

Semicontinuous Miniemulsion Terpolymerization: Effect of the Operation Conditions

MARÍA J. UNZUÉ and JOSÉ M. ASUA*

Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain

SYNOPSIS

The effect of solids content, initiator concentration, feed-flow rate, and amount of cosurfactant on the kinetics of the high solids content, semicontinuous miniemulsion terpolymerization of butyl acrylate, methyl methacrylate, and vinyl acetate was studied. In addition, the effect of the operation variables on the feasibility of obtaining a 65 wt % solids content latex with low amount of coagulum was investigated. The operation variables studied were: (1) partition of the monomer between the initial charge and the feed, (2) type and concentration of emulsifier; (3) feed-flow rate; and (4) sonication.

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INTRODUCTION

In recent years, a number of studies about miniemulsion polymerization have appeared in the literature.¹⁻²³ These works showed that in miniemulsion polymerization, particle formation occurs by nucleation of monomer droplets, the nucleation stage being much longer than that of the conventional emulsion polymerization. This was attributed to the low free-radical absorption efficiency of the monomer droplets.^{7,10} In addition, not all monomer droplets can be traced to polymer particles in the final latex. Therefore, monomer droplets must disappear by another mechanism other than nucleation such as monomer diffusion to growing particles and collision with polymer particles.^{18,21} Miniemulsion polymerization also differs from conventional emulsion polymerization because of the influence of the cosurfactant on the partition of the monomers between the different phases.²⁰ The presence of cosurfactant (hexadecane) in the monomer droplets reduces the free energy of mixing of the monomers in that phase. This increases the concentrations of the monomers in the monomer droplets; hence both the concentrations of the monomers in the polymer particles and the polymerization rate are reduced.

Most of the reported works¹⁻²³ are basic studies that elucidate the mechanisms involved in the miniemulsion polymerization process. Therefore, the experiments were carried out using solids content much lower than those of the commercial latexes. High solids content latexes offer numerous advantages for most commercial applications, e.g., low shipping costs and no need for removing water. High solids concentrations are used for coatings and adhesives and in many latexes and formulated products.²⁴ In addition, the production of most of these products involves the polymerization of several monomers of widely different reactivity ratios. On the other hand, the viscosity of the latex approaches infinity as the volume fraction of the polymer particles approaches the maximum concentration at which the system can still flow. Theoretically, this limiting volume fraction should be about 0.62 for spheres of uniform diameter.²⁵ However, the limiting volume fraction of polydisperse latexes is greater than 0.62 because the smaller particles fit within the voids of the array of large particles. Because of the distinct nucleation mechanism, the polymer particles produced in the miniemulsion process have a broader particle size distribution than those obtained in the conventional emulsion polymerization process.^{7,10,19} This suggests the possibility of obtaining highly concentrated latexes through miniemulsion polymerization.

* To whom correspondence should be addressed.

In the present work, the effect of the operation conditions on the kinetics of the high solids content, semicontinuous miniemulsion terpolymerization of butyl acrylate, methyl methacrylate, and vinyl acetate was investigated. Also, a preliminary study of the effect of the operation conditions on the feasibility of obtaining a 65 wt % solids content latex was carried out.

EXPERIMENTAL

Technical grade monomers were used. Methyl methacrylate (MMA) and butyl acrylate (BuA) contained 25 ± 10 and 50 ± 10 ppm of *p*-methoxyphenol as inhibitor, respectively. Vinyl acetate (VAc) contained hydroquinone (10–20 ppm) and acrylic acid (AA) contained 20 ppm of *p*-methoxyphenol. Hexadecane (HD), potassium persulfate (KPS), sodium lauryl sulfate (SLS), Alipal CO 436 (ammonium salt of sulfated nonylphenoxy (polyethyleneoxy) ethanol (4 ethyleneoxide), Rhône-Poulenc), Brij 35 ($C_{12}H_{25}-O-(C_2H_4O)_{23}$, ICI) and Brij 98 ($C_{16}H_{31}-O-(C_2H_4O)_{18}$, ICI) were also used as received. The water was deionized.

All the experiments were carried out at 80°C keeping the monomer molar ratio constant (MMA/BuA/VAc = 35/50/15). In addition, 1 wt % (based on monomers) of acrylic acid was included in the recipe. Two series of experiments were carried out. The recipes for the first series of polymerizations are given in Table I. All the experiments in this series were carried out using a 2 wt % (based on monomers) of Alipal CO 436. Polymerizations were carried out as follows: 10 wt % of the whole recipe, in a miniemulsion form, was initially charged into

Table I Recipes Used in the First Series of Experiments

Experiment	Solids Content (wt %)	$K_2S_2O_8$ (wt %) ^a	HD (wt %) ^a	Feeding Time (h)
1	33	1.05	2	6
2	55	0.52	2	6
3	55	1.05	2	6
4	55	1.05	4	6
5	55	1.05	2	9
6	55	1.05	2	4
7	60	1.05	2	6

