 (g)	water (g)	oxidant (g)	reductant (g)
initial charge (miniemulsion)	31.5	13.5	0.567	405	0.236 APS	
		semicontinuous process (3 h)				
SNM1	400		0.44		1[a]	1[a]
SNM2	400		0.88		1[a]	1[a]
SNM3	400		0.44		2[a]	2[a]
SNM4	400		0.20		1[a]	1[a]
SNM5	400		0.20		1[b]	1[b]

[a] APS/SBS. [b] TBHP/AsAc.

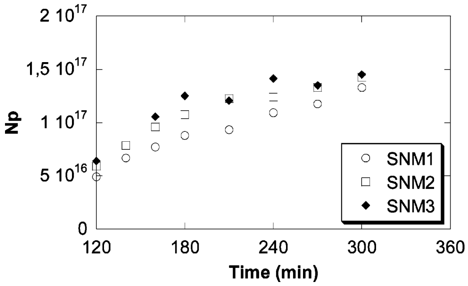


Figure 12. Number of particles evolution of different polymerization performed by semicontinuous polymerization with neat monomer feeding.

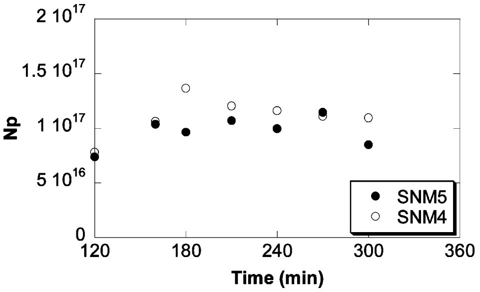
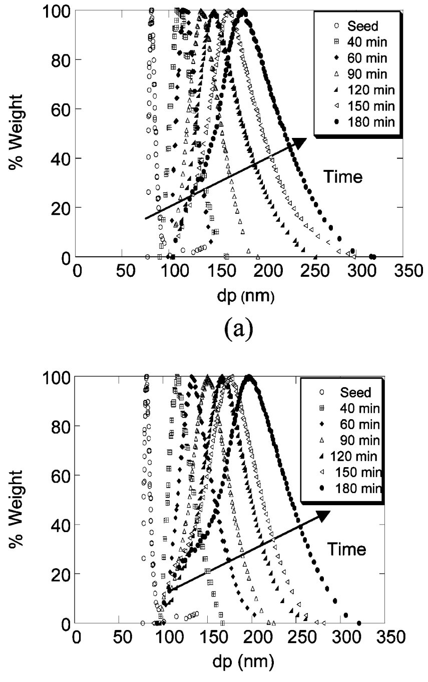


Figure 13. Evolution of the number of particles for polymerization performed by semicontinuous polymerization with neat monomer feeding (run SNM4, lower concentration of emulsifier in the feed, and SNM5, with TBHP/AsAc).



(a)

(b)

Figure 14. Particle size evolution for polymerization performed by semicontinuous polymerization with neat monomer feeding: (a) run SNM4, lower concentration of emulsifier in the feed; (b) run SNM5, with TBHP/AsAc.

initial charge, likely due to the formation of inactive radicals upon propagation with the vinyl groups of the PDMS.[25] The semicontinuous process was started at 120 min. Almost complete conversion was achieved at the end of the process. Figure 12 shows that a large number of new particles were nucleated during the semicontinuous process.

In order to reduce the extent of secondary nucleations, run SNM4 (Table 6) was performed using a lower concentration of emulsifier in the feed. Figure 13 shows that the number of particles was better controlled during most of the feeding process, although some nucleations occurred at the beginning. However, a close look to the evolution of the PSD indicates (Figure 14a) some secondary nucleation for most of the process. The surfactant concentration was not reduced any further due to the risk of latex coagulation.

Calculations using the particle size, the surface area covered by a molecule of surfactant under saturation conditions (a_s = 174 Å^2/molecule), and the volume of organic phase showed that no micelles were present in the reactor during the polymerization. Therefore, the formation of new particles occurred by homogeneous nucleation. Homogeneous nucleation is favored by the use of initiator systems that produce hydrophilic radicals. Hence, in order to minimize secondary nucleations, an initiator system that yields hydrophobic radicals (TBHP/AsAc) was used in run SNM5. The evolution of N_p and that of PSD presented in Figures 13 and 14b, respectively, showed that the use of TBHP/AsAc allowed reducing the number of newly formed particles.

Conclusions

In batch miniemulsion polymerization, droplets are efficiently nucleated provided that stable miniemulsions are used. Homogeneous nucleation may be important in systems with relatively small number (large size) of droplets. For the particular system used in this work, droplet stability increased with the PDMS content, allowing nucleation of most droplets. High PDMS contents yielded relatively large droplets, and hence particle formation by homogeneous nucleation was significant.

In semicontinuous polymerization using miniemulsion feeding, the fraction of the entering droplets that was nucleated decreased along the process because the increasing number of particles made radical entry in droplets less likely. In addition, the droplets that were nucleated give, as an average, small particles because in the time elapsed until they were nucleated they lost an important fraction of the monomer by diffusion to the existing particles, which grew further. This resulted in broad particle size distributions. The use of a thermal oil-soluble initiator (AIBN) did not improve droplet nucleation, likely due to both its slow decomposition rate and the low efficiency of the radicals produced in pairs within the droplets. Nucleation of a larger fraction of incoming droplets was possible by using initiator feeding rates during the semicontinuous process. On the other hand, the use of a small seed reduced the broadness of the PSD by lowering the size of the larger polymer particles.

In semicontinuous polymerization using neat monomer addition, the goal was to achieve efficient droplet nucleation of the miniemulsion used as initial charge (applying the concepts discussed for batch miniemulsion polymerization) and then avoiding particle coagulation and secondary nucleations. Coagulation was not observed in this work. Secondary nucleation could be minimized by using both a low concentration of emulsifier during semicontinuous operation and an initiator system (TBHP/AsAc) yielding hydrophobic radicals.

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References and Notes

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