

Minimum-Time Strategy to Produce Nonuniform Emulsion Copolymers. II. Open-Loop Control

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SYNOPSIS

An iterative approach was developed to determine the optimal monomer addition policies in real emulsion copolymerization systems in which only limited kinetic information is available. The approach was applied to obtain widely different copolymer composition profiles for the emulsion copolymerization of butyl acrylate and styrene. The approach involves a series of semicontinuous emulsion copolymerizations carried out in an open-loop control mode. Each reaction was used to obtain an estimation of the kinetics of the process that was used to calculate the monomer addition profiles for the next experiment. The method is model-independent and converges rapidly. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the first article of this series,¹ a method for calculating the optimal monomer addition policy to produce emulsion copolymers with a given composition profile was presented. The method was applied by simulation to obtain widely different composition profiles. The use of this approach for a real emulsion polymerization system requires one to have a good knowledge of both the mechanisms involved in the process and the values of the parameters of the kinetic model. This includes the nucleation process and the rate coefficients that control the average number of radicals per particle, namely, entry, exit, and termination rate coefficients. However, none of them can be accurately predicted. This makes the determination of the optimal monomer addition policies for a real emulsion copolymerization system difficult. A semiempirical iterative approach for the determination of the optimal monomer addition profile to obtain homogeneous copolymers in the case of emulsion copolymerization systems for which only limited information is available was applied to several emulsion copolymerization systems including some using technical monomers and reactors with limited capacity for heat removal.²⁻⁷

In this article, the semiempirical iterative approach² is used to implement in an open-loop control scheme the optimal monomer addition policies during the seeded emulsion copolymerization of butyl acrylate and styrene to obtain widely different copolymer composition profiles. The copolymer composition profiles obtained were those considered also in the first article of this series, i.e., a profile that goes through a maximum (profile 1), a continuously increasing profile (profile 2), and a continuously decreasing profile (profile 3).

EXPERIMENTAL

Monomers, butyl acrylate (BuA or A), and styrene (St or B) were washed with a 2.5*N* NaOH aqueous solution and then distilled under a reduced pressure of dry nitrogen. The purified monomers were stored at -18°C until use. The rest of materials were used as received. Deionized water was used throughout the work. Polymerizations were carried out in a 2 L reactor equipped with stirrer, reflux condenser, sampling device, and inlet system for nitrogen. The seeds were prepared in a batch process using the recipes given in Table I. These polymerizations were carried out at 70°C for 3 h. Then, the latices were heated to 90°C for 48 h to decompose the initiator. The diameters of the seeds are given in Tables II-

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Table I Recipes Used to Prepare the Seeds in a Batch Process

	Profile 1	Profile 2	Profile 3
Styrene (g)	500	620	500
Water (g)	1520	1225	1520
Sodium lauryl sulfate (g)	15	21	15
NaHCO ₃ (g)	1.4	1.74	1.4
K ₂ S ₂ O ₈ (g)	4	5.2	4

IV together with the recipes used for the optimal processes. The seed, all the initiator and buffer, as well as a fraction of the monomers, water, and emulsifier were initially charged into the reactor. The initial amounts of the monomers were calculated as detailed in the first article of this series.¹ Notice that this calculation only requires one to know the monomer partition coefficients and the values of reactivity ratios; therefore, it can be carried out a priori. The feed was divided into three streams: Two were neat monomers (butyl acrylate and styrene) and the other was an aqueous solution of the remaining surfactant. The three streams were fed into the reactor using computer-driven pumps. The feed rates of the monomers were calculated by means of the approach detailed below. The aqueous solution of the emulsifier was fed at a constant flow rate which was adjusted to finish the addition at the same time as that of the longer monomer addition. The amount of emulsifier was chosen attempting to avoid both coagulation and secondary nucleation. All the polymerizations were carried out at 70°C. Samples were withdrawn during the reaction, the polymerization short-stopped with hydroquinone, the overall conversion measured gravimetrically, and the cumulative copolymer composition determined by measuring the residual monomers by gas chroma-

tography. The particle size was measured by dynamic light scattering.

APPLICATION OF THE SEMIEMPIRICAL APPROACH

Arzamendi and Asua² considered that a reasonable estimation of the evolution of the average number of radicals per particle, \bar{n} , can be obtained from a semicontinuous emulsion copolymerization carried out using the right initial charge and monomer feed rates *not too different from the optimal ones*. Based on this assumption, they proposed the following semiempirical approach:

1. The initial charge required to produce the desired copolymer composition at the beginning of the process is calculated. This calculation only requires the values of the reactivity ratios and monomer partition coefficients that can be obtained from the literature or determined by independent experiments with a moderate amount of experimental work.
2. A semicontinuous emulsion polymerization using the initial charge of the reactor calculated in step 1 and arbitrary monomer feed rates is carried out. To obtain homogeneous copolymers, Arzamendi and Asua² used constant flow rates, but, as shown below, better choices can be made when copolymer composition profiles are desired. The time evolution of the overall conversion, copolymer composition, and number of polymer particles is measured.
3. From these results, the evolution of \bar{n} was determined and correlated with $(\phi_p^p x d_p^2)$