^a Based on the total amount of monomer. Other ingredients in the recipes: 2 wt % Alipal CO 436, 1 wt % acrylic acid, 35/50/15 molar ratio of methyl methacrylate/butyl acrylate/vinyl acetate.

the reactor, heated to 80°C (heating time = 15 min) and allowed to polymerize in batch for 15 min. Then, the rest of the recipe was fed as a miniemulsion into the reactor at a constant flow rate. After completion of the feeding, the reaction mixture was allowed to react in batch at the reaction temperature (80°C) for 1–2 h. Different emulsification processes were used for the initial charge and the feed. In order to prepare the initial charge, the emulsifier and the initiator were dissolved in water and a mixture of hexadecane and the monomers was added to the aqueous solution. The system was subjected to sonication (Branson Sonifier 450) under agitation provided by a magnetic-bar stirrer. The conditions for the sonications were as follows: output control: 7; duty cycle: 60%; sonication time: 5 min. The feed was a miniemulsion formed by flowing a mixture of monomers and hexadecane, and an aqueous solution of emulsifier and initiator through the sonifier equipped with a continuous-flow cell cooled with a water jacket. The conditions for the continuous sonication were: output control: 7; duty cycle: 60%; residence time in the flow cell: 20 min (for a total feeding time of 6 h).

In the second series of experiments, the effect of the operation variables on the feasibility of obtaining a 65 wt % solids content latex was investigated. The operation variables studied were:

1. Partition of the monomer between the initial charge and the feed;
2. type and concentration of emulsifier;
3. feed-flow rate; and
4. sonication.

The recipes for these reactions are given in Table II. In these reactions a 1.04 wt % of $K_2S_2O_8$ and a 2 wt % of HD (both based on monomers) were used. When the effect of the partition of the monomer between the initial charge and the feed was studied, the ratios emulsifier/monomer, initiator/monomer, and HD/monomer were the same in the initial charge as in the feed. In addition, the emulsification process was the same as in the first series of experiments.

Samples were withdrawn during the process and the polymerization was short-stopped with hydroquinone. The overall conversion was determined gravimetrically. The conversion of each monomer was determined by measuring the residual monomer by gas chromatography. In order to carry out these measurements the latex samples were diluted in an aqueous solution of surfactant (to avoid coagulation) and hydroquinone (to stop the polymerization) and

Table II Recipes Used in the Second Series of Experiments

Run	Initial Charge Solids Content (wt %)	Emulsifiers				Sonication		Feeding Time (h)
		Ionic	Wt % ^a	Non Ionic	Wt % ^a	Initial Charge	Feed	
8	65	Alipal CO 436	4	—	—	Yes	Yes	6
9	65	Alipal CO 436	2	Brij 35	2	Yes	Yes	6
10	55	Alipal CO 436	2	Brij 35	2	Yes	Yes	6
11	45	Alipal CO 436	2	Brij 35	2	Yes	Yes	6
12	55	Alipal CO 436	2	Brij 35	2	Yes	Yes	9
13	55	Alipal CO 436	4	—	—	Yes	Yes	6
14	55	Alipal CO 436	2	Brij 98	2	Yes	Yes	6
15	55	SLS	2	Brij 35	2	Yes	Yes	6
16	55	Alipal CO 436	1	Brij 35	1	Yes	Yes	6
17	55	Alipal CO 436	2	Brij 35	2	Yes	No	6
18	55	Alipal CO 436	2	Brij 35	2	No	No	6

^a Based on the total amount of monomer. Other ingredients in the recipes: 1.04 wt % $K_2S_2O_8$, 2 wt % hexadecane, 1 wt % acrylic acid, 35/50/15 molar ratio of methyl methacrylate/butyl acrylate/vinyl acetate.

injected into the gas chromatograph (GC). A glass insert filled with glass wool was inserted in the injection port to retain the polymer of the latex and avoid the clogging of the column. From the GC data, the cumulative terpolymer composition was calculated. No residual AA was measured. Independent experiments showed that the detection limit for AA was 0.2% (AA conversion = 0.8). Due to the small amount of AA used in the recipe, the extent of the AA conversion had a negligible effect on the values of both conversion and terpolymer composition. Therefore, in the calculations of conversion and terpolymer composition it was assumed that this monomer reacted instantaneously. The particle size was measured by dynamic light scattering (DLS). This value together with the overall conversion were used to estimate the number of polymer particles.

