

Agitation Effects in the Semicontinuous Emulsion Polymerization of Styrene and Butyl Acrylate

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ABSTRACT: The effect of agitation on the semicontinuous emulsion copolymerization of styrene and butyl acrylate was investigated. Both neat monomer addition and preemulsified feed were used. Experiments with and without a chain-transfer agent were carried out. For neat monomer addition, a mild degree of agitation ($\geq 0.1 \text{ kW/m}^3$) was required to avoid monomer mass-transfer limitations, but even a moderate degree of agitation (0.3 kW/m^3) was not enough to overcome the CTA mass-transfer limitations. Agitation was much less critical when preemulsified feeds were used. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 841–851, 2001

Key words: agitation; emulsion polymerization; mass transfer; styrene; butyl acrylate

INTRODUCTION

Emulsion polymerization in stirred tank reactors depends on agitation in several ways¹: It determines the emulsification of the monomers and affects the transport of the reactants to the polymerization loci (polymer particles). Agitation also affects the mixing time, which is critical to distribute homogeneously the entering flow streams in the reactor. Because polymerization is highly exothermic, an efficient agitation is required to ensure a uniform temperature throughout the reactor and to maximize the heat-removal rate. Agitation can also have a deleterious effect as it can promote coagulation.^{2,3}

Most of the works reported in the literature on the effect of agitation on emulsion polymerization

focused on batch reactors.^{4–9} Shunmukham et al.⁴ studied the effect of agitation on the emulsion polymerization of styrene and concluded that increasing the stirrer speed increased inhibition, decreased the polymerization rate, and lowered the average molecular weight of the polymer formed. Schoot et al.⁹ explained these results by the presence of oxygen traces in the nitrogen atmosphere under which the reaction was carried out. Oxygen may cause an induction period or may act as a terminator of the growing chain. For vinylidene chloride, Evans et al.⁵ observed different effects of the agitation for the three stages in which emulsion polymerization can be divided. During the nucleation, the rate of polymerization decreased with increasing stirring speed; during Interval II, the rate of polymerization increased with increasing stirring speed and Interval III was independent of stirring speed. According to Evans et al.,⁵ an increasing agitation rate during nucleation produced a better emulsification of the monomers, causing an augmentation of the interfacial area of the monomer droplets and thus increasing the amount of emulsifier adsorbed onto

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the monomer droplets. Therefore, less emulsifier was available for the stabilization of the new polymer particles. During Interval II, the emulsifier is desorbed from monomer droplets because of the increasing area of the growing particles. Therefore, monomer droplets coalesced, rendering monomer diffusion slower due to a reduction of the monomer droplets–aqueous-phase interfacial area. An increasing agitation degree improved droplet dispersion and thus led to an increase in the polymerization rate. In Interval III, all the monomer is in the polymer particles and diffusion is not affected by agitation.

Omi et al.⁶ observed that emulsion polymerization of styrene was not affected by stirring, as long as the emulsification conditions were the same. Nomura et al.⁷ found that emulsion polymerization is greatly influenced by impurities contained in the nitrogen atmosphere in contact with the emulsion. They found that in the presence of an imperfectly purified nitrogen atmosphere the polymerization rate decreased with agitation due to the absorption of oxygen traces. Under a pure nitrogen atmosphere, there was an optimum degree of agitation where emulsion polymerization was not affected by agitation. At low emulsifier concentrations near the critical micelle concentration, an increase in agitation caused a reduction of the effective emulsifier for the formation of micelles. At higher emulsifier concentrations, if agitation speed was higher than the above-mentioned level, the number of particles decreased by coagulation and thus the polymerization rate decreased. However, at lower speeds of stirring, the polymerization rate was controlled by the monomer transport rate from the monomer droplets to the aqueous phase. Bataille et al.⁸ studied the effect of agitation on the emulsion polymerization of vinyl acetate. These authors found that at low agitation rates there was phase separation and the maximum conversion was low because polymerization was controlled by the monomer diffusion rate. At higher agitation rates, no effect of the agitation on the polymerization rate was observed.

Despite the industrial importance of the semi-continuous process, only scarce studies on the effect of agitation on the semi-continuous process have been described. Thus, Donescu et al.¹⁰ reported that, in semi-continuous polymerization, an increasing agitation rate led to an increase of both the induction period and the final conversion.

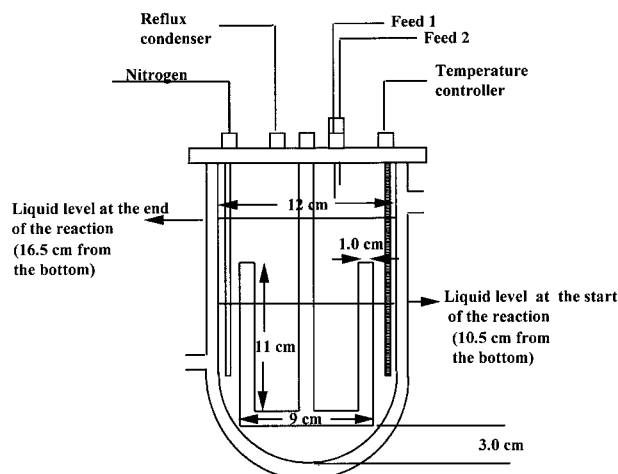


Figure 1 Reactor.