Table II Recipe Used for the Semicontinuous Emulsion Polymerizations to Obtain Profile 1; $T = 70^\circ\text{C}$

	Initial Charge	Stream 1	Stream 2	Stream 3
Styrene (g)	75	—	69	—
Butyl acrylate (g)	21.97	227	—	—
Water (g)	359	—	—	200
Sodium lauryl sulfate (g)	4.8	—	—	9
K ₂ S ₂ O ₈ (g)	0.80	—	—	—
NaHCO ₃ (g)	1.56	—	—	—
Seed (g)	306.8	—	—	—
dp_{seed} (nm)	60	—	—	—
Np_0 (no. polymer particles g ⁻¹) $\times 10^{15}$	2.00	—	—	—

Table III Recipe Used for the Semicontinuous Emulsion Polymerizations to Obtain Profile 2; $T = 70^\circ\text{C}$

	Initial Charge	Stream 1	Stream 2	Stream 3
Styrene (g)	102.67	—	190	—
Butyl acrylate (g)	11.75	238	—	—
Water (g)	725	—	—	200
Sodium lauryl sulfate (g)	5.32	—	—	12
$\text{K}_2\text{S}_2\text{O}_8$ (g)	0.80	—	—	—
NaHCO_3 (g)	1.56	—	—	—
Seed (g)	265	—	—	—
dp_{seed} (nm)	68	—	—	—
Np_0 (no. polymer particles g^{-1}) $\times 10^{15}$	1.89	—	—	—

through a polynomial fitting. The rationale for this choice is that \bar{n} depends on ϕ_p^p because the volume fraction of the polymer in the latex particles influences the termination rate constant in the polymer particles through the gel effect. In addition, \bar{n} increases with the latex particle diameter for Smith–Ewart Cases I and III.⁸ For the Smith–Ewart Case I, \bar{n} is proportional to d_p^2 because of the effect of dp on the desorption rate coefficient, and for the Smith–Ewart Case III, \bar{n} is proportional to $d_p^{3/2}$. Because the difference between these dependencies is not a large one, Leiza et al.^{3,5} chose to correlate \bar{n} with $(\phi_p^p x d_p^2)$. Implicit in this choice is the assumption that the effect of the composition of the monomer mixture on \bar{n} can be neglected. This assumption is reasonable for homogeneous copolymers because the composition of the monomer mixture has to be almost constant during the process.

4. The \bar{n} vs. $(\phi_p^p x d_p^2)$ relationship calculated in step 3 and the time evolution of Np measured in step 2 are used to calculate a new monomer addition profile by means of the adequate op-

timization method. This addition profile is used for the next experiment.

5. Steps 3 and 4 are repeated until the desired copolymer composition is obtained.

This approach was used to obtain homogeneous copolymers.^{2–7} When copolymers with a given composition profile are desired, the approach cannot be straightforwardly applied because the monomer addition rate at a given time depends on the rest of the process.¹ In addition, the effect of the composition of the monomer mixture on \bar{n} cannot be neglected. Therefore, a variation of the approach summarized above was used to determine the optimal monomer addition policies for the three copolymer composition profiles desired.

Three main changes have been included in the semiempirical approach. First, the initial charge and the monomer addition profiles of the first experiment of the series were calculated by means of the optimization method described in the first article of this series¹ using the kinetic model and the values of the parameters given in that article. Second, as \bar{n} depends on dp , ϕ_p^p , and the composition of the monomer mixture and all of them change substan-

Table IV Recipe Used for the Semicontinuous Emulsion Polymerizations to Obtain Profile 3; $T = 70^\circ\text{C}$

	Initial Charge	Stream 1	Stream 2	Stream 3
Styrene (g)	1.88	—	292	—
Butyl acrylate (g)	94.86	156	—	—
Water (g)	712.5	—	—	200
Sodium lauryl sulfate (g)	4.5	—	—	12
$\text{K}_2\text{S}_2\text{O}_8$ (g)	0.80	—	—	—
NaHCO_3 (g)	1.56	—	—	—
Seed (g)	250	—	—	—
dp_{seed} (nm)	64.5	—	—	—
Np_0 (no. polymer particles g^{-1}) $\times 10^{15}$	1.63	—	—	—

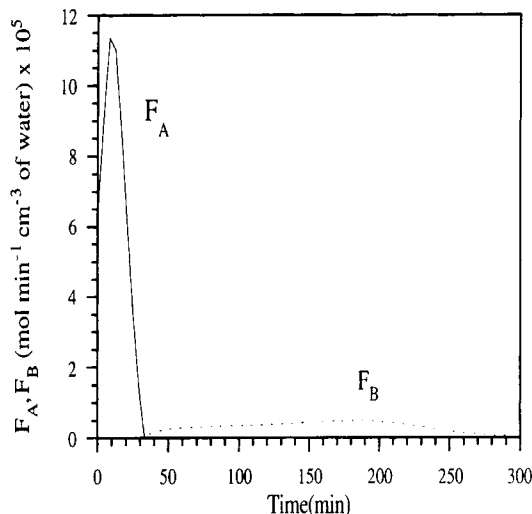


Figure 1 Monomer feed rates calculated from the theoretical model for run 1a during the semiempirical approach to obtain profile 1: (—) F_A ; (---) F_B .

