

Molecular Weight Development in Emulsion Copolymerization of *n*-Butyl Acrylate and Styrene

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ABSTRACT: The seeded emulsion copolymerization of *n*-butyl acrylate and styrene in a weight ratio of 50/50 was investigated. The effect of the type of process (batch vs. semicontinuous) and the amounts of initiator and emulsifier charged into the reactor on the time evolution of the fractional conversion, number of polymer particles, and weight-average molecular weight (M_w) was analyzed. It was found that the M_w depends to a slight extent on the type of process and the emulsifier concentration and to a larger extent on the initiator concentration. The molecular weight distributions (MWDs) and the gel content of the final latexes were also analyzed. In the absence of chain transfer agents (CTAs), the

fraction of gel was higher in the semicontinuous processes. It was also found that the gel content increased with increasing initiator concentration in the recipe. The addition of 1 wt % CTA avoided gel formation and led to an important reduction of the M_w . Nevertheless, the MWDs presented a shoulder or even a second peak at high molecular weights that was due to reactions of chain transfer to the polymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1918–1926, 2003

Key words: emulsion polymerization; styrene; butyl acrylate; kinetics; molecular weight distribution

INTRODUCTION

The properties of coatings based on acrylic resins are usually correlated with two variables, the molecular weight and the comonomer ratio. The mechanical properties resistance such as the toughness, abrasion resistance, or impact resistance of the final coatings improve with the increase of the molecular weight of polymers.¹ Nevertheless, the viscoelastic properties related to the mobility of chains such as tack² and wettability in adhesive applications require the presence of low polymer chains in the formulation. The incorporation of a comonomer^{1,3–6} commonly supposes the modification of the glass-transition temperature (T_g) of the formulation, and it can also modify the molecular weight⁷ and hence the mechanical properties of the final product. This is the case of *n*-butyl acrylate (*n*-BA), which is often copolymerized with styrene (St) in order to improve the hardness,¹ although this copolymerization decreases the flexibility of coatings and the tack in adhesive applications such as pressure sensitive adhesives (PSAs). Another factor

that has also been shown to influence the above-mentioned properties is the presence of crosslinked polymer chains, which in coatings leads to an increase in both the film hardness and its chemical resistance. Also, for PSA applications, gel fractions up to 30% significantly increases the shear resistance.² Polyacrylates for coatings and adhesives are mainly synthesized by emulsion polymerization,^{8,9} because the latex obtained through this technique can be directly applied.

Despite the industrial importance of *n*-BA/St copolymers, the literature about the relationship between polymerization conditions and molecular weights is scant.^{5,7,10–12} Most studies on *n*-BA/St copolymers deal with the kinetic aspects.^{13–21} Yang and Yang¹⁰ studied the influence of the comonomer ratio, initiator, emulsifier, and temperature on the polymerization rate and molecular weight under batch conditions. They found (in line with other authors^{5,11}) that an increase of *n*-BA content in the formulation led to an increase in both the polymerization rate and the molecular weights; the increase of temperature and initiator led to an increase of the polymerization rate and a decrease of the molecular weight. Cruz-Rivera et al.¹¹ obtained higher molecular weights in batch emulsion polymerization than in semicontinuous polymerization. Chrástova et al.¹² observed that polymerization using a water insoluble initiator produced much higher molecular weights than using a water soluble

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one. This fact was due to the low effective initiation rate in the case of the insoluble initiator, which caused a decrease of the termination rate.

Some authors reported insoluble polymer fractions (gel) being formed in the homopolymerization of *n*-BA^{5,22–25} and in some *n*-BA copolymerizations^{7,26,27} when formulations were rich in *n*-BA. The characterization of the molecular weight distribution (MWD) in gel forming systems requires the quantification of both the amount of gel polymer and the MWD of the soluble part (usually by size exclusion chromatography, SEC). However, only a limited number of studies^{7,24,25} have reported data on gel fractions for these polymerization systems in the open literature. The amount of gel formed in semicontinuous conditions could be significant because the reactions of chain transfer to the polymer are favored.²⁸ Recently, Plessis et al.⁷ quantified gel fractions in the seeded semicontinuous copolymerization of *n*-BA and St (<10 wt % St) that was carried out at 75°C. They found that the incorporation of St on *n*-BA formed during polymerization had profound implications on both the kinetics and microstructure of the formed copolymer (the higher the amount of St, the lower the gel fraction and the branching level and the higher the weight-average molecular weight of the sol polymer), and thus on the adhesive properties of the latex.

In this study, and in line with the studies of Plessis et al.,⁷ the effect of operational variables on the kinetics and microstructural properties (MWD and gel content) of the emulsion polymerization of *n*-BA and St for a typical coating and paint formulation (50/50 wt %) is investigated.

EXPERIMENTAL

The St (Aldrich) and *n*-BA (Aldrich) were purified by washing several times with a 10 wt % aqueous sodium hydroxide solution to eliminate inhibitors. The initiator (potassium persulfate, Merck), buffer, (sodium bicarbonate, Merck), emulsifier (sodium dodecyl sulfate, Sigma) and the chain transfer agent (CTA, *n*-dodecyl mercaptan, Merck) were used as supplied.

