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Seeded Semibatch Emulsion Polymerization of *n*-Butyl Acrylate. Kinetics and Structural Properties

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ABSTRACT: The seeded semibatch emulsion polymerization of *n*-butyl acrylate was investigated using potassium persulfate as initiator at 75 °C. The effect of initiator concentration and monomer feeding time (feed flow rate) on the kinetics, fraction of gel, molecular weight distributions, and level of branches were studied. It was found that the amount of gel formed was independent of initiator concentration and monomer feed flow rate if the process proceeded under starved conditions. On the other hand, the higher the initiator concentration and the feeding times, the higher the level of branches but the lower the molecular weights. A high level of branches was found, which was attributed to intramolecular transfer to polymer or backbiting.

Introduction

Latexes prepared by semibatch emulsion polymerization are widely used in a variety of applications such as adhesives, paper coatings, paints, varnishes, and synthetic rubbers. Acrylic and styrene−acrylic latexes account for an important part of commercial emulsion polymers. The end-use properties of these products are to a great extent due to their polymer chain microstructure. Thus, molecular weight distribution (MWD) strongly affects tack, resistance to peel, and resistance to shear of pressure-sensitive adhesives.[1,2] Also, the mechanical properties of the final latex film are influenced by the cross-linked fraction of the latex. For example, it was shown that the higher the gel content in the latex, the higher the stiffness or toughness of the film.[3,4]

Butyl acrylate is a monomer commonly used in acrylic formulations, and considerable effort has been devoted to study its emulsion polymerization.[5−12] However, the knowledge of the effect of the process variables on kinetics, MWD, gel fraction, and branching is scarce. Capek et al.[5,6] studied the effect of initiator type and reaction temperature on the kinetics and the molecular weights (measured by viscosimetry). It was shown that the average molecular weights decreased with increasing temperature and increased with conversion but did not vary with the initiator concentration. Several works[6,9,13,14] pointed out that the analysis of the MWD of poly(*n*-butyl acrylate) was almost impossible due to the formation of an insoluble network when the polymer was dried or washed, but none of them tried to quantify the fraction of gel formed during the polymerization.

In this work, the effect of initiator concentration and monomer feed rate on the kinetics and polymer microstructure (gel fraction, branching, and MWD of the sol fraction) during the seeded semicontinuous emulsion polymerization of *n*-butyl acrylate was investigated.

Experimental Section

Materials. *n*-Butyl acrylate (BA) and acrylic acid (Atochem), sodium lauryl sulfate (SLS, Merck), sodium hydrogen carbonate (Panreac), and potassium persulfate (Fluka) were all used as received. SLS was used to prepare the seed, and a mixture of ethoxilated anionic and nonionic surfactants (Rhodia) was used for the semicontinuous experiments. The composition of this system, which will be called surfactant A, cannot be disclosed due to proprietary reasons. Nevertheless, the knowledge of the composition of the surfactant system is not required for the understanding of the present work, because seeded emulsion polymerizations were used, and the only role of the surfactant was to maintain the stability of the seed polymer particles avoiding coagulation. Therefore, the surfactant had no direct effect on kinetics and polymer microstructure. All polymerizations were carried out using doubly deionized water (DDI).

Polymerizations. All reactions were seeded. The poly(*n*-butyl acrylate), *p*-BA, seed was prepared batchwise following the recipe shown in Table 1 in a Mettler-Toledo RC1 calorimeter at 65 °C and kept overnight at 90 °C in order to decompose the unreacted initiator. Initiator concentration and feeding time (flow rate) were varied in the semicontinuous emulsion polymerizations summarized in Table 2. The polymerizations were carried out at 75 °C in a 1 L glass reactor fitted with a reflux condenser, a sampling device, a nitrogen inlet, two feed inlet tubes, and a stainless steel stirrer with a set of three blade impellers (stirrer speed: 200 rpm). Table 3 shows the recipe used. The experimental procedure was as follows: the seed ($d_p = 97$ nm and solids content = 20.5 wt %) and a fraction of surfactant A, initiator, and water were initially charged into the reactor. The rest was fed in two streams having both the same feeding time. One was a monomer preemulsion and the other an initiator solution. Although in some experiments the total amount of initiator was varied, the partitioning of the initiator between the initial charge and the feed was kept constant.

Characterization. Samples withdrawn from the reactor during the polymerization were analyzed gravimetrically to determine the instantaneous conversion (based upon the total

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Table 1. Seed Recipe

butyl acrylate (g)	250
water (g)	1000
SLS (g)	5.0
$NaHCO_3$ (g)	1.25
$K_2S_2O_8$ (g)	1.25

Table 2. Summary of the Seeded Semicontinuous Polymerizations

	initiator concn (%)	feeding time (h)		initiator concn (%)	feeding time (h)
run 1	0.0188	3	run 6	0.0188	1
run 2	0.0375	3	run 7	0.075	1
run 3	0.075	3	run 8	0.30	1
run 4	0.15	3	run 9	0.30	2
run 5	0.30	3	run 10	0.30	4