Mechanical stabilities were determined at room temperature by means of a high-speed ($\approx 10,000$ rpm) stirrer. A three-blade propeller (diameter = 4 cm) was used. The latexes were subjected to high shear for 4 min in a 6-cm diameter unbaffled vessel, then filtered through a nylon cloth (63 mesh), and the retained solids washed with water. The dry weight of the coagulated material was determined as a measure of the mechanical stability. When no coagulated material was retained in the cloth, the particle size of the stirred latex was measured by DLS. An increase of the particle size suggests limited coagulation and hence the relative increase of the latex diameter was taken as a measure of the mechanical stability.

The salt tolerance of the latexes was determined by measuring either the amount of coagulum formed

or the increase in particle diameter when a 10-g sample of latex was mixed slowly under agitation with 10 cc of a salt solution and the mixture was kept at room temperature for 24 h. The salt solutions used were NaCl (0.1 M and 1 M); $CaCl_2$ (0.1 M and 1 M); and $Al_2(SO_4)_3$ (0.1 M and 0.5 M). In order to determine the freeze-thaw stability, the latexes were subjected to cycles where the samples were frozen at $-18^\circ C$ for 14 h and then allowed to thaw at room temperature for 14 h.

RESULTS AND DISCUSSION

First Series of Experiments

Kinetics

Figure 1 presents the effect of the initiator concentration on the evolution of the instantaneous conversion. It can be seen that the instantaneous conversion increased with the initiator content. In this figure, instantaneous conversion is defined as the fraction of the monomer already charged into the reactor converted to terpolymer

$$X_{ins} = \frac{M_{T_0} + F_M t - M_T}{M_{T_0} + F_M t} \quad (1)$$

where M_{T_0} is the amount of monomers in the initial charge, F_M the molar feed rate of the monomers, and M_T the amount of the unreacted monomers in the reactor at time t given by

$$\frac{dM_T}{dt} = -R_p + F_M \quad (2)$$

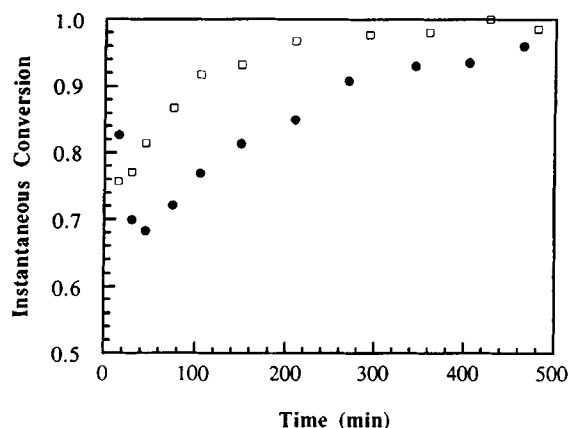


Figure 1 Effect of the initiator concentration on the time evolution of the instantaneous conversion. (□) Initiator = 1.05 wt %; (●) initiator = 0.52 wt %.

where R_p is the overall polymerization rate. Combining eqs. (1) and (2) the following equation for R_p can be obtained:

$$R_p = [M_{T_0} + F_M t] \frac{dX_{ins}}{dt} + F_M X_{ins}. \quad (3)$$

Equation (3) allows the calculation of the overall polymerization rate from the instantaneous conversion vs. time experimental curves. This calculation involves the difficulty of using differentials of data curves. These differentials were calculated from a low-order polynomial used to fit the data. High-order polynomials result in unstable values of the differentials. Figure 2 presents the evolution of the total number of latex particles in the reactor. It can be seen that new polymer particles were continuously nucleated during the process. This is in agreement

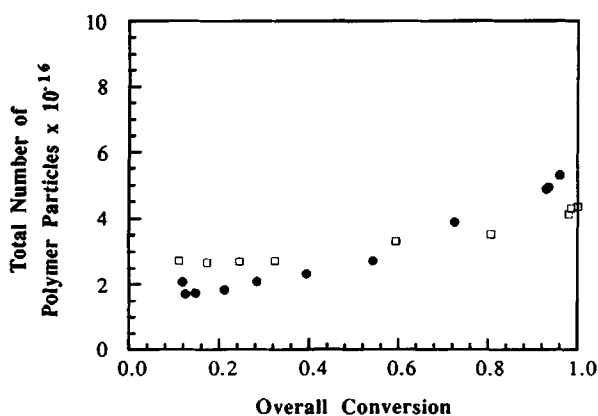


Figure 2 Effect of the initiator concentration on the total number of latex particles. (□) Initiator = 1.05 wt %; (●) initiator = 0.52 wt %.