All polymerizations were seeded to improve run to run reproducibility by avoiding the nucleation stage and in order to control the particle number.²⁹ The seed latex was prepared in a semicontinuous operation at

TABLE I
Recipe for Seed Preparation

K ₂ S ₂ O ₈ (g)	6.4
NaHCO ₃ (g)	6.4
SDS (g)	54.1
<i>n</i> -BA (g)	133.7
S (g)	1202
H ₂ O (g)	2272

TABLE II
Recipe for Seeded Emulsion Polymerizations

Seed (polymer) (g)	70 (25)
K ₂ S ₂ O ₈ (wt %) ^a	0.09–0.9
NaHCO ₃ (wt %) ^{a,b}	0.09–0.9
SDS (wt %) ^a	1.3–6.7
<i>n</i> -BA (g)	121
S (g)	121
<i>n</i> -Dodecyl mercaptan (wt %) ^a	0–1
H ₂ O (g)	365

^a Based on the monomer.

^b The ratio of initiator/buffer = 1.

70°C under starved conditions using the recipe given in Table I. The seed was rich in St to minimize the formation of nonlinear polymer by reactions of chain transfer to the polymer.⁹ Monomers were fed at a constant flow rate for 4 h. After that, the reactor was kept at 90°C for 12 h to decompose the remaining initiator. The seed latex that was characterized, as explained below, had an average particle diameter of 51 nm and a weight-average molecular weight (M_w) of 446,000 g/mol. An insoluble polymer fraction (gel) was not found.

Seeded polymerizations with a 50/50 *n*-BA/St weight ratio were carried out in a 1-L glass reactor at 60°C and a nitrogen atmosphere using the recipe given in Table II. Samples were withdrawn during the reaction and the polymerization was short-stopped with hydroquinone. Table III summarizes the four series of polymerizations that were conducted. In the first series, the influence of the monomer addition policy was studied. A batch and two semicontinuous reactions with different monomer feeding times were carried out (runs 1–3). The second series was conducted under semicontinuous conditions with a monomer feeding time of 4 h. In this series the amount of initiator in the recipe was varied (runs 3–5) and the buffer concentration was always kept at a 1/1 weight

TABLE III
Experimental Conditions of Seeded Emulsion Polymerizations

	Run	Feeding time (min)	Initiator (wt %) ^a	Emulsifier (wt %) ^a	CTA (wt %) ^a
Series 1 (FT)	1	0 (Batch)	0.45	1.3	0
	2	120	0.45	1.3	0
	3	240	0.45	1.3	0
Series 2 (I)	4	240	0.09	1.3	0
	3	240	0.45	1.3	0
	5	240	0.9	1.3	0
Series 3 (E)	3	240	0.45	1.3	0
	6	240	0.45	6.7	0
Series 4 (CTA)	7	240	0.09	1.3	1
	8	240	0.45	1.3	1
	9	240	0.9	1.3	1

^a Based on the monomer.

ratio with respect the initiator. In the third series the amount of emulsifier was varied while maintaining the rest of the parameters as in series 1 (runs 3 and 6).

Finally, the fourth series accounts for the effect of initiator when a CTA³⁰ (1 wt % *n*-dodecyl mercaptan) was included in the recipe. In order to avoid mass transfer limitations of the CTA, a preemulsion (monomers, CTA, emulsifier, and water) was fed in this last series.

Characterization of copolymer latexes

The conversion was calculated gravimetrically³¹ by drying a known sample from the latex under a vacuum at room temperature and after correction for the nonvolatile components. Two different conversions were considered with respect to the total amount of monomers in the formulation, hereafter called global conversion (X_g), and with respect to the amount of monomers that already had been fed into the reactor, hereafter called fractional conversion. The fractional conversion is directly related to the fraction of the polymer in the polymer particles.

The cumulative copolymer composition by weight was determined through the characterization of the unreacted monomers in the latex by gas chromatography.³¹

The particle size was determined by dynamic light scattering³² (Zetasizer 3000 HS). In order to measure the particle size, the samples were diluted in water leaving enough time to allow the monomer to diffuse out the polymer particles. Therefore, the measured particle size corresponds to that of the unswollen polymer particle. From this value and the value of the fractional conversion, the values of the average size of the swollen particles and the number of polymer particles can be calculated.

The MWD and M_w of the soluble fraction of polymer were determined by SEC^{31,33} at 40°C. A differential refractometer detector (Waters 410) was used. Three columns with pore sizes of 10², 10⁴, and 10⁶ Å (Waters HR2, HR4, and HR6) and tetrahydrofuran (THF) at a flow rate of 1 mL/min were used. Narrow polystyrene standards in the range of 4×10^2 to 10×10^6 were used for the calibration. No significant differences were obtained in referring the results to polystyrene or estimating the absolute molecular weight of the copolymer by means of using the Mark-Houwink parameters of the homopolymers and the molar composition of the copolymers. In the second case, the values of the Mark-Houwink parameters (K and α) used were 16.2×10^{-5} dL/g and 0.71 for St²⁰ and 7.4×10^{-5} dL/g and 0.75 for *n*-BA.³⁴

The amount of gel was quantified by means of an extraction process in THF under reflux conditions.³⁵