Table 3. Recipe Used in the Seeded Semicontinuous Emulsion Polymerizations

	initial charge	stream 1	stream 2
seed latex (g)	100		
water (g)	17.5	20	255
surfactant A (g)	1.25		2.5
butyl acrylate (g)			225.4
acrylic acid (g)			4.6
$K_2S_2O_8$ (wt %)[a]	0.0188−0.30[b]		

[a] Based on total monomer. [b] This amount was the sum of the initial charge plus that added in stream 1. The ratio of initiator between the initial charge and stream was 1/1.

monomer fed). Particle size was measured by dynamic light scattering spectroscopy, DLS (Coulter N4-Plus), and by capillary hydrodynamic fractionation, CHDF (Matec Applied Sciences, model 2000). For the DLS analysis samples were diluted to such low concentrations ($<1 \times 10^{-3}$ wt %) that one can safely assume that no monomer is present in the polymer particles, namely that unswollen particle sizes are measured. The analysis performed in the DLS equipment was carried out at 25 °C, and a run time of 120 s was used. Each sample was analyzed automatically six times, and only samples containing baseline error below 1% are considered to calculate the average. The unimodal analysis option was used. The results obtained by this technique were used to calculate the total number of particles of the latex.

Besides, CHDF was used to look for particles that might be created by secondary nucleation. The equipment was operated at the following conditions: flow rate, 1.4 mL/min; temperature, 35 °C; detector wavelength, 220 nm; sample concentration, <0,5 wt %; carrier fluid, 1X-6R500. Each sample was analyzed twice. None of the samples analyzed showed any tail or bimodal distribution. In addition, the average particle sizes calculated from the CHDF were in good agreement with those obtained by DLS.

Emulsion polymerization of BA yields a polymer containing a significant gel fraction. A modified version of Cohen Addad's process[15] was used to determine the gel content of the polymer. The process consisted of a continuous extraction with THF at 65 °C and during 7 h in a 1 L glass reactor. The gel fraction, G, can be calculated as follows:

$$G = w_g/w_p \tag{1}$$

where w_g and w_p are the weights of insoluble fraction and the whole sample, respectively.

The MWD of the sol was determined by size exclusion chromatography (SEC). Latex was added dropwise to tetrahydrofuran (THF) until a polymer concentration of approximately 0.3% w/v was reached. This yielded a colloidal dispersion of the gel fraction of the polymer in a solution of the sol polymer in THF. This dispersion was filtered (polyamide, $\Phi = 0.45\ \mu$m) before injection into the SEC instrument, which consisted of a pump (Waters model 510), three columns (Styragel of porosity 10^2, 10^4, and 10^6 Å), and a dual detector system formed by a differential refractometer and a viscometer (Viscotek model 250). Chromatograms were obtained at 40 °C using a THF flow rate of 1 mL min^{-1}. Polystyrene standards were used for calibration. The viscometer detector measured the intrinsic viscosity of the samples eluting at each retention time, and the average molecular weights were directly determined from calibration, without using the Mark−Houwink constants for the p-BA using the following expression:

$$[\eta]_i M_{wi} = c_i \tag{2}$$

where $[\eta]_i$ and M_{wi} are the intrinsic viscosity and the molecular weight of the polymer eluting at a retention volume v_i, and c_i is the same product $[\eta]_i M_{wi}$ calculated from the polystyrene standards. Attempts were made to measure long chain branching by this technique, but no consistent results were obtained when applying the Stockmayer[16] approach. Therefore, the level of branching was only quantified by solid-state ^{13}C NMR analysis. Final latexes were dried under vacuum at room temperature, and then the polymer samples were slightly swollen in THF before being analyzed. ^{13}C NMR spectra were obtained at 50 °C using a Bruker Avance DSX300 spectrometer at 75.5 MHz. Spectra were collected by using a 7 mm CP-MAS probe at a spinning rate of 1300 Hz. Inverse gated decoupling was used in order to avoid NOE effects. A composite pulse decoupling sequence was applied, consisting of an infinite cycle of two 180° pulses with phases of 0° and 15°. ^{13}C 90° pulses of 8 μs and a repetition time of 4 s between scans were also used. A few analyses made with a repetition time of 11 s gave the same ratio values, within the experimental error. At least 25 000 acquisitions were collected for each spectrum. A typical spectrum of the latexes produced during this work is presented in Figure 1. The peak assignments were made according to Lovell et al.[18,19] The percentage of branches was calculated as follows:

$$\%\ \text{branches} = \frac{A_H}{A_H + \dfrac{A_{E+F+G}}{2}} \tag{3}$$

where A_i is the area of the peak i in Figure 1.

Results and Discussion

Effect of Initiator Concentration. In runs 1−5, the initiator concentration was varied from 0.0188 to 0.30 wt % based on total weight of monomer, and the feeding time was 3 h. The other process variables were kept constant at the values given in Table 3.

Figure 2 shows the conversion evolution of the total number of particles in the different reactions. It can be seen that there was no significant effect of the initiator concentration on the total number of particles, N_p. The evolution of N_p was approximately the same for all the experiments and after a slight initial nucleation remained quite constant along the polymerization. Figure 3 presents the evolution of instantaneous conversion. It can be seen that these runs were conducted under starved conditions and that polymerization rate increased with initiator concentration. Because the number of particles did not depend on initiator concentration, the variation of the instantaneous conversion is attributed to the average number of radicals per particle that decreased as the initiator concentration was lowered.