with the results reported by Tang et al.²² who observed a significant secondary nucleation when the monomer was added as a miniemulsion. The values of R_p calculated from the data in Figure 1 together with the values of the total number of polymer particles presented in Figure 2 were used in an attempt to estimate the average number of radicals per particle, \bar{n} , from the following equation²⁸:

$$R_p = \{ (k_{pAA}P_A + k_{pBB}P_B + k_{pCA}P_C)[A]_p + (k_{pAB}P_A + k_{pBB}P_B + k_{pCB}P_C)[B]_p + (k_{pAC}P_C + k_{pBC}P_C + k_{pCC}P_C)[C]_p \} \frac{\bar{n}N_p}{N_A} \quad (4)$$

where $k_{p_{ij}}$ are the propagation rate constants, $[i]_p$ the concentration of monomer i in the polymer particles, N_p the total number of polymer particles in the reactor, and P_i is the time averaged probability of finding a growing chain with an ultimate unit of type i . Assuming the pseudo steady-state conditions for the free radicals, these probabilities are as follows:

$$P_A = \alpha / (\alpha + \beta + \gamma) \quad (5)$$

$$P_B = \beta / (\alpha + \beta + \gamma) \quad (6)$$

$$P_C = 1 - P_A - P_B \quad (7)$$

where

$$\alpha = (k_{pCA}k_{pBA}[A]_p + k_{pBA}k_{pCB}[B]_p + k_{pCA}k_{pBC}[C]_p)[A]_p \quad (8)$$

$$\beta = (k_{pAB}k_{pCA}[A]_p + k_{pAB}k_{pCB}[B]_p + k_{pCB}k_{pAC}[C]_p)[B]_p \quad (9)$$

$$\gamma = (k_{pAC}k_{pBA}[A]_p + k_{pBC}k_{pAB}[B]_p + k_{pAC}k_{pBC}[C]_p)[C]_p. \quad (10)$$

In order to calculate the concentrations of the monomers in the polymer particles the presence of HD should be taken into account in the equilibrium equations.¹⁴ Nevertheless, under the conditions used in the present work (high solids content, starved process), a rough estimation of the monomer concentrations can be obtained from the equilibrium equations and the overall material balances for the monomers by assuming that there is no HD in the system. For the sake of brevity these equations are not presented here.²⁸

The time evolution of the average number of radicals per particle calculated from Figures 1 and 2

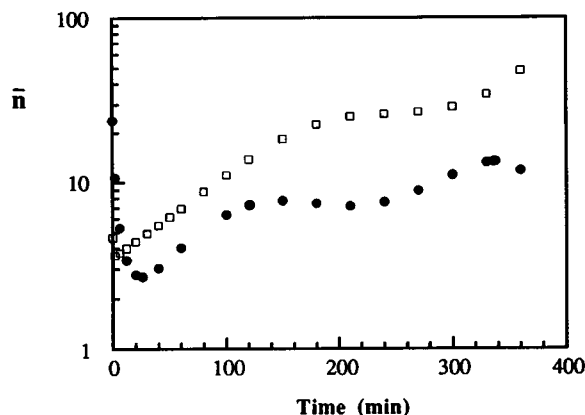


Figure 3 Effect of the initiator concentration on the average number of radicals per particle. (□) Initiator = 1.05 wt %; (●) initiator = 0.52 wt %.

using the approach described above is presented in Figure 3. The values of the propagation rate constants, k_p , and the partition coefficients, k_t^p , used in this calculation are given in Table III. In addition, Table IV presents the values of the reactivity ratios. It has to be pointed out that the \bar{n} values are affected by the inaccuracies involved in both the determination of the number of latex particles by DLS and the estimation of the concentrations of the monomers in the polymer particles. Nevertheless, these errors counteract one each other in some extent. Thus, the particle size measured by DLS is larger than the actual volume average diameter and this makes N_p to be underestimated and hence \bar{n} overestimated. On the other hand, the monomer concentrations calculated neglecting the effect of HD on the monomer partition are overestimated and therefore \bar{n} is underestimated. Figure 3 shows that polymerization proceeds according to Smith–Ewart Case 3 kinetics ($\bar{n} \gg 0.5$)²⁹ that is a result of large particle size (unswollen $dp_{t=75\text{min}} = 183\text{ nm}$) and the low termination rate constant of BuA ($k_{t\text{BuA}(60^\circ\text{C})} = 20 k_{p\text{BuA}}$ ³⁰). In addition, \bar{n} increased during polymerization because of the combined effect of the in-

Table III Values of the Parameters Used in the Calculation of \bar{n}

	A MMA	B BuA	C VAc
k_{pAA} (Ref. 32), k_{pBB} (Ref. 33), k_{pCC} (Ref. 32) ($\times 10^{-6}$) ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	1.12	0.416	4.26
k_A^p, k_B^p, k_C^p (Ref. 31)	0.025	0.0019	0.035

Table IV Reactivity Ratios (r_{ij})

$i \backslash j$	MMA	BuA	VAc
MMA	—	2.64 ^a	22.2 ^b
BuA	0.315 ^a	—	3.07 ^b
VAc	0.07 ^b	0.06 ^b	—

^a Estimated using the approach given in ref. 27.