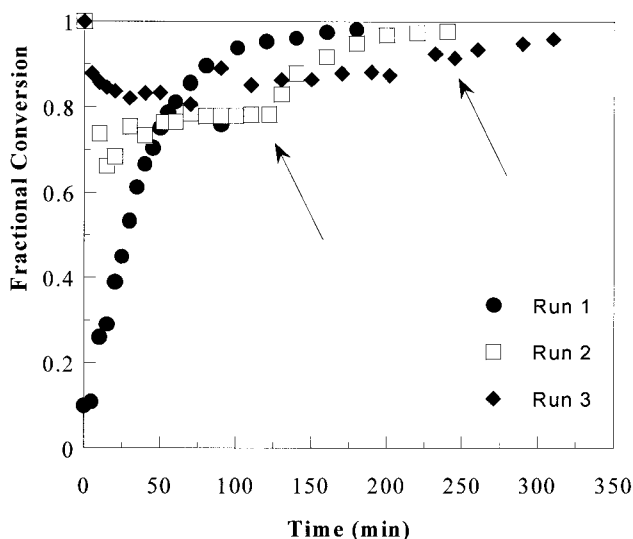


Figure 1 The effect of the monomer addition strategy on the fractional conversion for the seeded emulsion copolymerization of 50/50 *n*-BA/St at 60°C.

RESULTS AND DISCUSSION

Effect of monomer addition

Figure 1 shows the evolution of the fractional conversion (runs 1–3) for different strategies of monomer addition. Whereas in the batch process the totality of the monomer plus the seed was initially charged into the reactor, in the semicontinuous processes no monomer was initially charged. Because of the polymer contained in the seed the initial value of the fractional conversion was 0.1 for the batch reaction (run 1) and 1.0 for the semicontinuous reactions (runs 2 and 3). It can be seen that the batch reaction progresses with the lowest fractional conversion and consequently with the lowest polymer concentration. For the semicontinuous reactions the longer the feeding time the higher the fractional conversion and the lower the monomer concentration in the particles. This result, already described in the literature,^{36,37} had important consequences in the evolution of the molecular weight as will be explained later. The arrows in the figure indicate the end of the monomer addition period.

The time evolution of the cumulative copolymer composition for runs 1–3 is shown in Figure 2. It can be seen that *n*-BA content on the copolymer increased along the reaction. The line represents the copolymer composition calculated for the semicontinuous polymerization, assuming that the monomer fed reacted instantaneously. The composition of the copolymer deviated from this line, because St is more reactive than *n*-BA³⁸ ($r_{BA} = 0.2$, $r_{St} = 0.75$). The deviation was more acute in the batch process than in the semicontinuous processes because the ratio of *n*-BA/St in the latter case is controlled by the monomer feed rate.²⁹

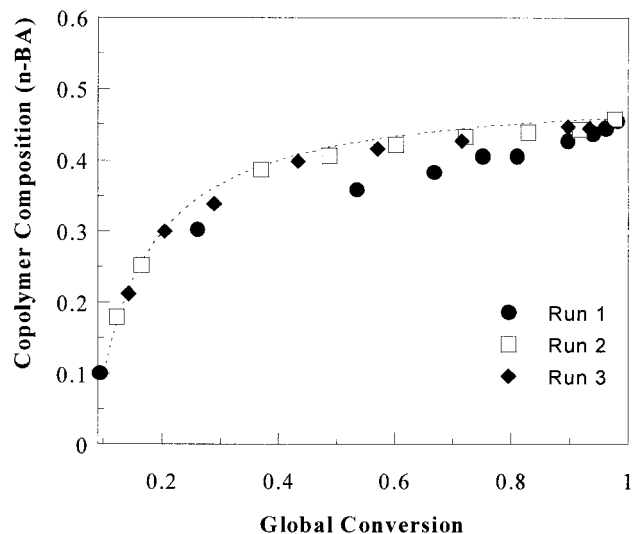


Figure 2 The effect of the monomer addition strategy on the cumulative copolymer composition (by weight).

Figure 3 shows the evolution of the number of polymer particles. The surfactant included in the initial charge is sufficient to maintain the colloidal stability of the seed particles as they grow through the polymerization.²⁹ Despite the use of a seed, new particles were formed during the process. The secondary nucleation was almost insensitive to the type of monomer addition.

The effect of the monomer addition strategy on the M_w of the sol fraction is shown in Figure 4. It can be observed that, in all the cases, the M_w increased along the process. Also, at intermediate conversions, $(M_w)_{batch} > (M_w)_{semicontinuous}$, although both processes led to a similar M_w value at the end of the process. In Figure 5 the sol MWD and the gel content of the final latexes

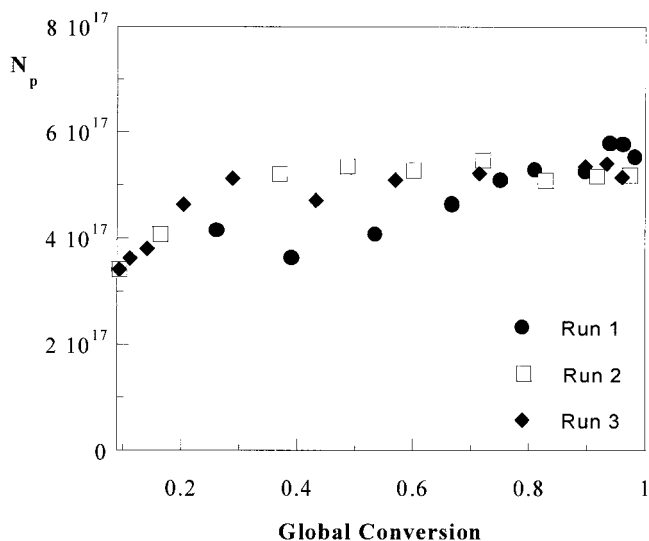


Figure 3 The effect of the monomer addition strategy on the number of polymer particles.

