Monomer Addition Policies for Copolymer Composition Control in Semicontinuous Emulsion Copolymerization

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Synopsis

The effect of various monomer addition policies on the composition of a copolymer synthesized by semicontinuous emulsion copolymerization, using monomers with widely different reactivity ratios, was studied by mathematical simulation. Three policies were considered. In the first, both monomers are added under starved conditions. In the second, the reactor is initially charged with all of the less reactive monomer plus the amount of the more reactive monomer needed to initially form a copolymer with the desired composition. Subsequent addition of the remaining monomer is made at a flow rate that ensures the formation of a copolymer of constant composition. In the third, the initial charge is the same as in the previous case with subsequent addition of the remaining monomer at a constant feed rate. The copolymer composition obtained under starved conditions was almost constant in the cases where low feed rates were used. However, this led to long process times. For the second policy, a mathematical model was developed to calculate the necessary addition rate of the more reactive monomer, that ensured the production of a copolymer of constant composition. It was found that the resulting process time was one third of that corresponding to the starved process. When variations in the copolymer composition were allowed, the third addition policy might prove to be a good alternative to the second addition policy because of its shorter process time and the advantage of working with a constant feed rate.

INTRODUCTION

High value specialty polymer latexes can be tailormade in semicontinuous reactors by the simple method of controlling the addition rate of the reactants. A homogeneous copolymer can be prepared from monomers with widely different reactivity ratios by carrying out the polymerization under starved conditions. In this process, a stream with a monomer molar ratio equal to the one desired for the copolymer is fed into the reactor at a feed rate that is lower than the polymerization rate corresponding to flooded conditions, namely, when there are monomer droplets present in the reactor. In this way, the polymerization becomes controlled by the addition rate and the reaction rate of both monomers is the same as the feed rate. Therefore, the copolymer produced has the same composition as the feed. However, under starved conditions, the concentration of the monomers in the polymer particles is low and consequently the slow polymerization rates can lead to long process times.

To overcome this problem, a different addition policy, hereafter referred to as the semistarved process, is envisaged by which the reactor is initially

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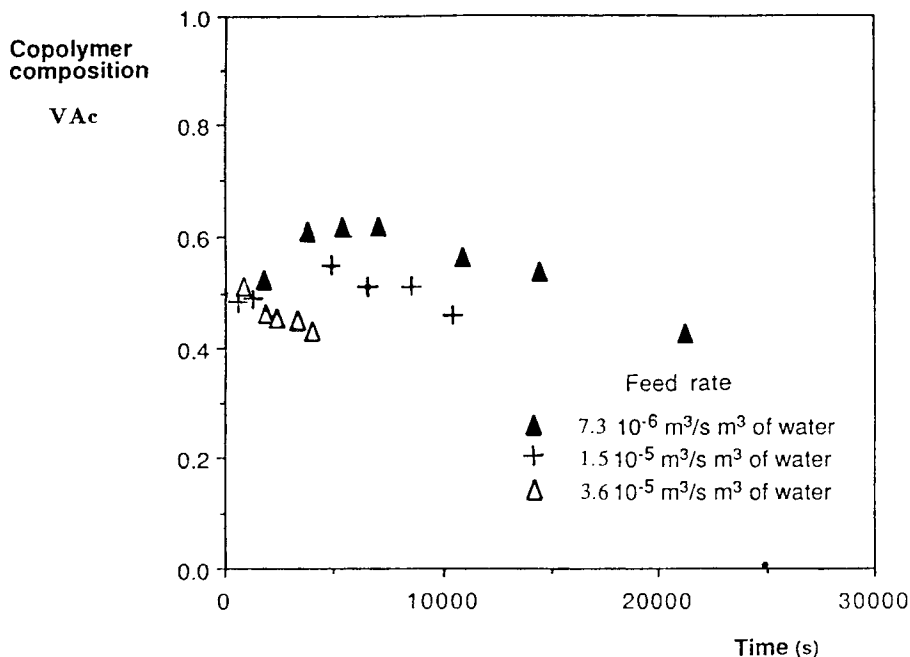
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Fig. 1. Effect of the methyl acrylate feed rate on the fraction of vinyl acetate in the copolymer. Experimental data from Ref. 1.