^b Reference 26.

creasing particle size and the decreasing monomer concentration in the polymer particles. The increase of the polymer size reduces radical desorption. On the other hand, the lower the monomer concentration the larger the gel effect and the lower the monomer chain transfer rate (the lower the radical desorption).

The evolution of the terpolymer composition is shown in Figure 4. In this figure, the overall conversion is defined as the fraction of the total monomer in the recipe converted to terpolymer. At the beginning of the process, the terpolymer was richer in MMA and BuA than the feed (horizontal lines in Fig. 4), this effect being more acute for the MMA. On the other hand, the terpolymer formed at the beginning of the process contained almost no VAc. This behavior was caused by the widely different reactivity ratios of these monomers. Thus, Table IV shows that the reactivities of these monomers are $r_{\text{MMA}} > r_{\text{BuA}} \gg r_{\text{VAc}}$. Figure 4 shows that the homogeneity of the terpolymer improved when the instantaneous conversion increased as a result of the increase of the initiator concentration. This was

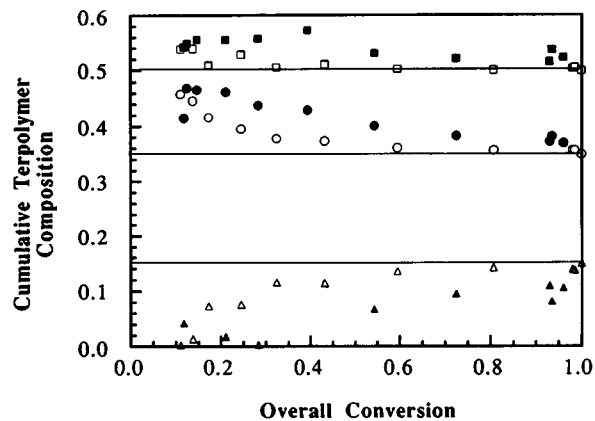


Figure 4 Effect of the initiator concentration on the cumulative terpolymer composition. 1.05 wt % initiator: (□) BuA; (○) MMA; (△) VAc. 0.52 wt % initiator: (■) BuA; (●) MMA; (▲) VAc.

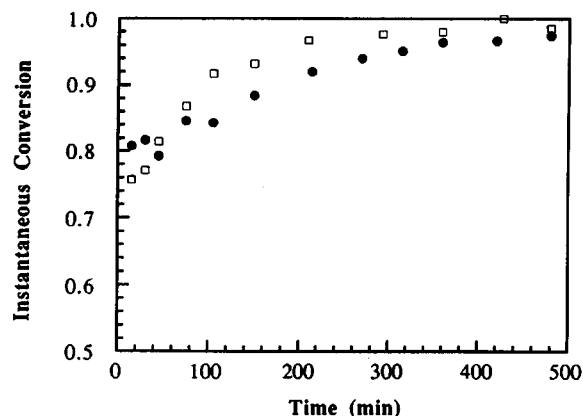


Figure 5 Effect of the amount of hexadecane on the instantaneous conversion. (□) HD = 2 wt %; (●) HD = 4 wt %.

caused by the fact that increasing polymerization rates brought the system nearer to the true starved conditions whereas the terpolymer formed has the same composition as the feed.

Figures 5 and 6 present the effect of the amount of cosurfactant on the polymerization rate and total number of polymer particles in the reactor. It can be seen that the polymerization rate decreased as the concentration of HD increased. On the other hand, calculations of the average number of radicals per particle showed that these polymerizations also proceeded according to Smith-Ewart Case 3 conditions.²⁹ For such a system, the only effect of the number of polymer particles on the kinetics is through the effect of the termination of free radicals in the aqueous phase (the extent of the aqueous phase termination increases as N_p decreases). However, the effect of HD concentration on N_p pre-

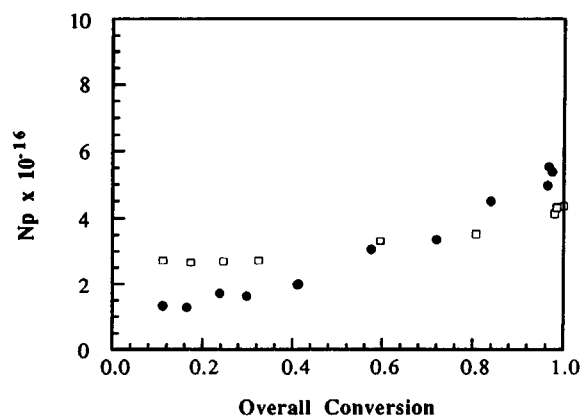


Figure 6 Effect of the HD concentration on the total number of polymer particles. (□) HD = 2 wt %; (●) HD = 4 wt %.

sented in Figure 6 cannot justify the polymerization rate change shown in Figure 5. This behavior can be explained by taking into account that the presence of HD in the monomer droplets reduces the free energy of mixing of the monomers in the monomer droplets. This increases the concentrations of the monomers in the monomer droplets and hence both the concentrations of the monomers in the polymer particles and the polymerization rate are reduced.²⁰ For these reactions, the evolution of the terpolymer composition showed a behavior similar to that found in the case of the effect of the initiator concentration, i.e., the homogeneity of the terpolymer improved when the polymerization rate increased and, at the beginning of the process, the terpolymer formed was richer in MMA and BuA than the feed.