In this article, the effect of the agitation on monomer conversion, number of polymer particles, and molecular weight distribution (MWD) in the semi-continuous emulsion polymerization of styrene and butyl acrylate was studied. Both neat monomer feed and preemulsified feed were used. Experiments with and without a chain-transfer agent (CTA) were carried out.

EXPERIMENTAL

Technical-grade monomers, styrene (S) and butyl acrylate (BuA), sodium lauryl sulfate (SLS, 90%, Merck, Darmstadt, Germany), potassium persulfate ($K_2S_2O_8$, 99%, Fluka, Buchs, Switzerland), sodium bicarbonate ($NaHCO_3$, 99.5%, Panreac, Barcelona, Spain), and dodecyl mercaptan ($C_{12}H_{25}S$, 98%, Aldrich, St. Louis, MO) were used as received. Deionized water (DI) was used throughout the work.

Polymerizations were carried out in a 2-L glass reactor fitted with a reflux condenser, stainless-steel anchor stirrer, sampling device, nitrogen inlet, and two feed inlet tubes. Dimensions of the reactor and the agitator are shown in Figure 1.

Table I presents the recipe used in the semi-continuous emulsion polymerizations carried out using a neat monomer addition and no CTA. Table II presents the recipes used in the runs carried out using preemulsified feed and no CTA. Table III shows the formulation used in the runs carried out using the neat monomer addition and a CTA, and Table IV, that of the runs using preemulsified feed and a CTA.

Table I Recipe Used in Polymerizations Carried Out Using Neat Monomer Addition and No CTA

	Initial Charge (g)	Stream 1 (g)	Stream 2 (g)
S	—	—	329.7
BA	—	—	270.3
SLS	9.0	3.0	—
KPS	1.0	—	—
NaHCO ₃	1.0	—	—
DI water	1050.0	150.0	—
Flow rate		0.85 g/min	3.33 g/min
Run	Agitation Rate (rpm)		
A1	70		
A2	100		
A3	150		
A4	220		

Polymerizations were carried out at 70°C using an initial charge made of the initiator, buffer, and a fraction of the emulsifier and water. When feeding neat monomers, the feed was divided into two streams: The first was a solution of the emulsifier, and the second, a mixture of S and BuA (S/BuA = 60/40 in a mol basis) and a CTA (in those polymerizations using a CTA). The monomer and aqueous feeds were adjusted to complete the addition in 3 h. Subsequently, the polymerization was continued in the batch for 1 h. When feeding a preemulsion, an aqueous emulsion of S, BuA, a CTA (if any), and the emulsifier was formed using a turbine at 300 rpm. All polymerizations were

carried out under a nitrogen atmosphere (purity 99.99).

Samples were withdrawn from the reactor at appropriate intervals and polymerization was short-stopped with hydroquinone. The conversion was determined gravimetrically. The particle size of the latex was measured by dynamic light scattering (Coulter N4 Plus from Coulter Corp., Fullerton, CA). At the end of the process, a sample was withdrawn to determine the particle-size distribution by a Disc Centrifuge Photosedimentation (BI-DCP from Brookhaven Instruments Corp., Holtsville, NY). The MWD was measured by size exclusion chromatography (SEC) using a

Table II Recipe Used in Polymerizations Carried Out Using Preemulsified Feeds and No CTA

	Initial Charge (g)	Stream (g)
S	—	329.7
BA	—	270.3
SLS	9.0	3.0
K ₂ S ₂ O ₈	1.0	—
NaHCO ₃	1.0	—
DI water	1050.0	150.0
Flow rate		4.18 g/min
Run	Agitation Rate (rpm)	
B2	100	
B3	150	

Table III Recipe Used in the Polymerizations Carried Out Using Neat Monomer Addition and CTA

	Initial Charge (g)	Stream 1 (g)	Stream 2 (g)
S	—	—	329.7
BA	—	—	270.3
Dodecyl mercaptane	—	—	2.0
SLS	9.0	3.0	—
K ₂ S ₂ O ₈	1.0	—	—
NaHCO ₃	1.0	—	—
DDI water	1050.0	150.0	—
Flow rate		0.85 g/min	3.34 g/min
Run	Agitation Rate (rpm)		
C1	70		
C2	100		
C3	150		
C4	220		

Waters 410 apparatus (Milford, MA), equipped with two detectors: a refractometer and a viscometer (Viscotek, Model 250) and three columns in series (10^2 , 10^4 , and 10^6 Å).