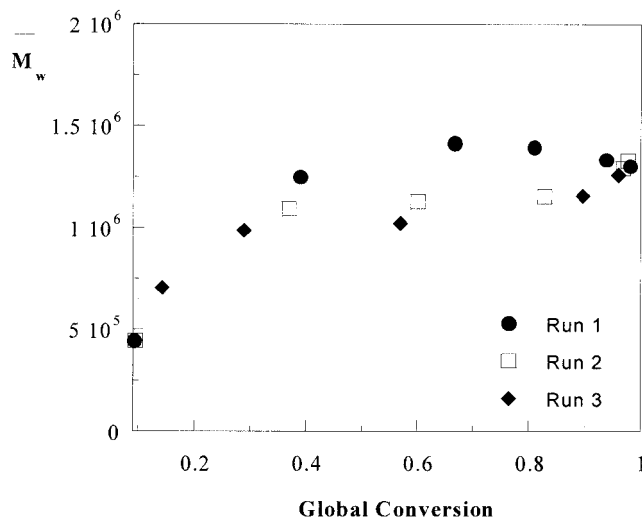


Figure 4 The effect of the monomer addition strategy on the evolution of the sol M_w .

are shown. It can be seen in Figure 5(a) that the MWDs were broad and the highest molecular weight did not exceed the value of 7 million. This agrees with the results reported by Plessis et al.^{7,24,25} This would sug-

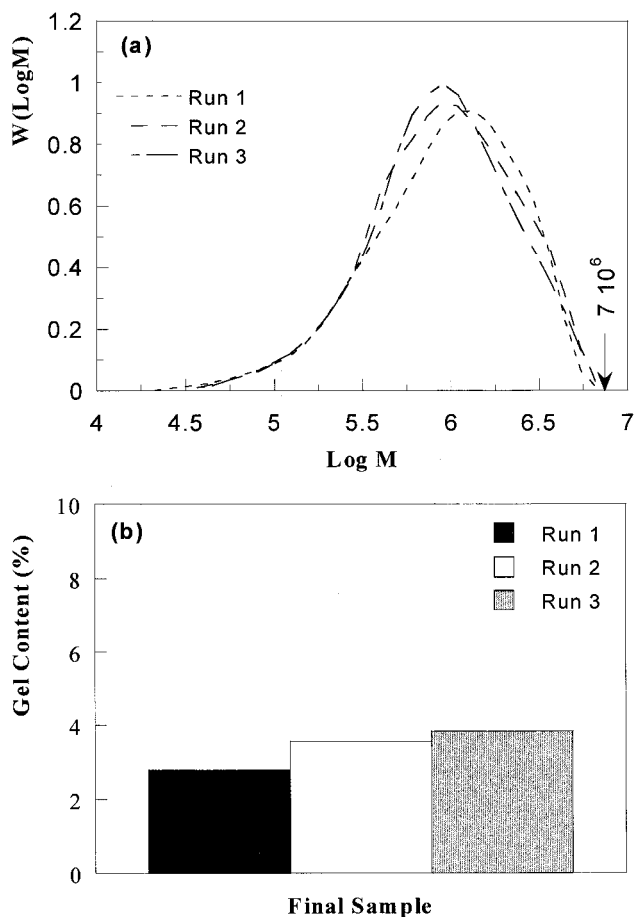


Figure 5 The effect of the monomer addition strategy on (a) the MWD and (b) the gel content of the final latex.

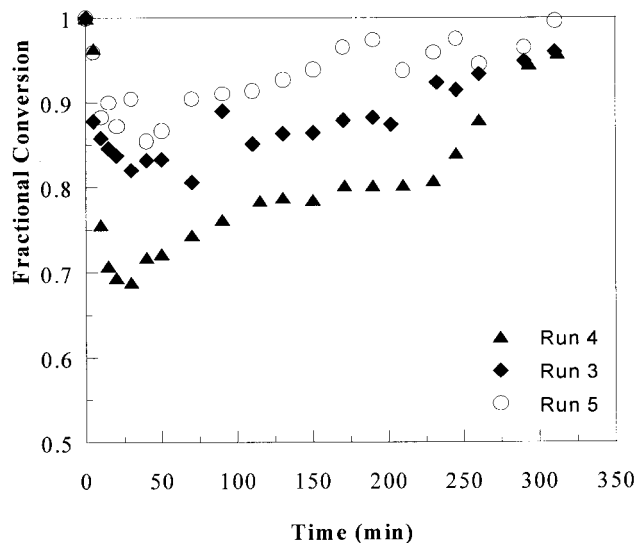


Figure 6 The effect of the concentration of the initiator on the fractional conversion for the seeded emulsion copolymerization of 50/50 *n*-BA/St at 60°C.

gest that the gel content measured by the extraction process determines the amount of insoluble polymer in the solvent used (THF) but not necessarily because of an infinite network as the classical theories of gel formation consider. Figure 5(b) shows that a low amount of gel was formed in the experiments. (Gel fractions were only found in the final samples.) The gel content was higher in the semicontinuous processes because of the larger polymer concentration in the polymer particles (Fig. 1). Thus, the gel content was also slightly greater in run 3 than in run 2. The formation of gel was probably due to reactions of chain transfer to the polymer plus reactions of termination, the combination of which became more important at the end of reaction when the ratio of BA/St units polymerized was high (Fig. 2) as was the concentration of the polymer (Fig. 1).