charged with all of the less reactive monomer as well as some of the more reactive monomer with the remaining more reactive being fed at a controlled rate. Arzamendi[1] carried out the seeded copolymerization of vinyl acetate (VAc) and methyl acrylate (MA) using an initial charge composed of all of the VAc and 12% of the MA (the more reactive monomer) and adding the remaining MA at a constant feed rate. The reported effect of the MA feed rate on the fraction of VAc in the copolymer is presented in Figure 1. This figure shows only the results obtained during the semicontinuous process, namely, while MA was being fed into the reactor. It was found that when high MA feed rates were used, the copolymer formed at the beginning of the process was rich in MA. The reverse behavior was found when low MA feed rates were used. Intermediate feed rates resulted in a more constant copolymer composition during the process. These results suggest that there should exist an addition rate profile for the more reactive monomer that ensures the production of a copolymer of constant composition during the polymerization.

The aim of the present work is to develop a mathematical model to calculate that addition rate profile and to compare its performance with the results obtained with other policies, namely, the starved process and the semistarved process using constant feed rate of the more reactive monomer.

SEMISTARVED PROCESS WITH VARYING FEED RATES

Suppose that a latex with a given solids content, Sc, and copolymer composition, Y_A, was desired. From Sc and Y_A, the total amount of each monomer per unit of volume of water is easily determined.

Let us consider a copolymerization with the following characteristics:
(i) Seeded copolymerization of monodisperse spherical particles with composition Y_A; (ii) Constant number of particles during the process; (iii) Aqueous phase polymerization negligible; and (iv) Monomer mass transfer much faster than the polymerization rate; therefore, distribution of the monomer between the different phases controlled by thermodynamic equilibrium

According to the proposed approach, the latex seed, monomer A and a certain amount of the more reactive monomer B are charged into the reactor together with the water and initiator. The problem is to calculate how much monomer B should be initially charged into the reactor to produce a copolymer of composition Y_A at the start of the process and the time-dependent addition rate of monomer B that ensures the formation of a copolymer with the same composition during the entire process. In the present work, both aspects will be solved in terms of the amount of monomer B that should be present in the reactor at any time to ensure the production of a constant copolymer composition.

If Rp_A and Rp_B are the rates of consumption of monomers A and B per unit of volume of water, the ratio Rp_A/Rp_B should be constant in order to obtain a copolymer of constant composition Y_A where

$$\frac{Rp_A}{Rp_B} = Y_A/(1 - Y_A) = K1 \tag{1}$$

The polymerization rates are

$$Rp_A = -(kp_{AA}P_A^p + kp_{BA}P_B^p)[A]_p \bar{n}N/N_A \tag{2}$$

$$Rp_B = -(kp_{AB}P_A^p + kp_{BB}P_B^p)[B]_p \bar{n}N/N_A \tag{3}$$

where kp_{ij} are the propagation rate constants; $[A]_p$ and $[B]_p$ the concentrations of the monomers in the polymer particles; $\bar{n}$ the average number of radicals per particle; N the number of particles per m³ of water; N_A the Avogadro's number; and P_i^p the time average probabilities of finding a free radical on a molecular unit of type i.[2-4] These probabilities are given by

$$P_A^p = kp_{BA}[A]_p/(kp_{BA}[A]_p + kp_{AB}[B]_p) \tag{4}$$

$$P_B^p = 1 - P_A^p \tag{5}$$

Substituting Eqs. (2)–(5) into Eq. (1) and rearranging, we obtain

$$K1 = \frac{r_A[A]_p/[B]_p + 1}{1 + \dfrac{r_B}{[A]_p/[B]_p}} \tag{6}$$

where r_A and r_B are the reactivity ratios of monomers A and B, respectively.