RESULTS AND DISCUSSION

Neat Monomer Addition and No CTA

Figure 2 presents the effect of the agitation rate on the instantaneous conversion for the reactions carried out using neat monomer addition and no

CTA. Instantaneous conversion was defined as the ratio between the polymer in the reactor and the monomer fed until the sampling time. The agitation rates used were 70, 100, 150, and 220 rpm. These agitations rates corresponded to Reynolds numbers of 9450, 13,500, 20,250, and 29,700, respectively, at the beginning of the reaction. At the end of the process, due to the increasing viscosity, the Reynolds numbers were 380, 540, 810, and 1190, respectively.

An agitation rate of 70 rpm led to a power per volume unit of 0.005 kW/m^3 at the beginning of

Table IV Recipe Used in the Polymerizations Carried Out Using Preemulsified Monomers and CTA

	Initial Charge (g)	Stream (g)
S	—	329.7
BA	—	270.3
Dodecyl mercaptane	—	2.0
SLS	9.0	3.0
K ₂ S ₂ O ₈	1.0	—
NaHCO ₃	1.0	—
DDI water	1050.0	150.0
Flow rate		4.19 g/min
Run	Agitation Rate (rpm)	
D2	100	
D3	150	

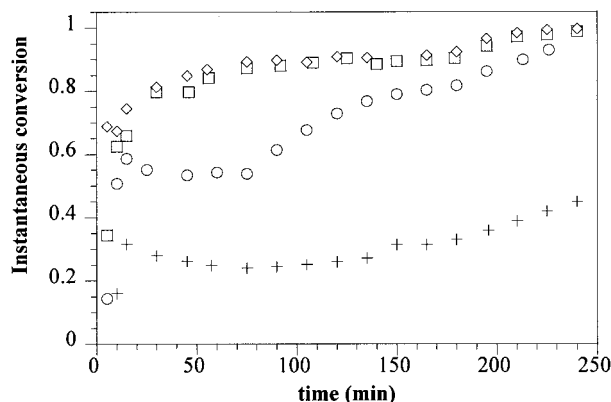


Figure 2 Time evolution of the instantaneous conversion for the reactions carried out using neat monomer addition and no CTA: (+) N equals; 70 rpm (A1); (O) N equals; 100 rpm (A2); (□) N equals; 150 rpm (A3); (◇) N equals; 220 rpm (A4).

the reaction. According to Rose,¹¹ this power value corresponded to a very gentle degree of agitation. An agitation speed of 100 rpm (0.01 kW/m³) corresponded to a gentle degree of agitation. Finally, 150 and 220 rpm corresponded to mild and moderate degrees of agitation (0.1 and 0.3 kW/m³, respectively). Agitator power was measured with a torque table.^{12,13} More intense degrees of agitation were not used because splashing, which led to the formation of a polymer film on the reactor wall, was observed.

Figure 2 shows that conversions of reactions A3 and A4 (carried out at agitation speeds of 150 and 220 rpm, respectively) had practically equal conversion evolutions. However, decreasing the agitator speed to 100 rpm (A2) and 70 rpm (A1) yielded much lower conversions.

The results presented in Figure 2 can be caused by the effect of the agitation rate on the mass transfer (reduction of monomer concentration on polymer particles) and/or on the nucleation (affecting the number of particles). Figure 3 shows that the particle number was independent of agitation speed; therefore, the differences in conversion observed in Figure 2 were not due to a change in the particle number. Consequently, it can be concluded that the increase in the polymerization rate as agitation increased was a consequence of a higher mass-transfer rate.

These results seem to be in conflict with previously reported results. Thus, Flory,¹⁴ Brooks,¹⁵ and Gilbert¹⁶ used characteristic time arguments to show that monomer replenishment from the aqueous phase is extremely rapid, more than

enough to maintain the equilibrium value of the monomer concentration in the particles. However, these authors considered only the monomer diffusion from the aqueous phase to the polymer particles, and Nomura et al.⁷ reported that the monomer diffusion from droplets to the aqueous phase represents the main resistance to monomer transport. Monomer diffusion from droplets to the aqueous phase depends on both the mass-transfer coefficient and the total area of the monomer droplets. When agitation is low, the monomer droplets coalesce and the interfacial area is small, leading to a slow monomer diffusion from droplets to the aqueous phase.

Figure 2 shows that at 70 and 100 rpm the kinetics of the process was controlled by the monomer mass-transfer rate from droplets to particles. Actually, at 70 rpm (A1) and in a lesser extent at 100 rpm (A2), it was observed that the monomer accumulated around the agitator shaft. Increasing the agitator speed improved the mass-transfer rate and conversion increased. Above a certain agitation rate (150 rpm), conversion was not affected by agitation, namely, the kinetics of the process was controlled by the chemical reaction.