The distinctive evolutions of the sol M_w (Fig. 4) between the batch and semicontinuous processes also stand out. The semicontinuous processes (runs 2 and 3) showed an initial increase in the M_w until reaching a plateau (slightly higher for the lower monomer feeding time experiment) and then a further increase in the last stage of the polymerization. For the batch process (run 1) the M_w initially increased to a maximum at about 70% global conversion and then slightly decreased. This behavior can be explained as follows: in a batch process the concentration of polymer in the polymer particles is low until a relatively high conversion is reached. Therefore, the probability of the reaction of chain transfer to the polymer is lower than in a semicontinuous process. Furthermore, in the batch process the copolymer formed at the beginning of the process was richer in St (for the larger reactivity of St, see Fig. 2), and consequently the probability of ab-

stracting H atoms from the copolymer backbone was lower than in the semicontinuous processes. Thus, the longer polymer chains formed in the semicontinuous process suffered chain transfer to the polymer and were transferred to the gel polymer; hence, the sol molecular weight decreased. This only occurred in the batch process at high conversions (>70%), leading to a simultaneous formation of gel and to a decrease of the molecular weights, although to a modest extent. This behavior agrees with the results recently published by Plessis et al. for the emulsion copolymerization of St and *n*-BA at lower contents of St and at a higher temperature (75°C).

Effect of initiator concentration

Figures 6–9 show the effect of the initiator concentration (runs 3–5) on the fractional conversion, the total number of polymer particles, the sol M_w , and the gel content for the seeded semicontinuous emulsion copolymerization of *n*-BA/St (see Table III).

Figure 6 shows that the greater the initiator concentration, the higher the fractional conversion. Secondary particle nucleation occurred in all runs. The extent of this process was stronger in the reactions with more initiator (Fig. 7). However, at the end of the reactions, a limited coagulation was observed that was more acute in the reaction with the highest initiator concentration. This coagulation increases with the initiator concentration because of the larger ionic strength of the medium and the larger surface area generated by the increase of the number of particles as the initiator concentration increases.

Figure 8 shows the effect of the initiator concentration on the evolution of the sol M_w . It may be seen that even though in all cases the M_w increased along the

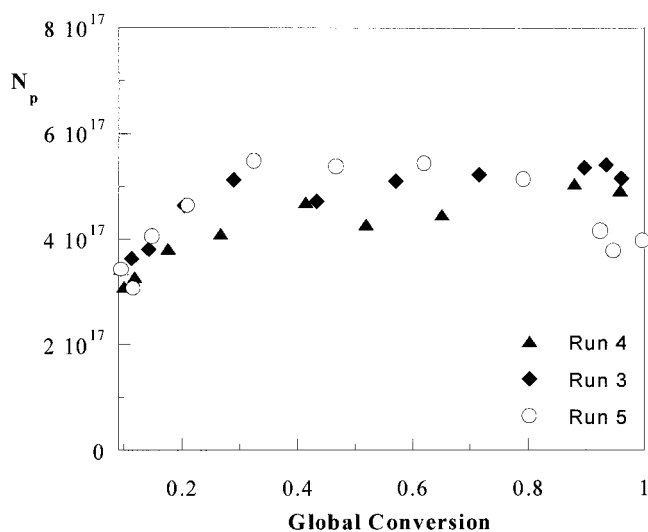


Figure 7 The effect of the concentration of the initiator on the evolution of the number of polymer particles.

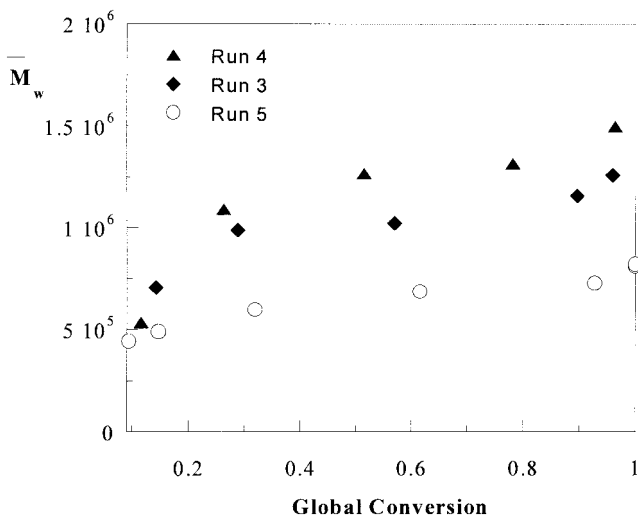


Figure 8 The effect of the initiator concentration on the evolution of the sol M_w .

reaction, the increase of the initiator concentration led to an important decrease of the final M_w . This behavior is typical for linear polymers because the radical concentrations have an important effect on the termina-