tially during the polymerization, no attempt to correlate \bar{n} with these variables was made. A more empirical alternative was chosen and $\bar{n}N_p/Np_0$ was correlated with the overall conversion, X_T , with N_p being the number of polymer particles, and Np_0 , the number of polymer particles in the seed. When neither coagulations nor secondary nucleations occur, $N_p = Np_0$. Third, the optimization approach developed by de la Cal et al.¹ has to be used to calculate the monomer feed rates for the next experiment. For homogeneous copolymers, this alternative is close to that adopted by Schoonbrood et al.⁷

Profile 1

The copolymer composition profile 1 presented a maximum and was given by the following equation:

$$Y_A = 0.2 + 2.3X_T - 2.3X_T^2 \quad (1)$$

where Y_A is the instantaneous copolymer composition referred to BuA, and X_T , the overall conversion.

The initial charge and the monomer addition profiles for the first experiment were calculated by means of the optimization method presented in the first article of this series¹ using the kinetic model and the values of the parameters presented in the appendix and Table I, respectively, of that article. The initial charge is given in Table II and the monomer feed rates presented in Figure 1. Run 1a was carried out under these conditions and the evolutions of the overall conversion, copolymer composition,

and number of polymer particles measured. Figure 2 presents a comparison between the experimental results and the desired values of the cumulative copolymer composition. The experimental values of the cumulative composition were calculated from the amounts of the unreacted monomers in the reactor measured by GC. Even through the experimental data were affected by some experimental noise, it seems from Figure 2 that the desired copolymer composition were almost achieved. However, to analyze these data, one has to bear in mind that substantial drifts of the instantaneous copolymer compositions are required for a modest change of the cumulative value and that the larger the overall conversion the more acute the effect. This behavior is illustrated in Figure 3 where the instantaneous copolymer compositions are compared. It has to be pointed out that the experimental instantaneous copolymer composition was determined by derivation of the experimental cumulative copolymer composition and, hence, affected by the error due to the derivation. Nevertheless, Figure 3 shows that experimental copolymer composition profile deviated significantly from the desired one. To have a better estimation of the kinetics of the process, the variation of $\bar{n}N_p/Np_0$ during run 1a was calculated (Fig. 4).

A polynomial was used to fit the $\bar{n}N_p/Np_0$ vs. X_T data of Figure 4. This polynomial was used to predict the kinetics of the system in the optimization approach employed to obtain the initial charge and the monomer addition profiles for the next experi-

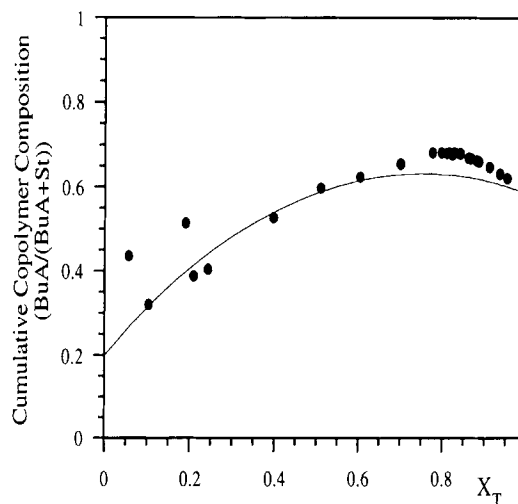


Figure 2 Comparison between (—) desired values and (●) experimental results of the cumulative copolymer composition obtained in run 1a during the semiempirical approach to obtain profile 1.

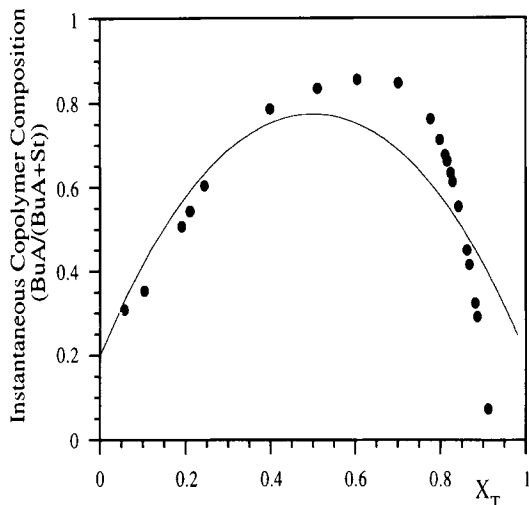


Figure 3 Comparison between (—) desired values and (●) experimental results of the instantaneous copolymer composition obtained in run 1a.

ment. It was found that the initial charge was the same that for run 1a. The monomer addition profiles are presented in Figure 5. These feed rate profiles were used in run 1b.