Figure 4 presents the velocity pattern in the reactor calculated by means of computational fluids dynamics using a commercially available code (CFX 4.1c) for the middle [Fig. 4(a)] and last stages [Fig. 4(b)] of run A1 (70 rpm). It can be seen that, at intermediate times, the liquid close to the shaft was rather stagnant. Therefore, the

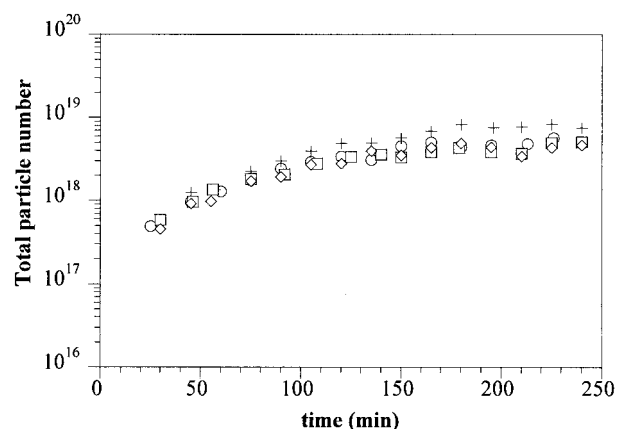
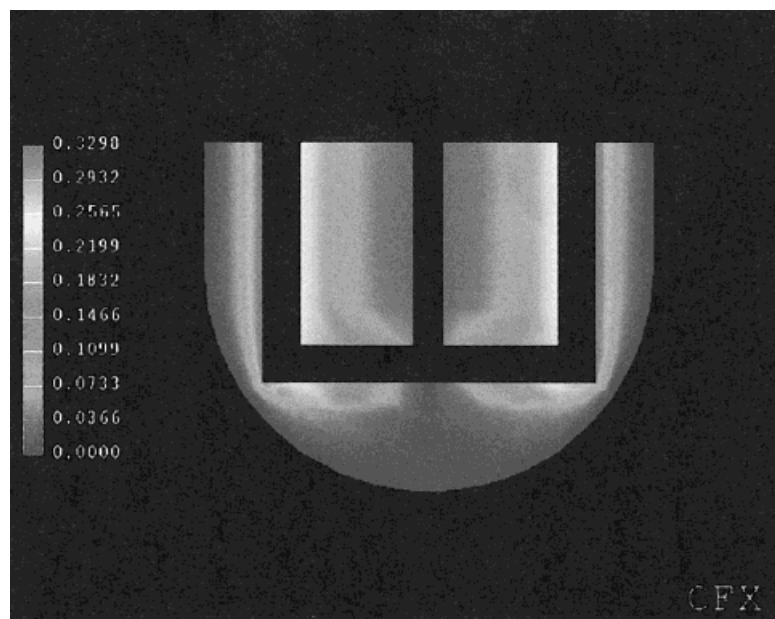
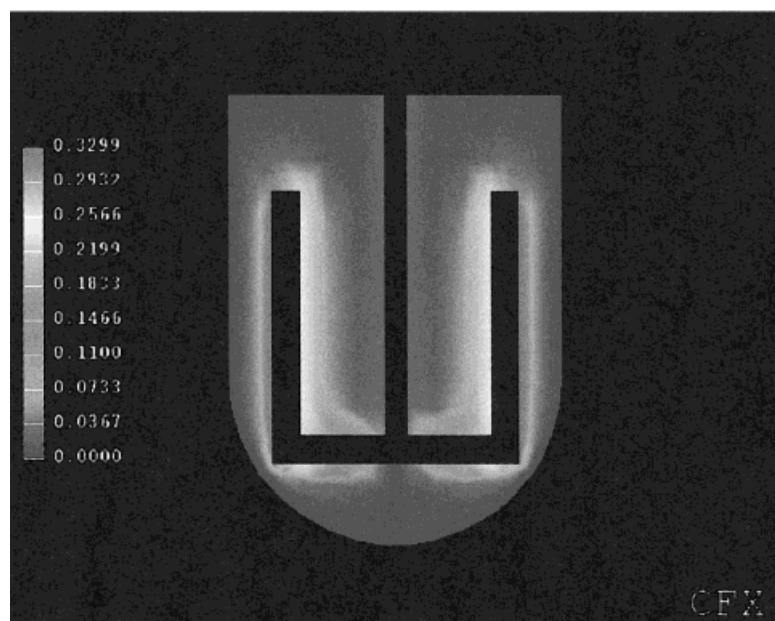


Figure 3 Time evolution of the particle number for the reactions carried out using neat monomer addition and no CTA: (+) N equals; 70 rpm (A1); (O) N equals; 100 rpm (A2); (□) N equals; 150 rpm (A3); (◇) N equals; 220 rpm (A4).



a)



b)

Figure 4 Velocity pattern in the reactor calculated by means of computational fluid dynamics using a commercially available code (CFX 4.1c) for the (a) middle and (b) last stages of runs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

monomer, which was fed as large droplets, was not well dispersed and, due to its lower density, remained at the liquid surface, forming monomer pooling. The situation was even worse once the

liquid level was above the agitator paddles [Fig. 4(b)]. The stagnation caused the monomer/aqueous-phase surface area to be rather low, leading to a low mass-transfer rate.