Figure 4 presents the evolution of gel fraction for the experiments in which different concentrations of initiator and a feeding time of 3 h were used (runs 1−5). It can be seen that the amount of gel increases from 10%, corresponding to the amount of gel present in the seed, to 55−65% without significant differences due to the different initiator concentrations used. The shape of gel

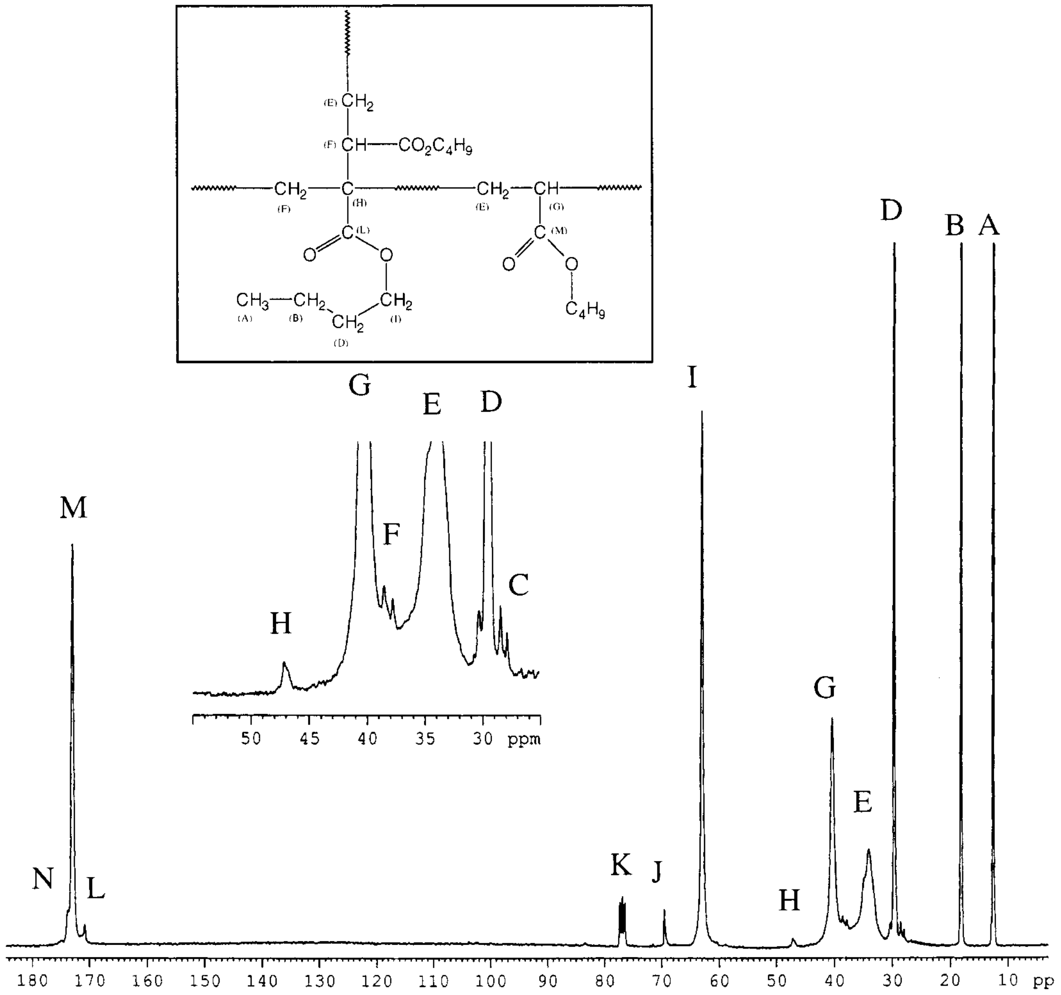


Figure 1. Solid-state ^{13}C NMR spectrum of polymer in THF. Peak assignments in refs 18 and 19.

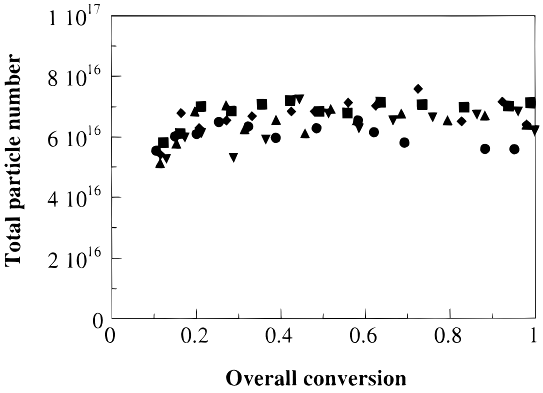


Figure 2. Evolution of the total number of polymer particles using different concentrations of initiator (feeding time = 3 h). Legend: (●) 0.0188% (run 1); (◆) 0.0375% (run 2); (▲) 0.075% (run 3); (■) 0.15% (run 4); (▼) 0.30% (run 5).