Figure 6 presents a comparison between the experimental results and the desired values of the cumulative copolymer composition. It can be seen that, at the beginning of the process, the copolymer was richer in styrene than desired and that the reverse occurred at the end of the polymerization. The variation of $\bar{n}N_p/Np_0$ during run 1b was calculated and this information used to calculate the initial charge and monomer addition profiles for run 1c. The initial charge was the same than for runs 1a and 1b and

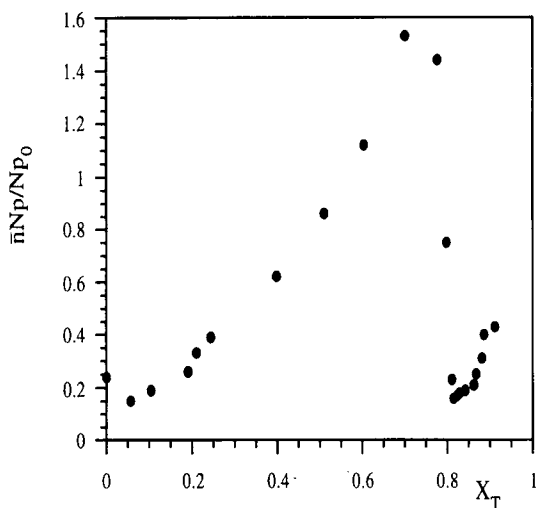


Figure 4 Variation of $\bar{n}N_p/Np_0$ in run 1a.

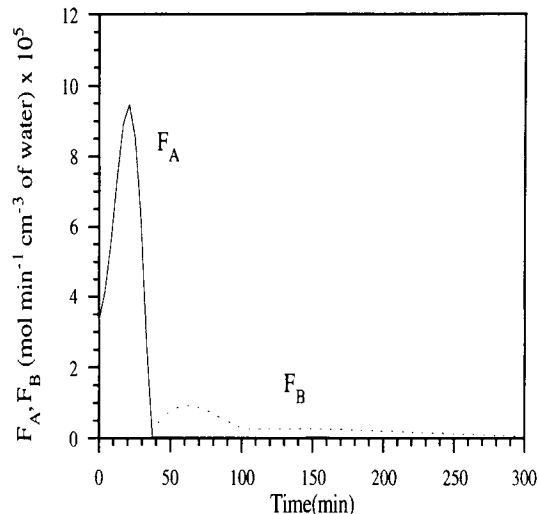


Figure 5 Monomer feed rates used in run 1b: (—) F_A ; (---) F_B .

the monomer feed rates are presented in Figure 7. Comparison of these monomer addition profiles shows that the initial feed rate of butyl acrylate was increased to avoid the formation of a copolymer too rich in styrene. However, Figure 8 shows that the improvement was not enough. Possibly, the difficulties in obtaining the desired copolymer composition profile at the beginning of the process were due to a poor determination of the starting time of the polymerization. The open-loop control is sensitive to errors in setting the exact time at which polymerizations begin. In the present work, the

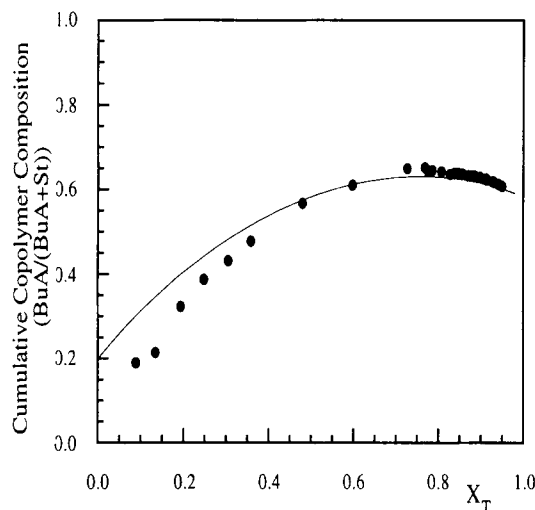


Figure 6 Comparison between (—) desired values and (●) experimental results of the cumulative copolymer composition obtained in run 1b during the semiempirical approach to obtain profile 1.

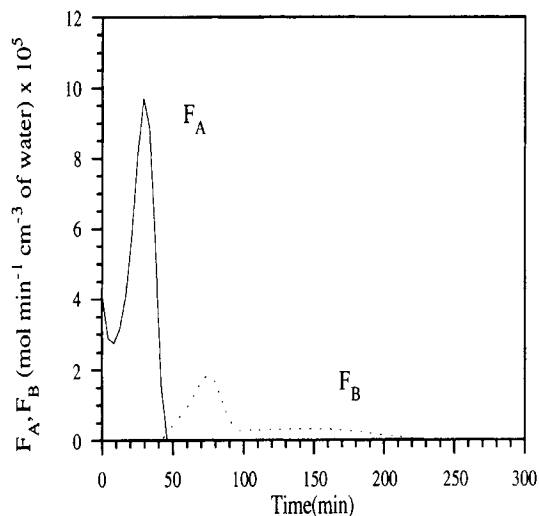


Figure 7 Monomer feed rates used in run 1c: (—) F_A ; (---) F_B .

starting time was taken as the time at which the reactor temperature increased 0.1°C . Therefore, this method allows for some batch polymerization before starting the monomer feeds. The batch polymerization of the styrene-rich initial charge would lead to initial copolymer compositions similar to those found in runs 1b and 1c.