From Eq. (6), the ratio $[B]_p/[A]_p$ which ensures a copolymer composition of Y_A can be obtained as a function of the reactivity ratios and $K1$:

$$\frac{[A]_p}{[B]_p} = \frac{(K1 - 1) + \left\{ (K1 - 1)^2 + 4r_A r_B K1 \right\}^{0.5}}{2r_A} \tag{7}$$

For a given amount of both monomer A and copolymer, the amount of monomer B which should be in the reactor to form a copolymer of composition Y_A may be calculated by solving Eq. (7) in conjunction with the equilibrium equations and the overall material balances.

Thermodynamic equilibrium is attained when the partial molar free energies of the monomers in the different phases are the same. Therefore, the following equilibrium equations can be written:

Polymer particles-aqueous phase

$$(\Delta G/RT)_A^p = (\Delta G/RT)_A^{aq} \tag{8}$$

$$(\Delta G/RT)_B^p = (\Delta G/RT)_B^{aq} \tag{9}$$

Aqueous phase-monomer droplets

$$(\Delta G/RT)_A^{aq} = (\Delta G/RT)_A^D \tag{10}$$

$$(\Delta G/RT)_B^{aq} = (\Delta G/RT)_B^D \tag{11}$$

$$(\Delta G/RT)_W^{aq} = (\Delta G/RT)_W^D \tag{12}$$

In these equilibrium equations, it was considered that water, W, is present in monomer droplets but not in the polymer particles. According to Ugelstad

TABLE I
Values of the Parameters Used in the Simulations[a]

Kp_{AA},[8] Kp_{BB},[9] Kp_{AB},[8-10] Kp_{BA}[9-10] (m^3 mol^{-1} s^{-1})	4.10	2.09	41.00	0.232
Kt_{AA}, Kt_{BB}, Kt_{AB}[11-13] (m^3 mol^{-1} s^{-1})	$2.9 \cdot 10^4$	$9.50 \cdot 10^3$	$1.7 \cdot 10^4$	
Kf_{AA},[14,15] Kf_{BB},[16] Kf_{AB}, Kf_{BA} (m^3 mol^{-1} s^{-1})	$4 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$6.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$
K_I (s^{-1})[17]	$1 \cdot 10^{-6}$			
χ_{Aw}, χ_{Bw}, χ_{AB}, χ_{BA}[5]	3.2	2.97	-0.139	-0.126
χ_{wA}, χ_{wB}[5]	8.65	4.37		
$(1 - m_{Aw})$, $(1 - m_{Bw})$, $(1 - m_{AB})$, $(1 - m_{BA})$[5]	0.63	0.32	-0.098	0.090
$(1 - m_{Ap})$, $(1 - m_{Bp})$, $(1 - m_{wA})$, $(1 - m_{wB})$[5]	1.0	1.0	-1.703	-0.471
χ_{ApA}, χ_{BpB}, χ_{ApB}, χ_{BpA}[18]	0.38	0.507	0.706	0.398
D_w, D_p(m^2 s^{-1})[29,20]	$1 \cdot 10^{-10}$	$1 \cdot 10^{-11}$		
F,[20] f[21]	$6 \cdot 10^{-2}$	0.4		
σ(N/m),[8] T (K)	$4.0 \cdot 10^{-3}$	333		

[a] kf_{AB} and kf_{BA} are estimated values. χ_{ApA}, χ_{BpB}, χ_{ApB}, and χ_{BpA} were determined from osmotic pressure measurements.[18]

et al.,[5] the partial molar free energies can be calculated as follows:

$$\left(\Delta G/RT\right)_j^i = \ln\phi_j^i + \sum_{k=1}^{n}\left(1 - m_{jk}\right)\phi_k^i + \sum_{\substack{k=1 \neq j}}^{n} \chi_{jk}\left(\phi_k^j\right)^2$$

$$+ \sum_{\substack{k=1 \neq j}}^{n-1} \sum_{\substack{l=k+1 \neq j}}^{n} \phi_k^i\phi_l^i\left(\chi_{jk} + \chi_{jl} - \chi_{kl}m_{jk}\right) + \frac{2\sigma v_j}{r_i RT} \quad (13)$$