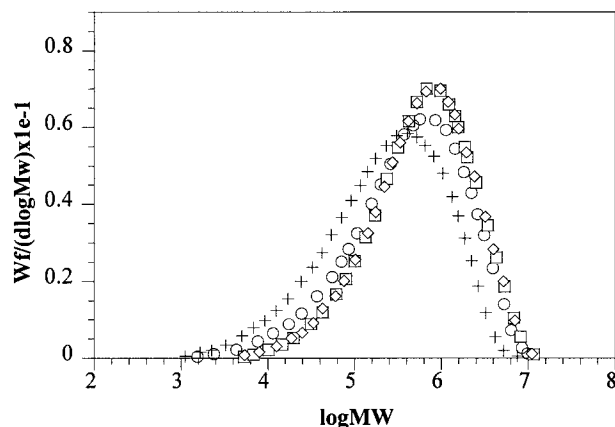


Figure 5 MWD of the final latexes for the reactions carried out using neat monomer addition and no CTA: (+) *N* equals; 70 rpm (A1); (O) *N* equals; 100 rpm (A2); (□) *N* equals; 150 rpm (A3); (◇) *N* equals; 220 rpm (A4).

Figure 5 shows the MWDs of the final latexes from reactions A1, A2, A3, and A4 as measured by SEC. It can be seen that up to 150 rpm an increasing agitation speed increased the molecular weight. This increase of molecular weight was due to a higher monomer concentration in latex particles at high agitation speeds. The results in Figure 2 suggest that, over 150 rpm, the agitation rate was enough to ensure that the monomer concentration in the polymer particles was at the thermodynamic equilibrium values. Therefore, additional increasing of the agitation had no effect on the monomer concentration in the polymer particles and, consequently, on the molecular weights.

Agitation may also affect the particle-size distribution because it can promote coagulation.^{2,3} Figure 6 shows the particle-size distributions of the final latexes of reactions A2, A3, and A4. The particle diameter of the latex obtained in reaction A1 was too small and it could not be measured by DCP. It can be observed that there was no effect of agitation on the final particle-size distributions.

Figure 7 presents the effect of the agitation rate on the copolymer composition. At 220 rpm, the cumulative copolymer composition was initially rich in S but it approached the feed composition when the starved conditions were reached. At 70 rpm, the cumulative copolymer composition is poorer in S than in the feed, because S was more affected by the diffusional limitations than was BuA (S is more water-insoluble than is BuA).

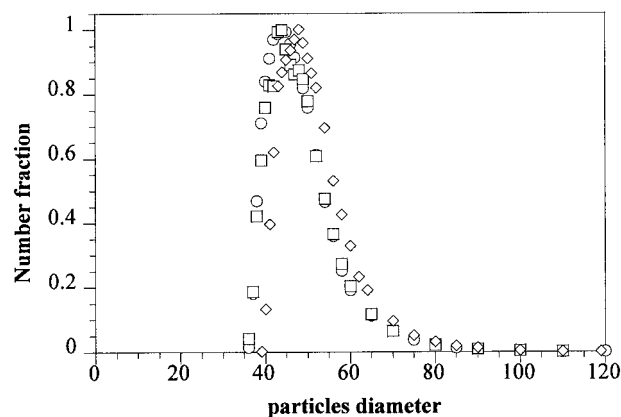


Figure 6 Particle-size distribution for the reactions carried out using neat monomer addition and no CTA: (O) *N* equals; 100 rpm (A2); (□) *N* equals; 150 rpm (A3); (◇) *N* equals; 220 rpm (A4).

Preemulsified Feed and No CTA

Figure 8 compares the conversion evolution for reactions A2 and A3 (carried out at 100 and 150 rpm, respectively, feeding neat monomers) with that of reactions B2 and B3 (100 and 150 rpm, respectively, and feeding preemulsified monomers). It can be observed that, when preemulsified feed was used, high monomer conversion was achieved even at relatively low agitation rates (100 rpm). This effect was not due to a change in the number of polymer particles (Fig. 9) but to an improved mass-transfer rate. When preemulsified monomers were fed, the stirrer was required to blend the entering preemulsion with the reac-

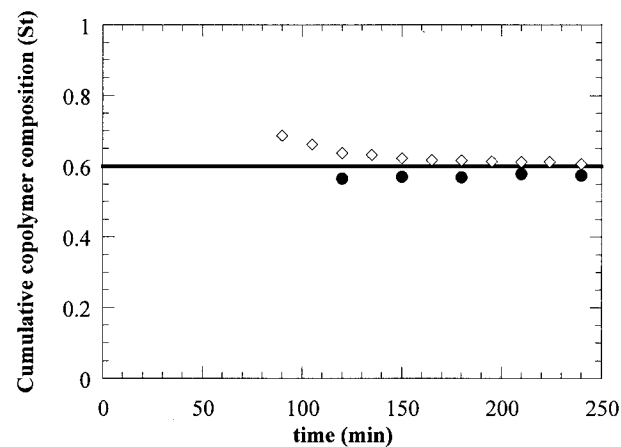


Figure 7 Cumulative copolymer composition for the reactions carried out using neat monomer addition and no CTA: (●) *N* equals; 70 rpm (A1); (◇) *N* equals; 220 rpm (A4); (—) desired composition.