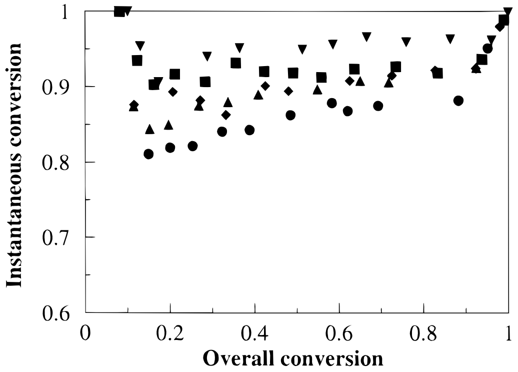


Figure 3. Evolution of the instantaneous conversion using different concentrations of initiator (feeding time = 3 h). Legend: (●) 0.0188% (run 1); (◆) 0.0375% (run 2); (▲) 0.075% (run 3); (■) 0.15% (run 4); (▼) 0.30% (run 5).

fraction curve, increasing rapidly up to a plateau, was similar to that obtained by simulation by Arzamendi and Asua.[20] In the absence of cross-linking agents, gel can be produced by intermolecular chain transfer to polymer coupled with either propagation to terminal double bonds or termination by combination. For *n*-butyl acrylate polymerization, chain transfer to polymer can occur to a monomeric unit belonging to the same polymer chain or to other polymer chain, which may surround the radical.[18,19,21,26,30] In the first case, the chain transfer to polymer is intramolecular, the so-called backbiting mechanism which leads to short chain branches, SCB.The second process is intermolecular and leads to long chain branches, LCB. Only LCB leads to gel formation. Terminal double bonds might be produced by chain transfer to monomer or termination by disproportionation. It is unlikely that chain transfer to monomer occurred to a significant extent because the monomer chain transfer rate constant is small,[22] and polymerizations were carried out under rather starved conditions, namely, at low monomer concentrations. On the other hand, it has been reported that *n*-butyl acrylate mainly terminates by combination.[23] Therefore, gel was produced by intermolecular chain transfer to

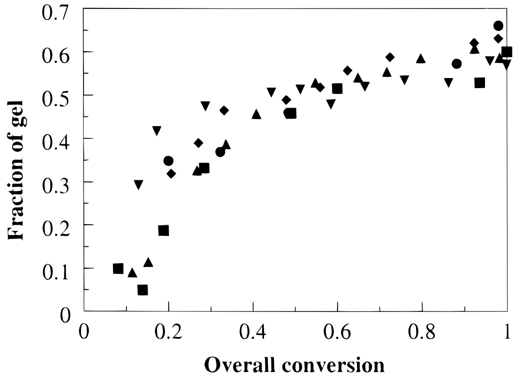
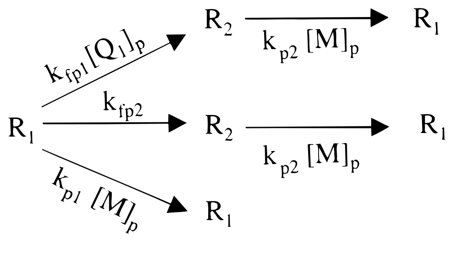


Figure 4. Evolution of the fraction of gel using different concentrations of initiator (feeding time = 3 h). Legend: (●) 0.0188% (run 1); (◆) 0.0375% (run 2); (▲) 0.075% (run 3); (■) 0.15% (run 4); (▼) 0.30% (run 5).

polymer coupled with termination by combination of large macroradicals.

In a compartmentalized system, such as emulsion polymerization, termination by combination of large macroradicals can only occur in a significant extent if the average number of radicals per particle ($\bar{n}$) is close to or greater than 0.5, namely, if there is a substantial number of polymer particles with two or more radicals. Estimations of $\bar{n}$ from Figures 2 and 3 by using the propagation rate constant determined by pulsed laser polymerization, PLP ($k_{p,75°C}$ = 44 289 L/(mol/s)),[24,25] yields a value of $\bar{n}$ close to 0.1, which would result in a negligible extent of the termination by combination of large macroradicals. Therefore, the effective propagation rate ($\bar{k}_p$) constant should be lower than the PLP value. Plessis et al.[26] proposed that low reactive tertiary radicals produced by intramolecular chain transfer to polymer are responsible for the reduction of the $\bar{k}_p$ value. Actually, both intermolecular and intramolecular chain transfer to polymer yield tertiary carbon radicals with much lower reactivity than the secondary carbon radicals involved in the linear growth of the poly(*n*-BA) chain.[21] Therefore, the reaction scheme proposed by Plessis et al.[26] should be modified as follows:



(4)

where R$_1$ and R$_2$ are the secondary and tertiary radicals, k_{fp1} is the intermolecular chain transfer to polymer rate constant, [Q$_1$]$_p$ is the concentration of polymer in the polymerization loci (polymer particles), k_{fp2} is the intramolecular chain transfer to polymer rate constant, k_{p1} and k_{p2} are the propagation rate constants of radicals R$_1$ and R$_2$, respectively, and [M]$_p$ is the concentration of the monomer in the polymer particles. According to scheme 4, the effective propagation rate constant is

$$\bar{k}_p = k_{p1}P_1 + k_{p2}P_2 \tag{5}$$

where P_1 and P_2 are the probabilities of having a radical of type R$_1$ and R$_2$, respectively. Assuming that a pseudo-steady state applies to these radicals, one obtains

$$(k_{fp2} + k_{fp1}[Q_1]_p)R_1 = k_{p2}[M]_pR_2 \tag{6}$$

$$R = R_1 + R_2 \tag{7}$$

Combining eqs 6 and 7, the probabilities of having a radical of type R$_1$ or R$_2$ can be obtained:

$$P_1 = \frac{R_1}{R} = \frac{k_{p2}[M]_p}{k_{p2}[M]_p + k_{fp2} + k_{fp1}[Q_1]_p}; \quad P_2 = 1 - P_1 \tag{8}$$

Equation 8 is more general than that proposed by Plessis et al.[26] for P_1 and P_2, as the contribution of the intermolecular chain transfer is included. It can be shown[29] that for BA $k_{fp1}[Q_1]_p \ll k_{p2}[M]_p + k_{fp2}$, and eq 8 reduces to the relationship used by Plessis et al.:[26]

$$P_1 = \frac{k_{p2}[M]_p}{k_{p2}[M]_p + k_{fp2}}; \quad P_2 = 1 - P_1 \tag{9}$$

Equations 5 and 9 show that the effective polymerization rate constant depends on monomer concentration. Thus, under starved semicontinuous emulsion polymerization, [M]$_p$ is low and P_2 increases, leading to a decrease of $\bar{k}_p$. Using this low value of $\bar{k}_p$, values of $\bar{n}$ close to or greater than 0.5 are obtained from Figures 2 and 3. This allows for a substantial termination by combination and hence for the formation of gel.

Table 4 shows the final level of branches achieved for each concentration of initiator as well as the final gel content. It can be seen that the frequency of branching is very high and comparable to that of LDPE and PVC. Feucht et al.[27] reported for LDPE a frequency of short branching of 2−4% (based on the number of monomer molecules in the polymer) and a 0.01−0.04% for long branching. For PVC a frequency of short branches up to 0.5% and a 0.05% for long branches have been found.[28] The high number of branching points with a gel fraction of only 60% suggests extensive backbiting, namely that the simplified mechanism proposed by Plessis et al.[26] applies. Table 4 shows that total number of branches increased with increasing initiator concentration. According to the mechanism proposed by Plessis et al.,[26] the probability of a backbiting event is

$$P_2 = \frac{k_{fp2}}{k_{fp2} + k_{p2}[M]} \tag{10}$$

Figure 3 shows that monomer concentration decreased as the initiator concentration increased, and according to eq 10 this should lead to higher frequency of branches, which agrees well with the experimental findings.

Table 4 and Figure 4 show that for a feeding time of 3 h the initiator concentration had no effect on the gel content of the final latex. This is somehow surprising because increasing initiator concentration yielded higher polymer/monomer ratios (see Figure 3), and this would increase the probability of intermolecular chain transfer to polymer, which promotes gel formation. At this point, no explanation of this result can be offered, and these results will be discussed in depth with the help of a mathematical model of the process in the subsequent paper of this series.[29]

Figure 5 shows the evolution of the weight-average molecular weights for the experiments in which different concentrations of initiator were used (runs 1−5). It

Table 4. Branching Level of the Final Latexes

expt	initiator concn[a] (wt %)	feeding time (h)	% branches[b]	% gel
1	0.0188	3	1.71	66
2	0.0375	3	1.78	63
3	0.075	3	2.03	59
4	0.15	3	2.37	60
5	0.30	3	2.80	55
6	0.0188	1	1.66	36
7	0.075	1	1.40	49
8	0.30	1	0.87	52
9	0.30	2	2.08	57
10	0.30	4	3.37	59

[a] Based on total monomer. [b] Number of branched carbons per 100 monomer molecules.

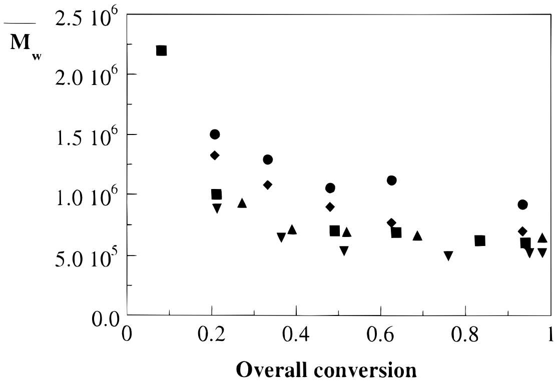


Figure 5. Evolution of the weight-average molecular weight using different concentrations of initiator (feeding time = 3 h). Legend: (●) 0.0188% (run 1); (◆) 0.0375% (run 2); (▲) 0.075% (run 3); (■) 0.15% (run 4); (▼) 0.30% (run 5).

can be seen that $\overline{M_w}$ decreased along each reaction whereas the gel fraction increased (Figure 4). Arzamendi and Asua[20] predicted the same relation between sol molecular weight and gel fraction through mathematical modeling. The reason for this behavior is that because long polymer chains have a higher probability of suffering intermolecular chain transfer to polymer, the gel incorporates preferentially the longer chains, provoking a reduction of the molecular weight of the sol fraction. In addition, increasing the initiator concentration produces a slight decrease on the average molecular weights. This decrease of $\overline{M_w}$ could be due to the increase of the number of radicals (which reduces the kinetic chain length) and the reduction of the concentration of the monomer in the polymer particles (which promotes chain transfer to polymer and incorporation of long chains into gel).