where j represents the various components (monomers, water, and polymer); i refers to the phase involved (polymer particles, aqueous phase, and monomer droplets); ϕ_j^i is the volume fraction of component j in phase i; m_{ij} is the ratio of the equivalent number of segments of components j and i; v_j is the molar volume of component j; r_i the radius of phase i; σ the interfacial tension; R the gas constant; T the temperature; and χ_{jk} the interaction parameters. The interaction parameter of monomer i with the copolymer was calculated as follows:

$$\chi_{ip} = Y_A\chi_{ipA} + (1 - Y_A)\chi_{ipB} \quad (14)$$

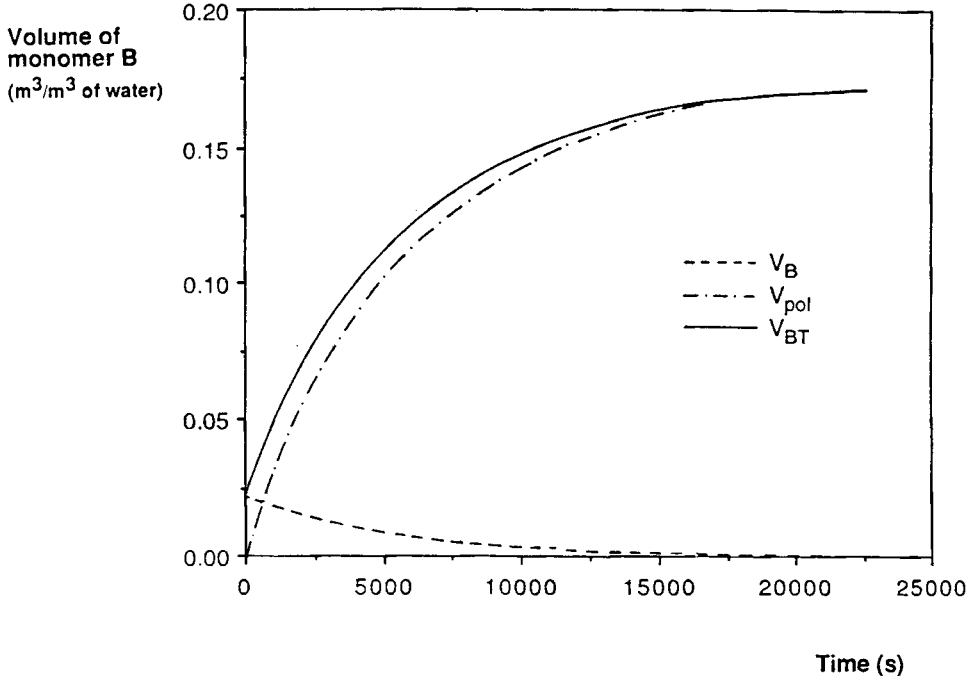where χ_{ipj} is the interaction parameter of monomer i with homopolymer j.

Fig. 2. Volume of monomer B versus process time for the production of a copolymer of constant composition through a semistarved process with varying feed rates. V_{BT}: Total volume of monomer B added to the reactor; V_B: Volume of B as a free monomer; V_{Bpol}: Volume of B in the copolymer. $Y_A = 0.5$; $A_0 = 1,937$ mol/m^3 of water; N = 5 · 10^{20} part/m^3 of water.