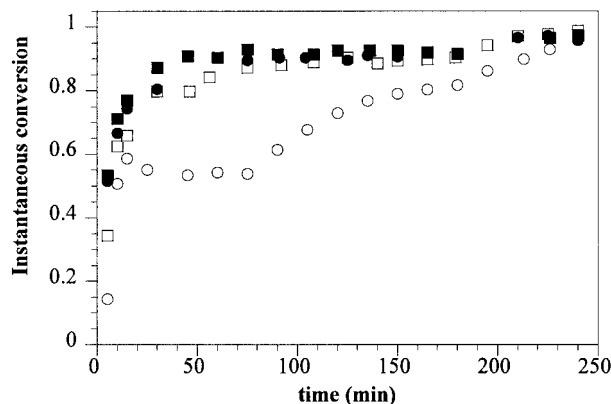


Figure 8 Effect of using preemulsified feed and no CTA on the evolution of the instantaneous conversion:

Reaction	Agitation Rate (rpm)	Feed	Symbol
A2	100	Neat	○
A3	150	Neat	□
B2	100	Preemulsified	●
B3	150	Preemulsified	■

tion mixture, but no emulsification was needed. The results in Figure 8 show that the anchor provided a high enough circulation flow (which gave short blending times) but rather poor turbu-

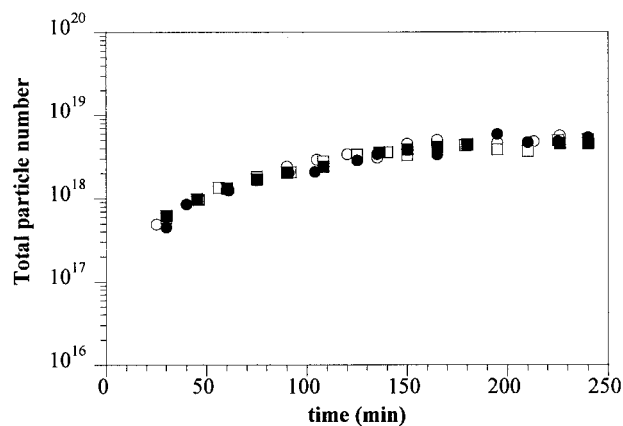


Figure 9 Effect of using preemulsified feed and no CTA on the evolution of the particle number:

Reaction	Agitation Rate (rpm)	Feed	Symbol
A2	100	Neat	○
A3	150	Neat	□
B2	100	Preemulsified	●
B3	150	Preemulsified	■

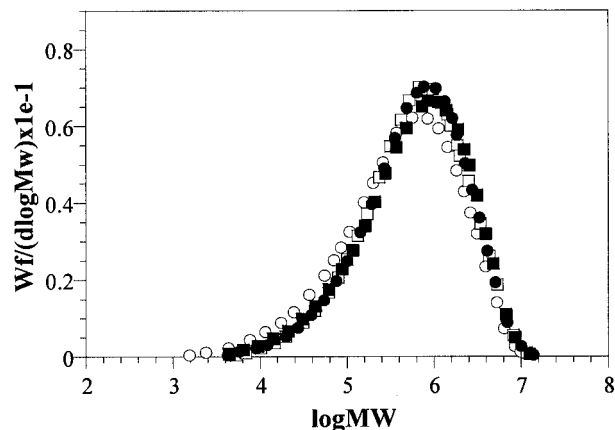


Figure 10 Effect of using preemulsified feed and no CTA on the molecular weight distribution of the final latexes:

Reaction	Agitation Rate (rpm)	Feed	Symbol
A2	100	Neat	○
A3	150	Neat	□
B2	100	Preemulsified	●
B3	150	Preemulsified	■

lence (which is needed for emulsification). Figure 10 presents the MWDs of the final latexes from reactions A2, A3, B2, and B3 and further supports the idea that when preemulsified feed was used the monomer concentrations were at the thermodynamic equilibrium values.