Figures 7 and 8 present the effect of the feed-flow rate on the evolution of the instantaneous conversion and cumulative terpolymer composition, respectively. In these figures, the relative time is defined as the ratio between the current time and the total feeding time of each polymerization. For relative times greater than 1, the polymerizations proceeded in batch. At the beginning of the process when the monomers accumulate in the reactor, the instantaneous conversion is quite sensitive to the polymerization conditions whereas the sensitivity is substantially reduced afterward. This is shown in Figure 7 where it can be seen that the amount of monomers accumulated in the reactor at the beginning of the process decreased when the feed-flow rate decreased, namely, the system was closer to the complete starved conditions. For relative times greater than 0.5, the data are too close to allow a distinction between them. On the other hand, Figure

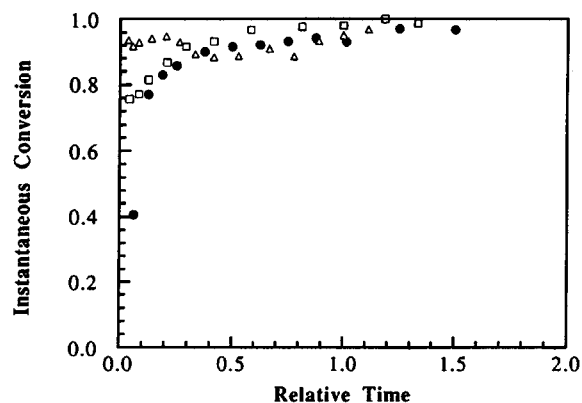


Figure 7 Effect of the feed-flow rate on the evolution of the instantaneous conversion. (●) Feeding time = 4 h; (□) feeding time = 6 h; (△) feeding time = 9 h.

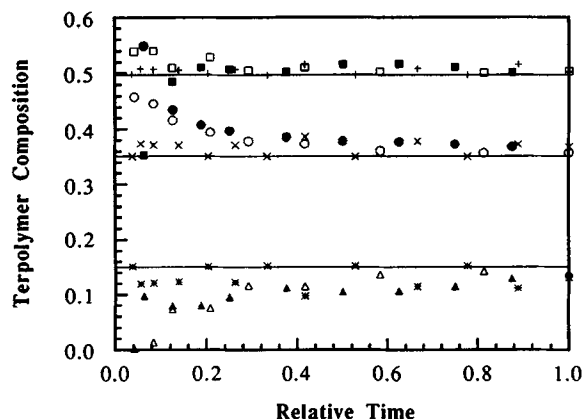


Figure 8 Effect of the feed-flow rate on the cumulative terpolymer composition. Feeding time 4 h: (■) BuA; (●) MMA; (▲) VAc. Feeding time 6 h: (□) BuA; (○) MMA; (△) VAc. Feeding time 9 h: (+) BuA; (×) MMA; (*) VAc.

8 shows that the closer the system to the starved conditions the more homogeneous the terpolymer formed.

Figure 9 presents the evolution of the instantaneous conversion for three different solids contents 33 wt %, 55 wt %, and 60 wt %. In these experiments the amount of initiator was proportional to the amount of monomer, i.e., to the solids content. On the other hand, calculations of the average number of radicals per particle showed that these polymerizations also proceeded according to Smith-Ewart Case 3 conditions. This means that polymerizations proceed under pseudo-bulk conditions and, for systems in which the monomer/initiator ratio is kept constant, one would expect to have the same conversion evolution if no radical termination in the aqueous phase occurs. However, Figure 9 shows that the instantaneous conversion increased with the solids content. This suggests that a significant radical termination occurred in the aqueous phase. These results were analyzed using the model developed by Urretabizkaia et al.³¹ for emulsion terpolymerization. This model showed that, for the conditions used in the experiments of Figure 9, the extent of the radical termination increased when the solids content decreased because the probability that