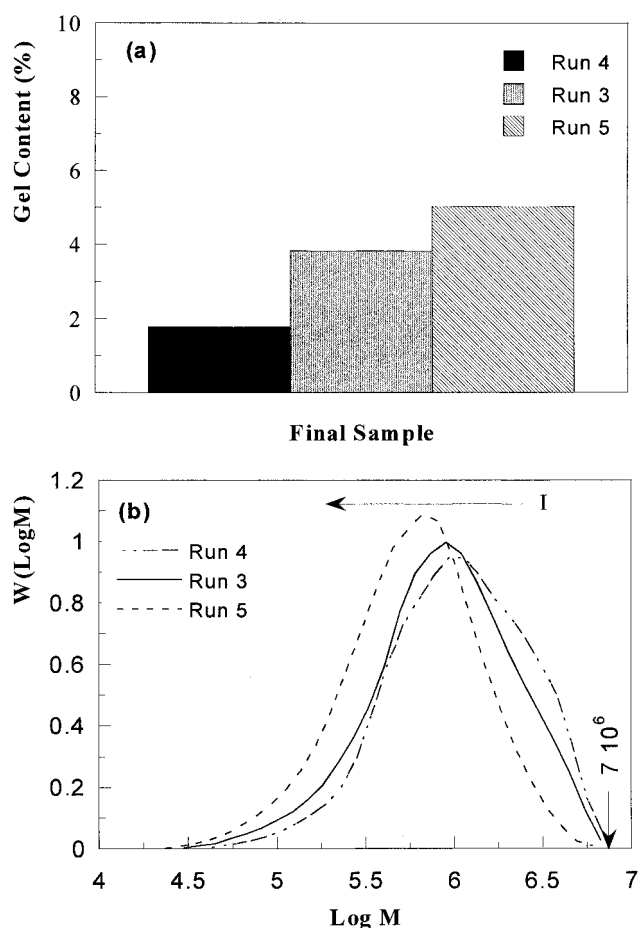


Figure 9 The effect of the initiator concentration on (a) the gel content and (b) the MWD of the final latex.

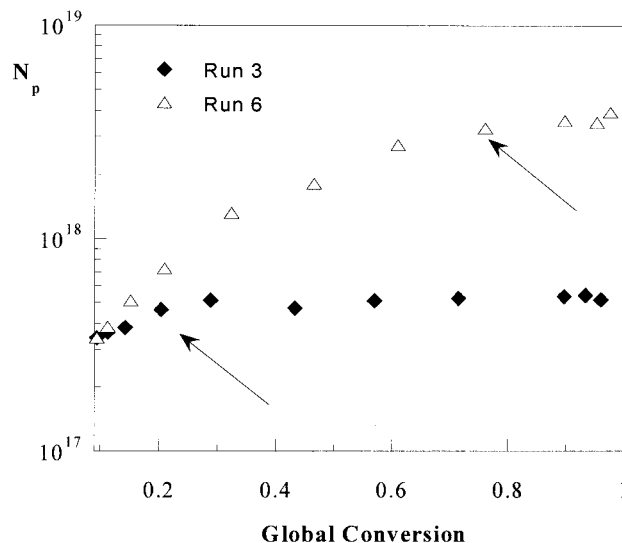


Figure 10 The effect of the emulsifier concentration on the number of polymer particles.

tion rate, and hence on the kinetic chain length of the growing radical. In this present case, this effect was enhanced by gel formation. Thus, an increase of the initiator concentration also led to a high polymer concentration in the polymer particles (Fig. 6) and consequently to a larger extent of the reactions of transfer to the polymer that finally generated extremely high molecular weight polymer chains leading to gel formation.

Figure 9 shows that the gel fraction increased with the initiator concentration and this contributed to the disappearance of the shoulder of the high molecular weights as the initiator concentration increased.

Effect of emulsifier concentration

Figures 10 and 11 show the effect of the increase of the initial emulsifier concentration on the evolution of the total number of polymer particles and the fractional conversion, respectively. It can be seen that the increase of the emulsifier concentration led to a stronger secondary nucleation, which in turn provoked an increase in the polymerization rate and the fractional conversion. In Figure 10 the arrows mark the moments at which micelles disappeared. These points were calculated from the values of the area covered by the emulsifier molecule (determined to be 0.47 nm²/molecule by conductimetric measurements), the size and number of polymer particles, and the value of the critical micelle concentration (determined in this work as 9.75 × 10⁻³ mol/L). In both reactions the nucleation of particles continued in spite of the absence of micelles. Nevertheless, beyond these points the particle formation that presumably occurred by homogeneous nucleation became slighter.

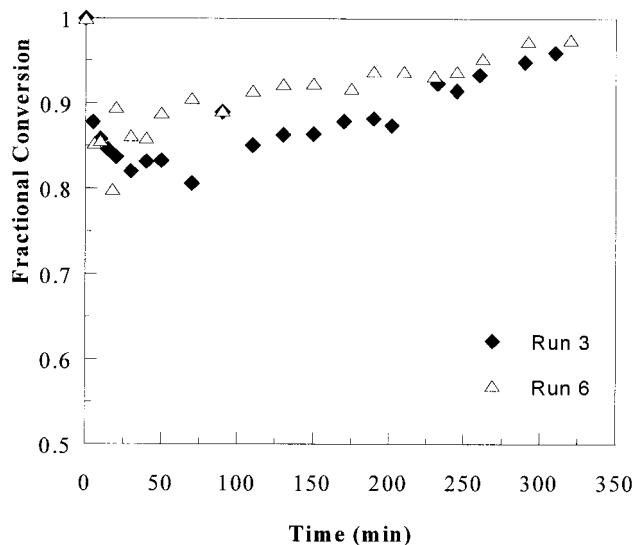


Figure 11 The effect of the emulsifier concentration on the fractional conversion.