Neat Monomer Addition and CTA

Mercaptans are common CTAs used to control the molecular weights in emulsion polymerization. Mercaptans are efficient CTAs, but they have an unpleasant odor. Therefore, long-chain mercaptans which have low vapor pressure are commonly used. Long-chain mercaptans are highly water-insoluble, and, hence, it is expected that they are affected by diffusional limitations. The presence of a highly water-insoluble compound in the monomer droplets may also cause a slower diffusion of the monomer from the droplets to the aqueous phase, in a way similar to miniemulsion polymerization.^{17,18}

Figure 11 shows the monomer conversions for reactions C1, C2, C3, and C4 carried out feeding neat monomers at agitation speeds of 70, 100, 150, and 220 rpm, respectively. These results are similar to those obtained in reactions carried out without a CTA (Fig. 2): At 70 and 100 rpm, the

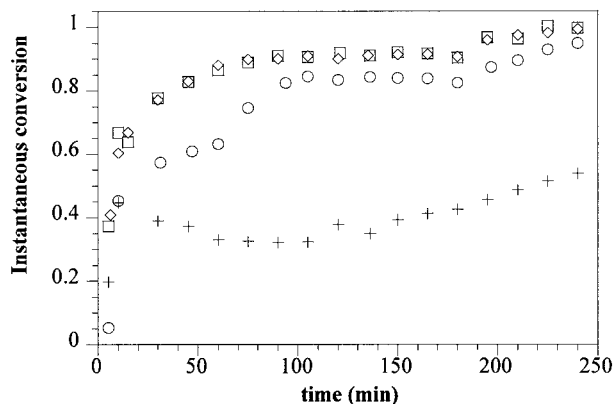


Figure 11 Time evolution of the instantaneous conversion in the reactions carried out with CTA and feeding neat monomers: (+) N equals; 70 rpm (C1); (O) N equals; 100 rpm (C2); (□) N equals; 150 rpm (C3); (◇) N equals; 220 rpm (C4).

kinetics of the process was controlled by the monomer mass transfer, whereas above 150 rpm the chemical reaction was the rate-determining step. Comparison between Figures 2 and 11 and Figures 3 and 12 shows that the presence of dodecyl mercaptan did not affect the polymerization rate and number of particles. This means that monomer diffusion is not retarded by the presence of a highly water-insoluble CTA. On the other hand, these results indicate that the radicals formed by chain transfer to a CTA are not significantly less active than are the monomer radicals and that they do not desorb from the polymer particles.

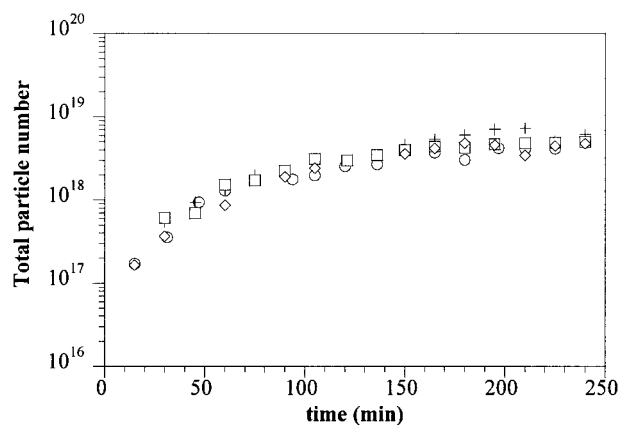


Figure 12 Time evolution of the particle number for the reactions carried out with CTA and feeding neat monomers: (+) N equals; 70 rpm (C1); (O) N equals; 100 rpm (C2); (□) N equals; 150 rpm (C3); (◇) N equals; 220 rpm (C4).

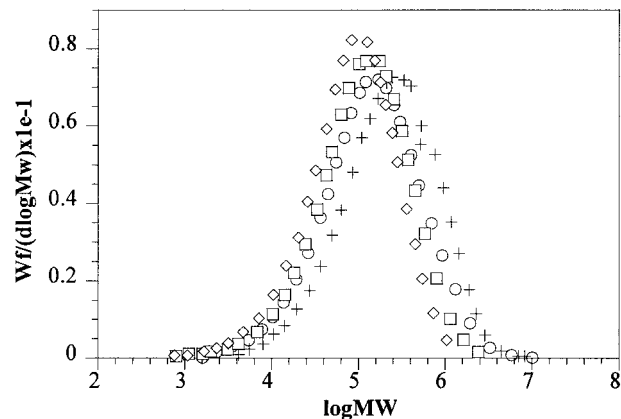


Figure 13 MWD of the final latex for the reactions carried out with CTA and feeding neat monomers: (+) N equals; 70 rpm (C1); (O) N equals; 100 rpm (C2); (□) N equals; 150 rpm (C3); (◇) N equals; 220 rpm (C4).