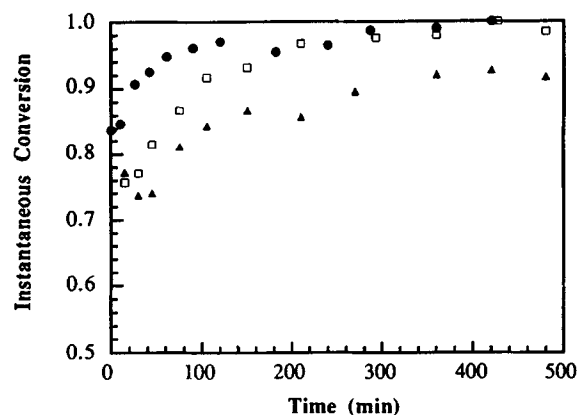


Figure 9 Evolution of the instantaneous conversion for different solids contents: (▲) 33 wt %; (□) 55 wt %; (●) 60 wt %.

a free radical entered into a polymer particle decreased. For these reactions the terpolymer composition evolved as in the previous cases: the greater the amount of monomer accumulated in the reactor the less homogeneous the terpolymer.

Latex Properties

All miniemulsion latexes were stable upon addition of the 0.1 M and 1 M solutions of NaCl and upon addition of the 0.1 M solution of CaCl₂. On the other hand, all latexes were coagulated by the 1 M solution of CaCl₂ as well as by the 0.1 M and 0.5 M solutions of Al₂(SO₄)₃. No coagulum was observed for all the latexes after the mechanical stability test. In addition, Table V presents the effect of the high shear on the particle size. It can be seen that a slight increase of the particle size was observed after the test indicating limited coagulation. All the latexes coagulated completely after the first cycle of the freeze-thaw test.

Second Series of Experiments

The goal of the second series of experiments was to investigate the effect of the operation variables on the feasibility of obtaining a 65 wt % solids content

Table V Effect of the High Shear on the Particle Size

Run	1	2	3	4	5	6	7
Solids Content	33	55	55	55	55	55	60
dp _{before test} (nm)	225	231	246	236	246	257	257
dp _{after test} (nm)	225	212	262	256	263	263	276

latex with low amount of coagulum. In this region, the latex viscosity shows a tremendous sensitivity toward the solids content and hence the achievement of a 65 wt % solids content is much more difficult than the 55 and 60 wt % runs shown in Table I. The operation variables studied were:

1. partition of the monomer between the initial charge and the feed;
2. feed flow rate;
3. type and concentration of emulsifier; and
4. sonication.

The polymerizations were carried out using the recipes given in Table II.

The results obtained in these series of experiments are summarized in Table VI. In order to show the difficulties in obtaining a 65 wt % solids content latex, run 8 was carried out using the same procedure as the first series of experiments but the concentration of anionic emulsifier was increased to 4 wt % (based on monomers). This experiment could not be completed because the latex completely coagulated during the batch preperiod. Some improvement was obtained using a mixture of anionic emulsifier (Alipal CO 436; 2 wt %) and nonionic emulsifier (Brij 35; 2 wt %) but still a 10 wt % of coagulum was formed (run 9).

The effect of the partition of the monomer between the initial charge and the feed was investigated in Experiments 9–11. In these experiments

Table VI Results Obtained in the Second Series of Experiments

Experiment	Coagulum (wt %)	Final Overall Conversion ^a	Solids Content Based on Conversion (wt %)
8	100	—	—
9	10	—	64.0
10	2.8	0.99	64.8
11	100	—	—
12	2.7	0.97	63.3
13	100	—	—
14	0.7	0.99	63.2
15	4.2	0.97	63.7
16	1.7	1.00	64.8
17	1.8	1.00	65.0
18	4.0	0.99	64.6

^a Including coagulum.

initial charges with different solids contents were used: 65 wt %, 55 wt %, and 45 wt %. The solids contents of the feeds were: 65 wt %, 66.1 wt %, and 68 wt %, respectively. In addition, a mixture of anionic emulsifier (Alipal CO 436; 2 wt %) and nonionic emulsifier (Brij 35; 2 wt %) was used. Table VI shows that a 10 wt % of coagulum was formed in Experiment 9 (initial charge: 65 wt %), the formation of coagulum starting early in the batch polymerization of the initial charge. The amount of coagulum was significantly reduced in run 10 in which a 55 wt % solids content initial charge was used. The coagulum was mainly located at the stirrer and could not be observed during the process. The solids content of the initial charge was additionally lowered to 45 wt % in run 11. In this run, the 68 wt % solids content feed was a highly viscous emulsion that hindered the heat transfer in the continuous flow cell of the sonifier and polymerization occurred after 60 min plugging the cell. Experiments 9–11 showed that when a high solids content miniemulsion was used as initial charge, coagulum was formed during the batch polymerization of the initial charge, whereas when a low solids content initial charge was employed, the solids content of the feed was excessive and the continuous flow cell was plugged. A compromise between these situations was obtained using a 55 wt % solids content initial charge and a 66.1 wt % solids content feed.

Comparison between the results obtained in runs 10 and 12 showed that the increase of the feeding time from 6 h (run 10) to 9 h (run 12) had no effect on the amount of coagulum.