A slight effect of the emulsifier concentration on the sol M_w can be observed in Figure 12. The M_w was smaller for the lower emulsifier concentration. In addition, the M_w increased along the polymerization as was also observed for the other runs. Another factor to take into account in these reactions is that the presence of a high amount of emulsifier could cause chain transfer reactions to this compound.

The MWD of the final sample of two runs is shown in Figure 13(a). It can be seen that for the higher emulsifier concentration the molecular weights are shifted to smaller molecular weights. Figure 13(b) shows that the gel content also decreased when the emulsifier was increased. This is the opposite of what was observed for the effects of feeding time and initiator concentration, namely, the lower the molecular

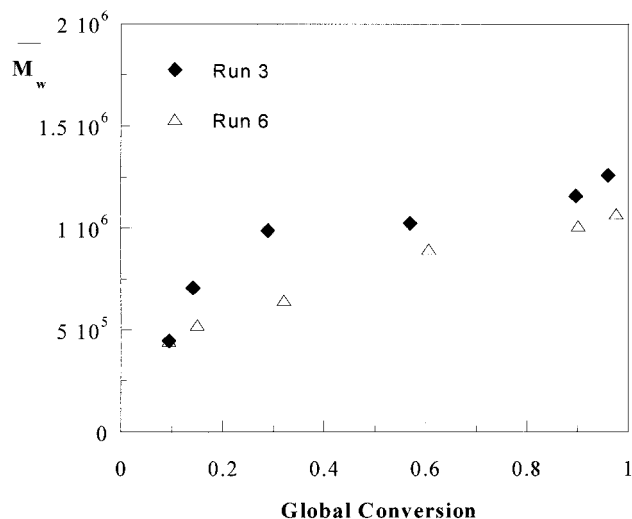


Figure 12 The effect of the emulsifier concentration on the evolution of the sol M_w .

weight, the higher the gel fraction. An explanation for the different behavior could be that, as a consequence of the high number of polymer particles generated along run 6, the average number of radicals per particle was significantly reduced; hence, although chain transfer to the polymer might take place, termination by combination is somewhat reduced. Thus, termination in the polymer particles occurred preferentially by monomolecular mechanisms (chain transfer to the monomer and/or chain transfer to the emulsifier), which led to a decrease in the gel content.

Effect of initiator concentration in polymerizations with CTAs

The effect of the concentration of the initiator when 1 wt % *n*-dodecyl mercaptan (CTA) was included in the recipe was considered. It should be pointed out that the monomers and the CTA were fed as a preemulsion to minimize mass transfer limitations, which can be particularly important for a hydrophobic species such as the CTA we employed. The evolution of the fractional conversion for runs 7–9 is similar (not shown) to

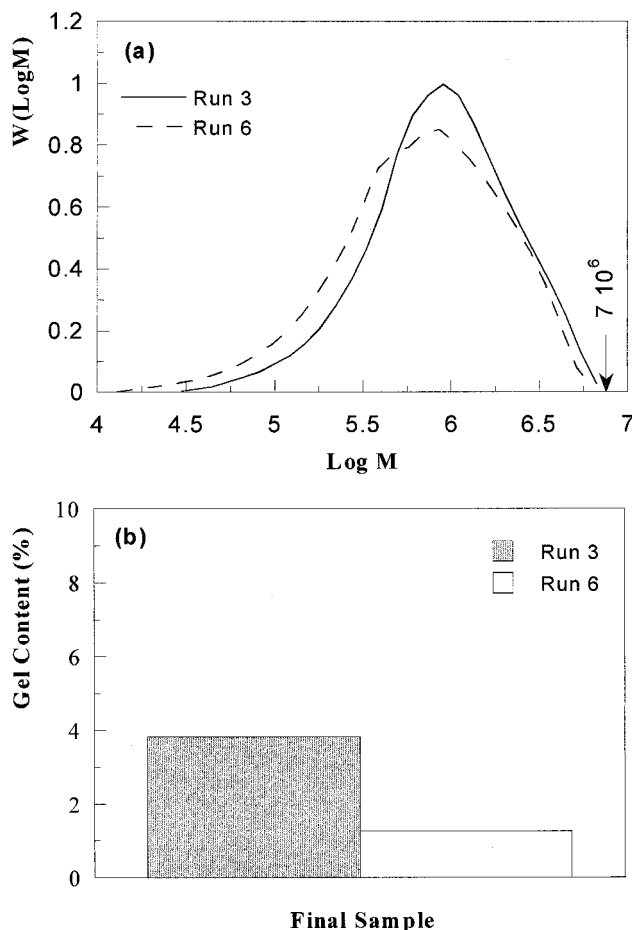


Figure 13 The effect of the emulsifier concentration on (a) the MWD and (b) the gel content of the final sample.