Figure 13 presents the MWDs of the final latexes obtained in reactions C1, C2, C3, and C4. It can be observed that the molecular weights were lower than in the polymerizations carried out without a CTA (Fig. 5) and that compared with those reactions the order of molecular weights decreased with the agitation speed. Increasing agitation yielded a better monomer emulsification that promoted mass transfer because both the interfacial area and the mass-transfer coefficient increased. Figure 13 shows that the molecular weights decreased with agitation for the whole range of agitation rates. This result contrasts with that found for the monomer conversion (Figs. 2 and 11) where the chemical reaction became the rate-determining step over 150 rpm. This result is likely due to the low water solubility of dodecyl mercaptan. This suggests that the polymerization of water-insoluble monomers like 2-ethylhexyl acrylate, Veova10, *p*-methylstyrene, vinyl hexanoate, vinyl *n*-decanoate, and vinyl estearate can be very sensitive to agitation.

Preemulsified Feed and CTA

Figure 14 presents the time evolution of conversion in reactions C2 and C3 (carried out feeding neat monomers and using 100 and 150 rpm, respectively) and reactions D2 and D3 (carried out feeding a preemulsion and using 100 and 150 rpm, respectively). It can be observed that preemulsification minimized the mass-transfer resistances and the chemical reaction became the rate-determining step.

Figure 15 shows the MWDs of the final latexes obtained in reactions C2, C3, D2, and D3. The highest molecular weight corresponded to latex C2 because, although the monomer concentration in the particles was low in this reaction, dodecyl mercaptan diffusion was very slow, and, hence, the chain-transfer rate was limited. When feeding a preemulsion, the surface area of the droplets increased, and the resistance to CTA mass transfer decreased, leading to the decrease of molecular weight in reactions D2 and D3. Comparison of the molecular weight in reaction D2 with those in reactions C2 and C3 shows that the reduction of molecular weight obtained feeding a preemulsion was more acute than that obtained by increasing the agitation speed from 100 to 150 rpm. This effect is also observed comparing the molecular weight of reaction D2 (Fig. 15) with reaction C4 (Fig. 13).

CONCLUSIONS

In this work, the effect of the agitation speed and the type of monomer feed on the semicontinuous emulsion copolymerization of S and BuA, with and without a CTA (dodecyl mercaptan), was investigated. It was found that when neat monomer

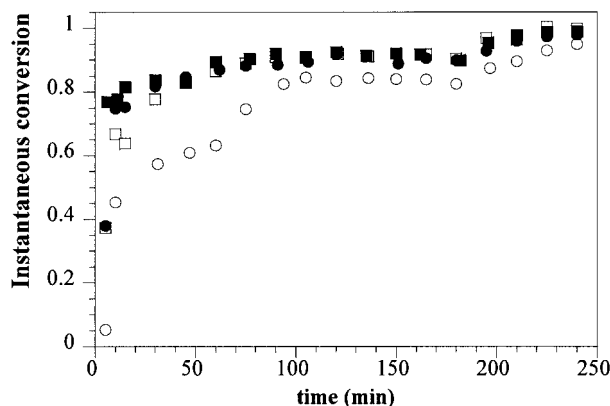


Figure 14 Effect of using preemulsified feed on the evolution of the instantaneous conversion of the reactions carried out with a CTA:

Reaction	Agitation Rate (rpm)	Feed	Symbol
C2	100	Neat	○
C3	150	Neat	□
D2	100	Preemulsified	●
D3	150	Preemulsified	■

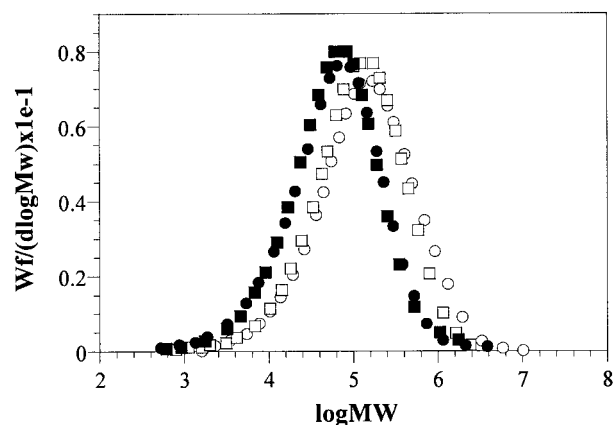


Figure 15 Effect of using preemulsified feed on the MWD of the final latexes of the reactions carried out with a CTA:

Reaction	Agitation Rate (rpm)	Feed	Symbol
C2	100	Neat	○
C3	150	Neat	□
D2	100	Preemulsified	●
D3	150	Preemulsified	■

addition was used, a mild degree of agitation (0.1 kW/m^3) was needed to overcome monomer mass-transfer limitations. However, a moderate degree of agitation (0.3 kW/m^3) was not enough to avoid mass-transfer limitations for dodecyl mercaptan. Preemulsification of the feed was allowed to minimize mass-transfer limitations of both the monomer and the CTA, even at gentle degrees of agitation (0.01 kW/m^3). It was also observed that the effect of the diffusional limitations on the molecular weights depends on the presence of a CTA. In the presence of a CTA, the molecular weights decreased with the agitation rate, whereas they increased in the absence of a CTA. No effect of the agitation rate on the particle-size distribution was observed.

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