The effect of the type and concentration of emulsifier on the feasibility of the process was investigated in runs 10 and 12–16. Table VI shows that a mixture of anionic and nonionic emulsifiers was needed to stabilize the system. The process could not be carried out using only the anionic emulsifier (Alipal CO 436; 4 wt %), run 13, because the viscosities of the initial charge and the feed were too high and a large amount of coagulum was formed in both the reactor and the continuous flow cell. On the other hand, a significant reduction of the amount of coagulum was observed when the HLB of the nonionic emulsifier was reduced by using Brij 98 instead of Brij 35. However, when Alipal CO 436 was substituted by SLS the amount of coagulum increased (run 15). Surprisingly, the amount of coagulum decreased when the total amount of the emulsifier was reduced in run 16. Comparison between run 10 and run 17 shows that the amount of coagulum decreased when the feed was not subjected

Table VII Salt Tolerance of the 65 wt % Latexes

Run	Coagulum (wt %)					
	NaCl		CaCl ₂		Al ₂ (SO ₄) ₃	
	0.1M	1M	0.1M	1M	0.1M	1M
8 ^a	—	—	—	—	—	—
9 ^a	—	—	—	—	—	—
10	< 0.1	1.4	< 0.1	3	0.7	5.1
11 ^a	—	—	—	—	—	—
12	1.3	1.9	1.0	2.4	1.3	19.7
13 ^a	—	—	—	—	—	—
14	0.4	0.6	0.5	1.3	0.5	100
15	0.1	0.1	0.2	0.1	< 0.1	100
16	0.3	0.3	0.2	1.1	0.3	6.8
17	< 0.1	< 0.1	< 0.1	0.2	< 0.1	16.2
18	< 0.1	0.1	0.1	0.2	0.1	42.2

^a Latexes completely coagulated during polymerization.

to sonication. However, the amount of coagulum increased when neither the initial charge nor the feed were sonicated, run 18.

Table VII summarizes the results of the chemical stability test. Comparison with the results obtained for the latexes from the first series of experiments showed that chemical stability was significantly increased by using a mixed surfactant system. In addition, Table VII shows that the latexes were quite stable upon addition of NaCl, CaCl₂, and 0.1M solution of Al₂(SO₄)₃ but coagulated with a 0.5M solution of Al₂(SO₄)₃. All the latexes coagulated completely after the first cycle of the freeze-thaw test.

CONCLUSIONS

The effect of the operation conditions on the kinetics of the high solids content, semicontinuous miniemulsion terpolymerization of butyl acrylate, methyl methacrylate, and vinyl acetate was investigated. It was found that continuous nucleation occurred during the polymerization that proceeded according to Smith-Ewart Case 3 kinetics. In addition, the composition of the polymer formed at the beginning of the process was richer in MMA and BuA than the feed and the polymer contained almost no VAc. The homogeneity of the terpolymer improved when the amount of monomer accumulated in the reactor decreased.

A preliminary investigation of the effect of the operation variables on the feasibility of obtaining a

65 wt % solids content latex with low amount of coagulum was carried out. This goal was achieved by using a 55 wt % solids content initial charge with a 66.1 wt % solids content feed and mixed emulsifier system [Alipal CO 436 (2 wt %) and Brij 98 (2 wt %)]. The amount of coagulum formed increased when either the anionic emulsifier was used alone (4 wt %) or the Alipal CO 436 was substituted by SLS. The feed-flow rate had no effect on the amount of coagulum formed. The amount of coagulum increased when neither the initial charge nor the feed were sonicated. In addition, solids contents of the initial charge greater (65 wt %) and less (45 wt %) than 55 wt % led to complete coagulation.

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NOMENCLATURE

dp	Polymer particle diameter (nm)
F_M	Molar feed rate of the monomers (mol s ⁻¹)
$[i]_p$	Concentration of monomer i in the polymer particles (mol cm ⁻³)
k_i^p	Partition coefficient: ϕ_i^w/ϕ_i^p
k_{pji}	Propagation rate constant (cm ³ mol ⁻¹ s ⁻¹)
M_{T_0}	Initial amount of monomers in the reactor (mol)
M_T	Amount of unreacted monomers (mol)
\bar{n}	Average number of radicals per particle
N_A	Avogadro's number
N_p	Total number of polymer particles in the reactor
P_i	Time averaged probability of finding a free radical with ultimate unit of type i in the polyme particles
R_p	Overall polymerization rate (mol s ⁻¹)
t	Time (s)
X_{ins}	Instantaneous conversion

Subscripts

p	Particle phase
w	Aqueous phase

Greek Symbols

α	Parameter given by eq. (8)
β	Parameter given by eq. (9)
γ	Parameter given by eq. (10)
ϕ_i^j	Volume fraction of component i in phase j

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