Two more polymerizations were needed to achieve the convergence of the iterative approach. Figure 9 presents the monomer feed rates used in run 1e in which the desired copolymer composition profile was obtained (Fig. 10). Five experiments were required to determine the optimal policy. This is a very modest amount of work as compared with that required to develop a kinetic model for a emulsion polymerization process.⁹⁻¹¹

Profile 2

Profile 2 was a continuously increasing copolymer composition profile given by the following equation:

$$Y_A = 0.1 + 0.25X_T + 0.55X_T^2 \quad (2)$$

where Y_A is the copolymer composition referred to BuA, and X_T , the overall conversion.

The initial charge and the monomer addition profiles for the first experiment were calculated by means of the optimization method presented in the first article of this series¹ using the kinetic model and the values of the parameters detailed in the appendix and Table I, respectively, of that article. The initial charge is given in Table III and the monomer feed rates presented in Figure 11. Run 2a was carried

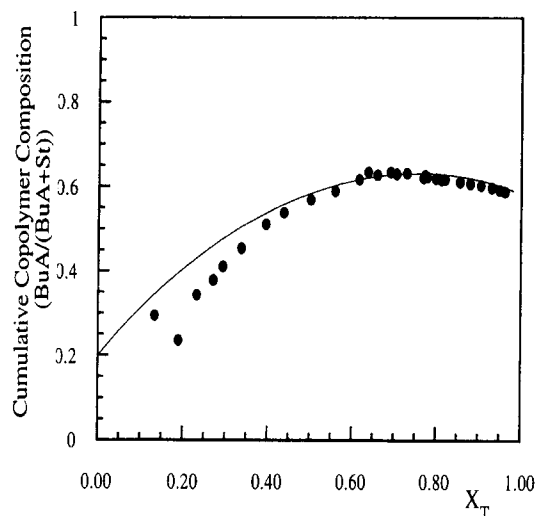


Figure 8 Comparison between (—) desired values and (●) experimental results of the cumulative copolymer composition obtained in run 1c during the semiempirical approach to obtain profile 1.

out under these conditions and the evolutions of the overall conversion, copolymer composition, and number of polymer particles were measured. Figure 12 presents a comparison between experimental results and desired values of the cumulative copolymer composition. It can be seen that the initial styrene content of the copolymer was higher than the desired one, whereas the reverse occurred at the end of the polymerization. The evolution of $\bar{n}N_p/N_{p0}$ during run 2a was calculated and this information used to calculate the initial charge and the monomer addition profiles for the next experiment. It was found

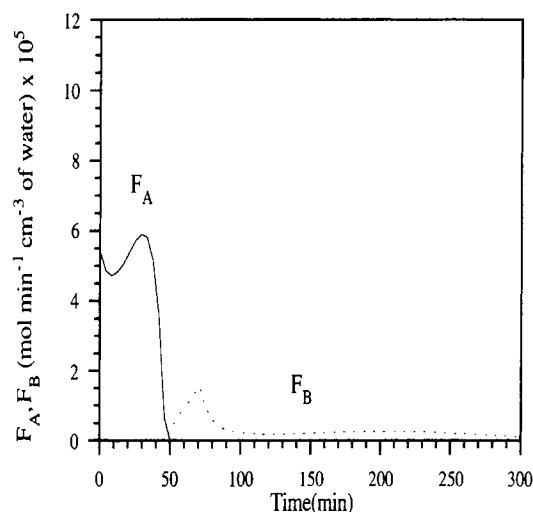


Figure 9 Monomer feed rates used in run 1e: (—) F_A ; (---) F_B .

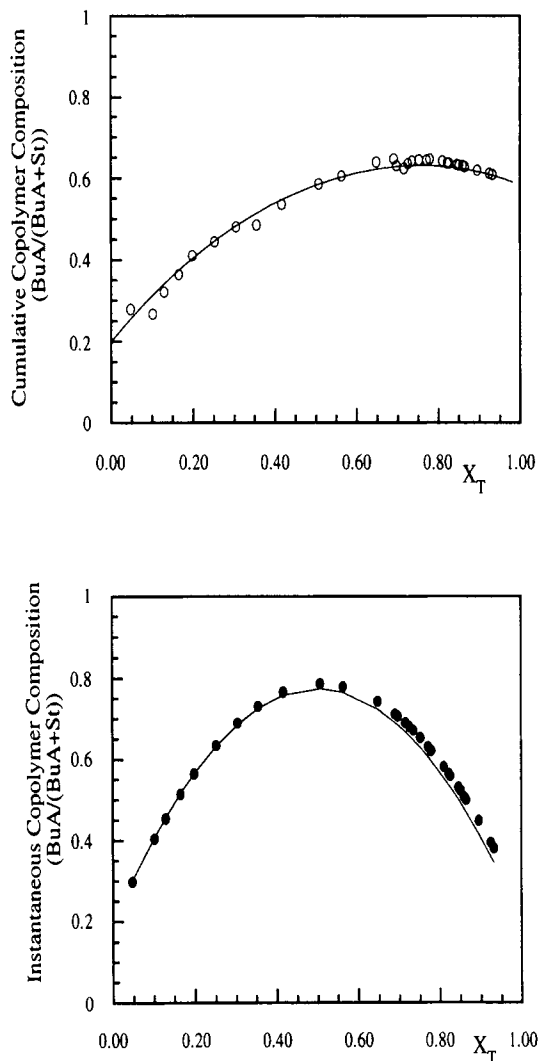


Figure 10 Comparison between (—) desired values and experimental results of the (○) cumulative and (●) instantaneous copolymer composition obtained in run 1e during the semiempirical approach to obtain profile 1.

that the initial charge was the same as that for run 2a that is presented in Table III. The monomer addition profiles are presented in Figure 13. These feed rate profiles were used for the next experiment.