To investigate the effect of the initiator concentration in a broader range of instantaneous conversions, a series of experiments using a short feeding time (1 h) were carried out (runs 6–8). Figures 6, 7, and 8 show the evolution of the instantaneous conversion, the fraction of gel, and the weight-average molecular weights, respectively. Table 4 shows the final level of branches and gel amount obtained in these experiments. Figure 6 shows that, in runs 6 and 7 carried out with low initiator concentrations (0.075% and 0.0188%, respectively), monomer accumulated in the reactor probably due to the low radical flux, which was not able to overcome the effect of the inhibitor contained by the monomer added at a high flow rate. The accumulation of monomer in the reactor resulted in a decrease of the gel content (Figure 7), likely due to the reduction of the polymer/monomer ratio that minimized the occurrence of intermolecular chain transfer to polymer. During the first stages of the process, a comparable gel fraction was obtained in runs 6 (0.0188 wt %) and 7 (0.075 wt %) because both runs proceeded with similar polymer/monomer ratios. Later run 7 reached starved conditions, yielding an increasing amount of gel. At the end of the process, the gel fraction ranked according to the average polymer/monomer ratio in the process.

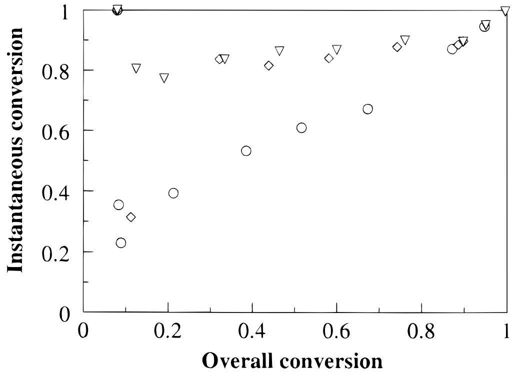


Figure 6. Evolution of the instantaneous conversion for different initiator concentrations (feeding time = 1 h). Legend: (○) 0.0188% (run 6); (◇) 0.0375% (run 7); (▽) 0.30% (run 8).

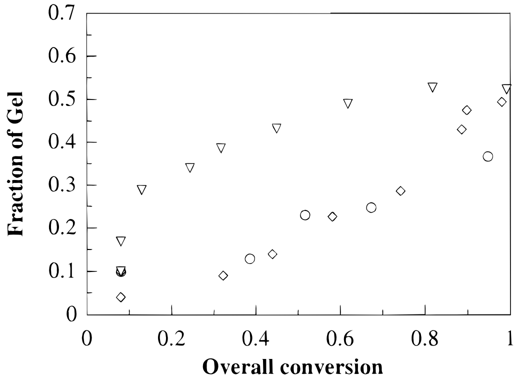


Figure 7. Evolution of the gel fraction for different initiator concentrations (feeding time = 1 h). Legend: (○) 0.0188% (run 6); (◇) 0.0375% (run 7); (▽) 0.30% (run 8).

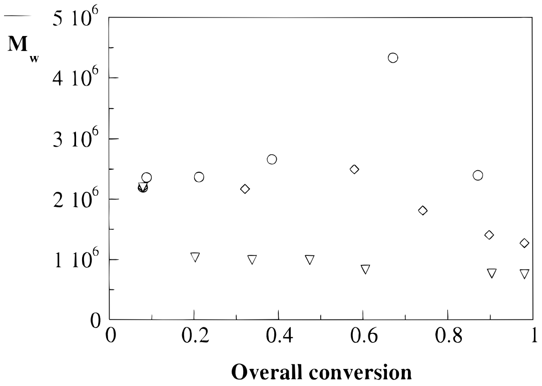


Figure 8. Evolution of the weight-average molecular weight for different initiator concentrations (feeding time = 1 h). Legend: (○) 0.0188% (run 6); (◇) 0.0375% (run 7); (▽) 0.30% (run 8).

Table 4 shows that monomer accumulation also lowered the number of branches, in agreement with the predictions of the mechanism proposed by Plessis et al.[26]

Figure 8 shows that the higher the initiator concentration, the lower $\overline{M_w}$. This is the result of the com-

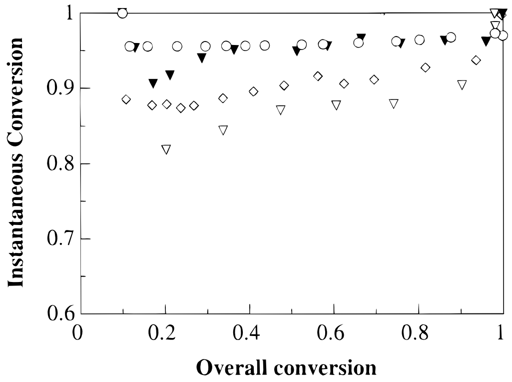


Figure 9. Evolution of the instantaneous conversion for experiments with different feeding time (initiator concentration = 0.3 wt %). Legend: (▽) 1 h (run 8); (◇) 2 h (run 9); (▼) 3 h (run 5); (○) 4 h (run 10).

bined effect of a decrease of the kinetic chain length and an increase of gel fraction as initiator concentration increased.