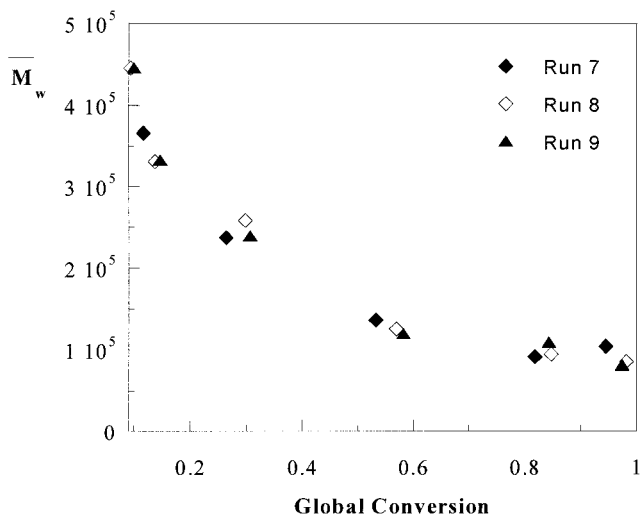


Figure 14 The effect of the initiator concentration in the presence of the CTA on the evolution of the M_w .

their counterparts carried out without the CTA (runs 3–5).

Figure 14 shows the effect on the M_w of the inclusion of 1 wt % CTA in the formulation. It can be seen that the addition of the CTA significantly reduced the M_w of the latexes almost independently of the initiator concentration. In addition, the gel fraction of these polymer latexes was zero. Figure 15 presents the MWDs of the final samples for runs 7–9. In all cases the MWDs were similar and bimodal. In order to determine the cause of the presence of two populations of polymers chains with such different molecular weights, the evolution of the MWD along the reactions was studied (Fig. 16). The MWDs were normalized in such a way that the areas under the curves were proportional to the polymer produced up to the mo-

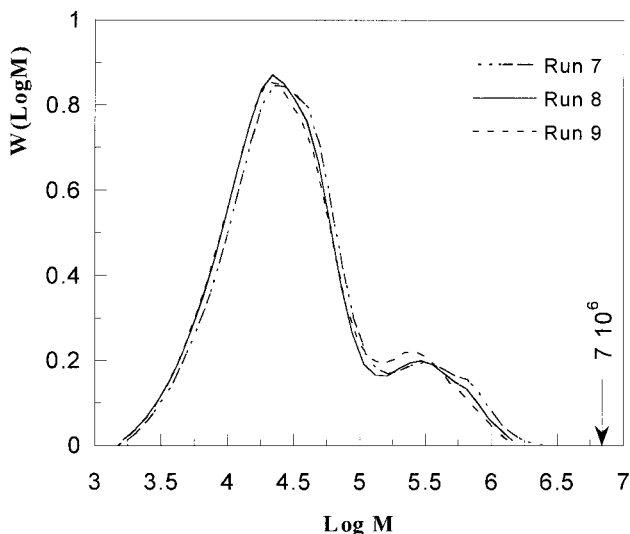


Figure 15 The effect of the initiator concentration in presence of the CTA on the MWD of the final latex.

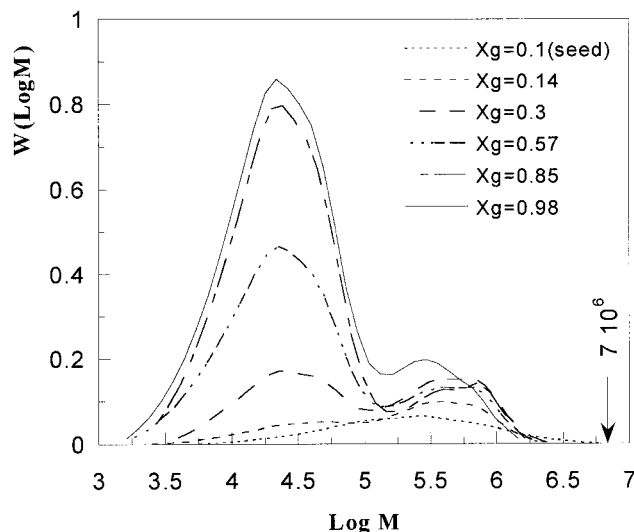


Figure 16 The evolution of the MWD along the reaction for run 8 (with the CTA).

ment when the sample was taken. Note that the polymer that was initially produced had a molecular weight that was higher than that of the seed. It seems that the CTA did not reach the polymer particles as fast as the monomer. From $X_g = 0.3$ – 0.85 the molecular weight was mainly controlled by the chain transfer to the CTA and the amount of polymer in the peak corresponding to that molecular weight increased with conversion. At the end of the reaction some high molecular weight was produced, which was very likely due to chain transfer to the polymer.

CONCLUSIONS

The effect of different operational variables (concentration of initiator and emulsifier and monomer feeding time) on the kinetics and copolymer microstructure in a seeded emulsion copolymerization of *n*-BA/St (50/50 wt % ratio) was investigated. The results show evidence of nonlinear reaction mechanisms that produced high molecular weights. Gel polymer was found but at levels that might not significantly affect the final properties of the latexes. In the absence of CTA, the initiator concentration allows the control of the molecular weight and gel content of the copolymer. The monomer feeding strategy and emulsifier concentration do not allow any control of the microstructural properties.

In the experiments carried out with 1 wt % CTA, gel polymer was not produced and the molecular weights were controlled by the CTA concentration. The bimodal shape of the MWD of the latexes produced in these experiments stands out. The bimodality was attributed to the mass-transfer limitations of the CTA in order to reach the polymerization loci at the beginning of the feeding time.

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