A semicontinuous emulsion copolymerization run 2b was carried out using the recipe given in Table III and the feed rate profiles presented in Figure 13. Figure 14 presents a comparison between the experimental results and the desired values of the cumulative copolymer composition. It can be seen that a fairly good agreement was obtained, namely, that run 2b was carried out under optimal conditions. In this case, only two experiments were required to determine the optimal policy.

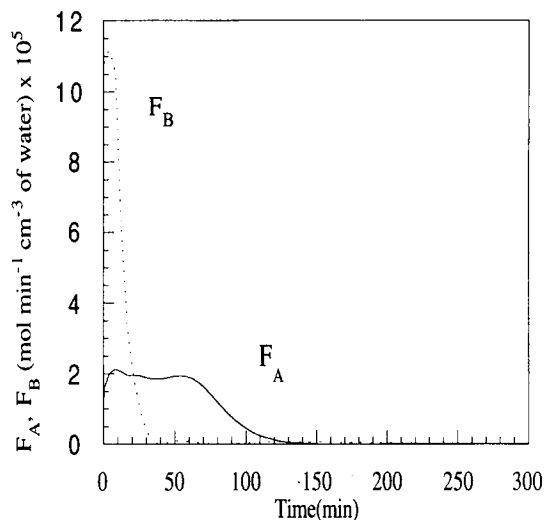


Figure 11 Monomer feed rates calculated from the theoretical model for run 2a during the semiempirical approach to obtain profile 2: (—) F_A ; (---) F_B .

Profile 3

Profile 3 was a continuously decreasing copolymer composition profile given by

$$Y_A = 0.9 - 1.35X_T + 0.55X_T^2 \quad (3)$$

The initial charge and the monomer addition profiles for the first experiment were calculated using the theoretical model described in the first article of this series.¹ Figure 15 presents the monomer addition profiles and the initial charge is given in Table

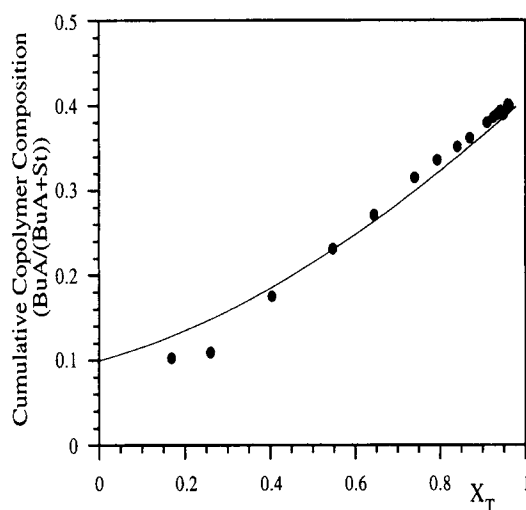


Figure 12 Comparison between (—) desired values and (●) experimental results of the cumulative copolymer composition obtained in run 2a during the semiempirical approach to obtain profile 2.

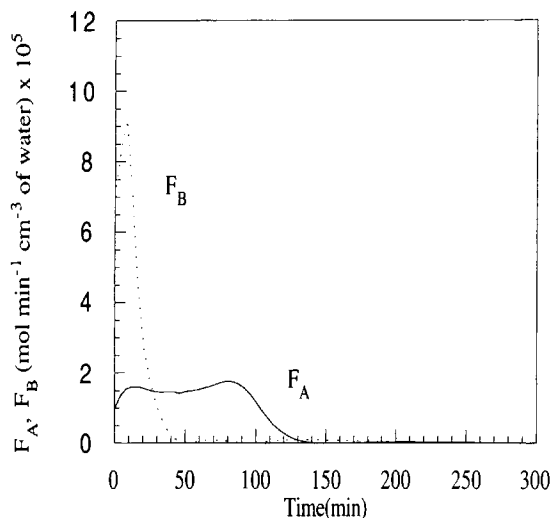


Figure 13 Monomer feed rates used in run 2b during the semiempirical approach to obtain profile 2: (—) F_A ; (---) F_B .

IV. Run 3a was carried out under these conditions and the cumulative copolymer composition obtained is presented in Figure 16. It can be seen that the experimental copolymer composition deviated significantly from the desired profile. The variation of $\bar{n}Np/Np_0$ during run 3a was calculated and this information used to calculate the initial charge and monomer addition profiles for run 3b.