In run 8 (initiator concentration 0.3 wt %), $\overline{M}_w$ decreased continuously during the process, the maximum decrease being located at overall conversion, *X*, in the range 10−20%, which is the region where the gel fraction increased sharply. Run 7 (initiator concentration 0.075 wt %) showed a roughly constant $\overline{M}_w$ up to *X* = 0.4−0.5 and then a continuous decrease, in agreement with the evolution of the gel fraction (Figure 7). Run 6 carried out with the lowest initiator (0.0188 wt %) yielded the higher molecular weight. The effect of the gel formation on the sol molecular weights can also explain the differences between Figures 5 and 8, in which the same variation of the initiator concentration led to a higher effect on $\overline{M}_w$ for the runs presented in Figure 8. In the experiments carried out with 3 h feeding time (Figure 5), the gel content was roughly the same (Figure 4), and hence all the sol MWDs were similarly affected by gel formation. On the other hand, in the experiments carried out in 1 h (Figure 8) large differences in gel content were observed (Figure 7), which resulted in wider differences in sol $\overline{M}_w$.

Effect of Monomer Feeding Time. To study the effect of this variable, a series of experiments (runs 5, 8−10) were carried out varying the feeding time from 1 to 4 h, keeping constant the other process variables. The total number of polymer particles was not affected by the monomer feeding time (not shown) and was roughly constant during each experiment. Figure 9 shows the evolution of the instantaneous conversion. It can be seen that the lower the monomer feeding time, the lower the instantaneous conversion, although all experiments proceeded under starved conditions.

Figure 10 presents the evolution of the fraction of gel for the experiments in which the monomer feeding time was varied. For all the experiments, the fraction of gel increases from 10% to 52−60%, and no significant effect of the feeding time was observed, likely due to the fact that all runs were carried out under starved conditions.

Table 4 shows that the level of branches for the final latex was affected by the feeding time whereas the fraction of gel was not. As for the experiments carried out with different initiator concentrations, the level of branches increased with increasing instantaneous conversion, i.e., decreasing monomer concentration in the polymer particles. This is in agreement with eqs 5−9.

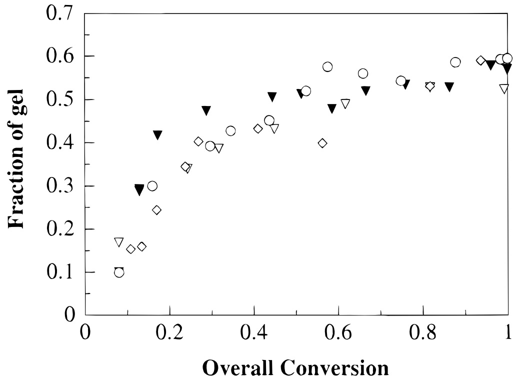


Figure 10. Evolution of the gel fraction for experiments in which different feeding time (initiator concentration = 0.3 wt %). Legend: (▽) 1 h (run 8); (◇) 2 h (run 9); (▼) 3 h (run 5); (○) 4 h (run 10).

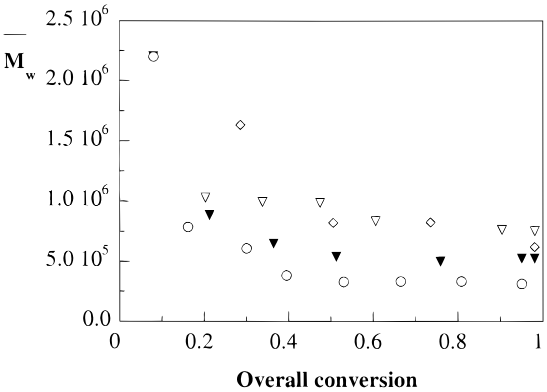


Figure 11. Evolution of weight-average molecular weight for experiments with different feeding time (initiator concentration = 0.3 wt %). Legend: (▽) 1 h (run 8); (◇) 2 h (run 9); (▼) 3 h (run 5); (○) 4 h (run 10).

On the other hand, the fraction of gel was not affected by this increase in the level of branching, which might be considered as an additional indication of that most of branches were short chain branches produced by the backbiting process.

Figure 11 presents the conversion evolution of the weight-average molecular weight for the experiments in which the feeding time was varied. It can be seen that the molecular weight decreased during the reaction as a result of the increase of gel fraction. In addition, the greater the feeding time, the smaller the average molecular weights. This result is due to the fact that faster feed rates yielded higher monomer concentrations, which resulted in longer chains. The higher the monomer concentration also resulted in a reduction of the number of polymer chains that were transferred to the gel through chain transfer to polymer and termination by combination.