Figure 17 presents the evolution of the cumulative copolymer composition in run 3b. Comparison with Figure 16 shows that the copolymer composition

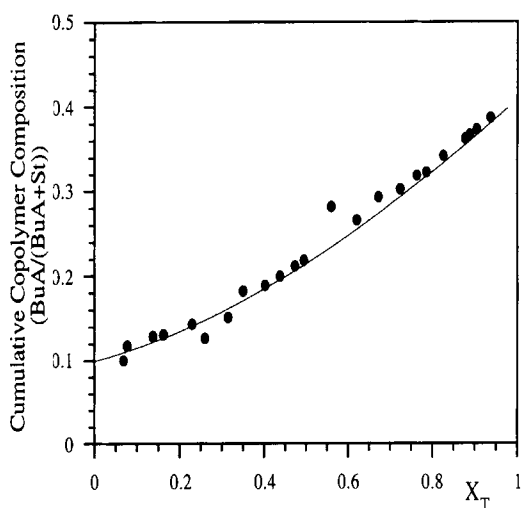


Figure 14 Comparison between (—) desired values and (●) experimental results of the cumulative copolymer composition obtained in run 2b during the semiempirical approach to obtain profile 2.

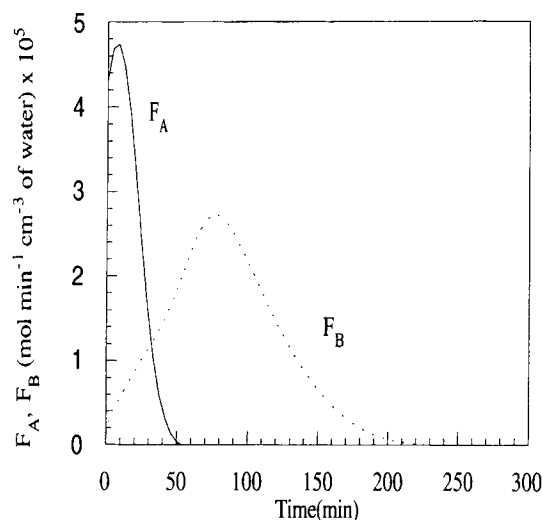


Figure 15 Monomer feed rates used in the semiempirical approach to obtain profile 3: (—) F_A ; (---) F_B .

profile obtained in run 3b deviated from the desired one by more than that obtained in run 3a, namely, it seemed that the approach diverged. Therefore, it was suspected that some error was made during run 3b. To check this point, run 3b was repeated (run 3b'). The results are presented in Figure 17. It can be seen that a good reproducibility was obtained and no other cause of this apparent divergence was found. The variation of $\bar{n}Np/Np_0$ during run 3b was calculated and the initial charge and monomer addition profiles for run 3c determined. It was found

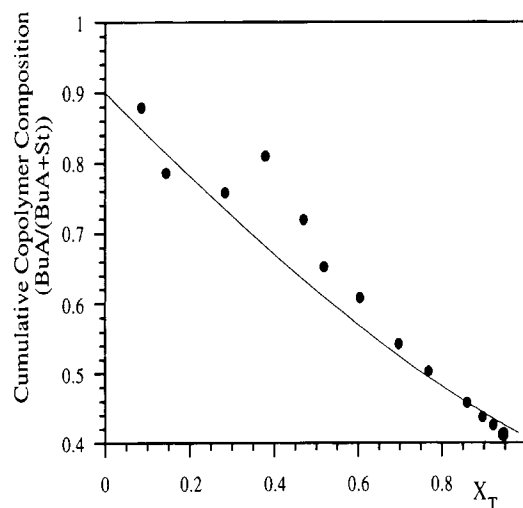


Figure 16 Comparison between (—) desired values and (●) experimental results of the cumulative copolymer composition obtained in run 3a during the semiempirical approach to obtain profile 3.

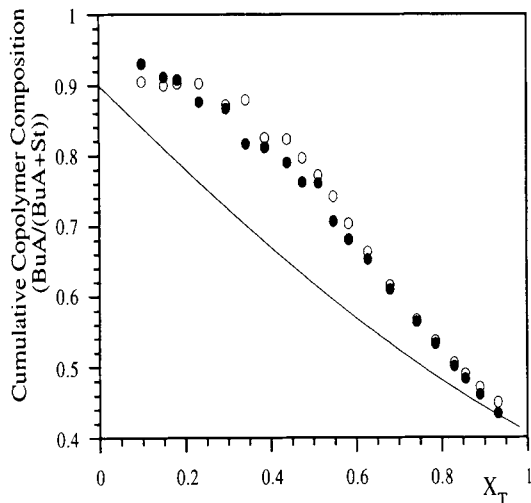


Figure 17 Comparison between (—) desired values and experimental results of the cumulative copolymer composition obtained in runs (●) 3b and (○) 3b' during the semiempirical approach to obtain profile 3.

that the initial charge was the same than for runs 3a and 3b.

Figure 18 presents the evolution of the cumulative copolymer composition in run 3c. It can be seen that the correction of the monomer feed rates was excessive. The variation of $\bar{n}Np/Np_0$ during run 3c was calculated and this information used to calculate the initial charge and monomer addition profiles for run 3d. The initial charge was the same as that for the other experiments in this series and the monomer addition profiles are given in Figure 19. The evolution of the copolymer composition during run 3d is presented in Figure 18. It can be seen that the desired copolymer composition profile was obtained, namely, run 3d was carried out under optimal conditions.

COMPARISON WITH THE POWER FEED PROCESS

The results obtained under the optimal conditions were compared with those obtained by means of the power feed processes in which the feeding times were equal to the process time of the optimal processes and the feed composition equal to the desired copolymer composition profile. Therefore, the end conversion is achieved with a larger time process. When the feed time was finished, the polymerization was continued for about 60 min to achieve the same conversion as that of the optimal approach. Simulations carried out in part one of this series¹ showed

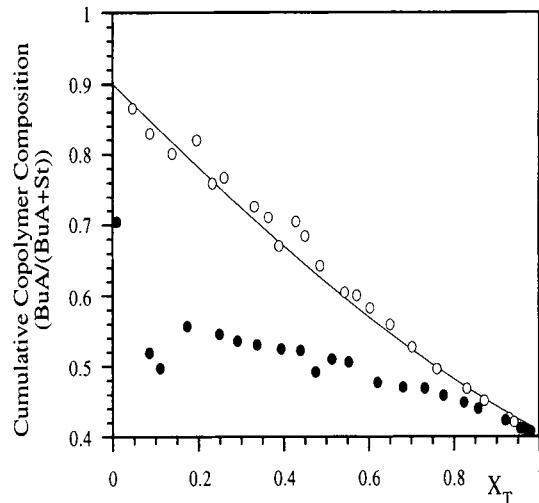


Figure 18 Comparison between (—) desired values and experimental results of the cumulative copolymer composition obtained in runs (●) 3c and (○) 3d during the semiempirical approach to obtain profile 3.

that the differences in copolymer composition between the optimal process and the power feed method were larger for profile 1 than for the other profiles. Therefore, profile 1 was chosen for comparison. Figure 20 presents a comparison between the copolymer composition profiles obtained by means the optimal and the starved processes for profile 1. It can be seen that the desired copolymer composition profile was obtained through the optimal process, whereas significant deviations were found for the power feed process.

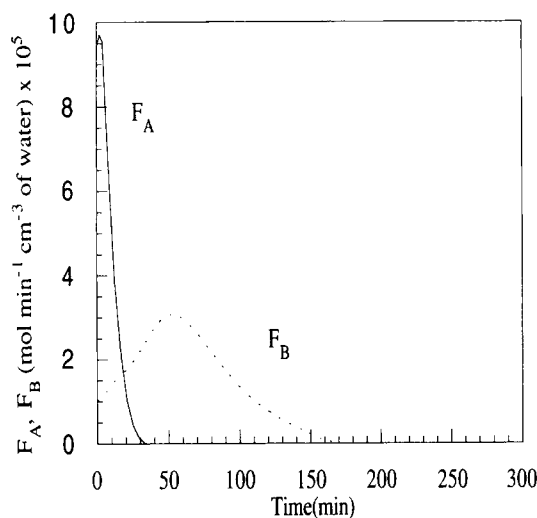


Figure 19 Monomer feed rates used in run 3d during the semiempirical approach to obtain profile 3: (—) F_A ; (---) F_B .

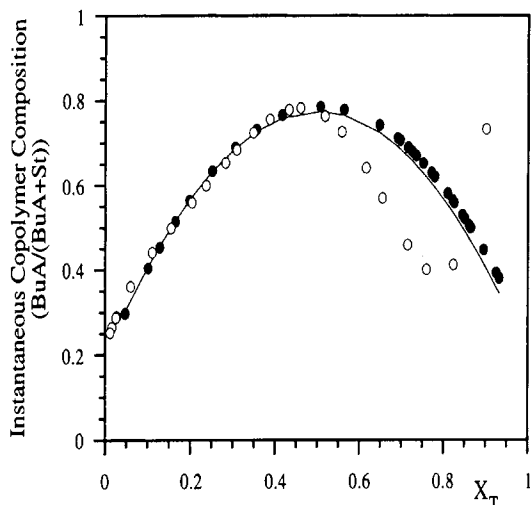


Figure 20 Comparison between the desired instantaneous copolymer composition profile and those obtained by means of (●) the optimal process and (○) the power feed process for profile 1.

CONCLUSIONS

The method for the calculation of the optimal monomer addition policy to produce emulsion copolymers with well-defined composition profiles developed in the first part of this series cannot be readily implemented in a real emulsion copolymerization system because the values of the kinetic model and the values of the parameters of this model are not usually available. To overcome this difficulty, a semiempirical approach was developed and applied to determine the optimal monomer addition policies to produce widely different copolymer composition profiles during the emulsion copolymerization of butyl acrylate and styrene. The method involves a series of semicontinuous emulsion copolymerizations carried out in an open-loop control mode. Each reaction was used to obtain an estimation of the kinetics of the process. This information was used to calculate the butyl acrylate and styrene addition profiles for the next experiment. The approach converged after a few (2–5) polymerizations. The results obtained with the optimal process were compared with those obtained under power feed conditions. It was found that the optimal process always allowed

one to obtain the desired copolymer composition profiles, whereas this is not the case for the power feed process using the same process time. Finally, it is worth pointing out that open-loop control cannot deal with batch-to-batch variations due to several reasons such as differences in raw materials. For systems in which batch-to-batch variations are frequent, a close-loop control system such as that used by Urretabizkaia et al.¹² should be used.

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