Conclusions

The seeded semicontinuous emulsion polymerization of *n*-butyl acrylate initiated by potassium persulfate at 75 °C was investigated. For the first time in the open literature structural molecular properties of the poly(*n*-butyl acrylate), such as branching level and molecular weight distribution of the sol and amount of gel, are reported. In addition, the effect of operational variables (initiator concentration and monomer feed flow rate) in both the kinetics and the architecture of the polymer are presented. Thus, it was found that the gel formed during the process was not affected by the initiator concentration or the monomer feeding time, whereas the instantaneous conversion, molecular weight distribution, and level of branching were. Increasing initiator concentration increased the polymerization rate and level of branching and slightly reduced the final molecular weights of the sol. In addition, increasing the feeding time increased instantaneous conversion and level of branches and decreased sol molecular weights. These results have technological implications because the amount of gel produced cannot be modified if one wishes to proceed under starved conditions (which are commonly used to control reactor temperature and copolymer composition). The amount of gel can be controlled by working under flooded conditions. Also noticeable is the fact that the high level of branching encountered was predominantly due to intramolecular transfer to polymer, so-called backbiting, which has important kinetic implications due to the low reactivity of the tertiary radical formed in this transfer mechanism. This led to a decrease of the effective polymerization rate as the monomer concentration decreased.

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References and Notes

(1) Satas, D. *Adhesives Tapes, Polymer Conference Series*; Wayne State University: Detroit, MI, June 12–16, 1967.
(2) Satas, D. In *Handbook of Pressure Sensitive Adhesive Technology*; Van Nostrand Reinhold: New York, 1989.
(3) Back, A. L. *Ind. Eng. Chem.* **1947**, *39*, 1339.
(4) Czlonkowka-Kohutnicka, Z.; Razsczuk, A. *J. Appl. Polym. Sci.* **1975**, *19*, 1269.
(5) Capek, I.; Kostrubova, J.; Barton, J. *Chem. Zvesti* **1984**, *38*, 803.
(6) Capek, I. *Polymer* **1994**, *26*, 1154.
(7) Maxwell, I. A.; Napper, D. H.; Gilbert, R. G. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 1449.
(8) Mallya, P.; Plamthottam, S. S. *Polym. Bull.* **1989**, *21*, 497.
(9) Potisk, P.; Capek, I. *Angew. Makromol. Chem.* **1994**, *218*, 53.
(10) Zirkee, H. F.; van den Enden, M. J. W. A.; van Kilsdonk, W. T.; van Herk, A. M.; German, A. L. *Acta Polym.* **1996**, *47*, 441.
(11) Ozdeger, E.; Sudol, E. D.; El Aasser, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3827.
(12) Maeder, S.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 4410.
(13) Dube, M. A.; Rilling, K.; Penlidis, A. *J. Appl. Polym. Sci.* **1991**, *43*, 2137.
(14) Wunderlich, W.; Schulz, G. V. *Makromol. Chem.* **1976**, *177*, 973.
(15) Cohen-Addad, J. P.; Bogonuk, C.; Granier, V. *Macromolecules* **1994**, *27*, 5032.
(16) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(17) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. In *Tablas para la elucidación estructural de compuestos orgánicos por métodos espectroscopios*; Alhambra: Madrid, 1980.
(18) Lovell, P. A.; Shah, T. H.; Heatley, F. *Polym. Commun.* **1991**, *32*, 4, 98.
(19) Ahmad, N. M.; Heatley, F.; Lovell, P. A. *Macromolecules* **1998**, *31*, 2822.
(20) Arzamendi, G. Asua, J. M. *Macromolecules* **1995**, *28*, 7479.
(21) McCord, E. F.; Shaw, W. H.; Hutchinson, R. A. *Macromolecules* **1997**, *30*, 246.
(22) Maeder, S.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 4410.
(23) Moad, G.; Solomon, D. H. In *Comprehensive Polymer Science*; Esarmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, 1989; Vol. 3, p 147.
(24) Lyons, R. A.; Hutovic, J.; Piton, M. C.; Christie, D. I.; Clay, P. A.; Manders, B. G.; Kable, S. H.; Gilbert, R. G. *Macromolecules* **1996**, *29*, 1918.
(25) Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. *Macromolecules* **1996**, *29*, 4206.
(26) Plessis, C.; Arzamendi, G.; Leiza, J. R.; Schoonbrood, H. A. S.; Charmot, D.; Asua, J. M. *Macromolecules* **2000**, *33*, 4.
(27) Feucht, P.; Tilger, B.; Luft, G. *Chem. Eng. Sci.* **1985**, *40*, 1935.
(28) Odian, G. In *Principles of Polymerization*; Wiley: New York, 1970; p 242.
(29) Plessis, C.; Arzamendi, G.; Leiza, J. R.; Schoonbrood, H. A. S.; Charmot, D.; Asua, J. M. *Ind. Eng. Chem. Res.*, in press.
(30) Chiefari, J.; Jeffery, J.; Mayadune, R. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 7700.

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