Additionally, the radius of the polymer particles is given by

$$r_p = \left(3V_{pol}/4\pi N\phi_p^P\right)^{1/3} \tag{15}$$

The overall material balances are

$$\phi_A^P + \phi_B^P + \phi_p^P = 1 \tag{16}$$

$$\phi_A^{aq} + \phi_B^{aq} + \phi_W^{aq} = 1 \tag{17}$$

$$\phi_A^D + \phi_B^D + \phi_W^D = 1 \tag{18}$$

$$\phi_A^{aq}V_{aq} + \phi_A^P V_p + \phi_A^D V_D = V_A \tag{19}$$

$$\phi_B^{aq}V_{aq} + \phi_B^P V_p + \phi_B^D V_D = V_B \tag{20}$$

$$\phi_W^{aq}V_{aq} + \phi_W^D V_D = V_W \tag{21}$$

$$V_p = V_{pol}/\phi_p^P \tag{22}$$

where V_{aq}, V_p, and V_D are the volumes of the aqueous phase, monomer swollen polymer particles and monomer droplets, respectively; V_A, V_B, and V_W are the volumes of A, B and water; and V_{pol} the volume of the copolymer. In all the calculations $V_W = 1$ m^3.
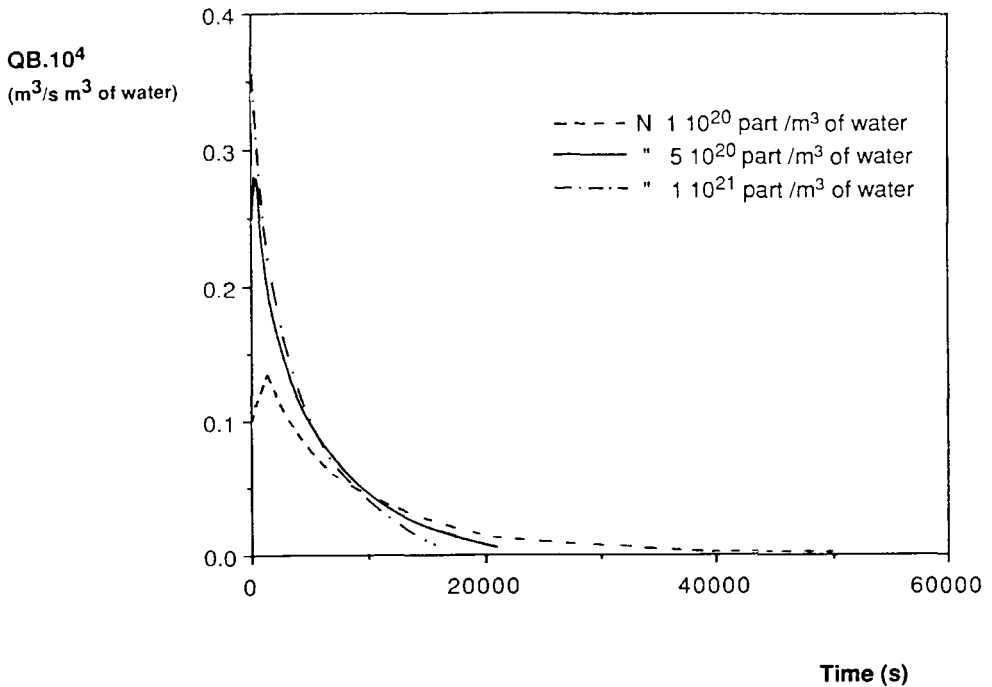

Fig. 3. Effect of the number of particles in the seed on the monomer B feed rate profile. $Y_A = 0.5$; $A_0 = 1{,}937$ mol/m^3 of water.

In terms of the volume fractions, Eq. (7) may be written as:

$$\frac{\phi_A^p v_B}{\phi_B^p v_A} = \frac{(K1 - 1) + \left\{(K1 - 1)^2 + 4r_A r_B K1\right\}^{0.5}}{2r_A} \qquad (23)$$

Equations (8)–(23) are a system of 14 nonlinear algebraic equations with 14 unknowns, namely, ϕ_A^p, ϕ_B^p, ϕ_p^p, ϕ_A^{aq}, ϕ_B^{aq}, ϕ_W^{aq}, ϕ_A^D, ϕ_B^D, ϕ_W^D, V_{aq}, V_p, V_D, r_p, V_B. The simultaneous solution gives, among other interesting results, the volume of B per m^3 of water that should be in the reactor in order to obtain a copolymer of the desired composition. The amount of monomer B that has to be initially charged into the reactor, for a given initial amount of monomer A and copolymer, can be readily calculated by solving the system of nonlinear algebraic equations. However, since the volumes of both monomer A and copolymer vary during polymerization, the system of equations has to be coupled to the differential equations describing the consumption of initiator and monomer A:

$$\frac{dI_2}{dt} = -K_I I_2 \qquad (24)$$

$$\frac{dA}{dt} = -(kp_{AA}P_A^p + kp_{BA}P_B^p)[A]_p \bar{n} N / N_A \qquad (25)$$
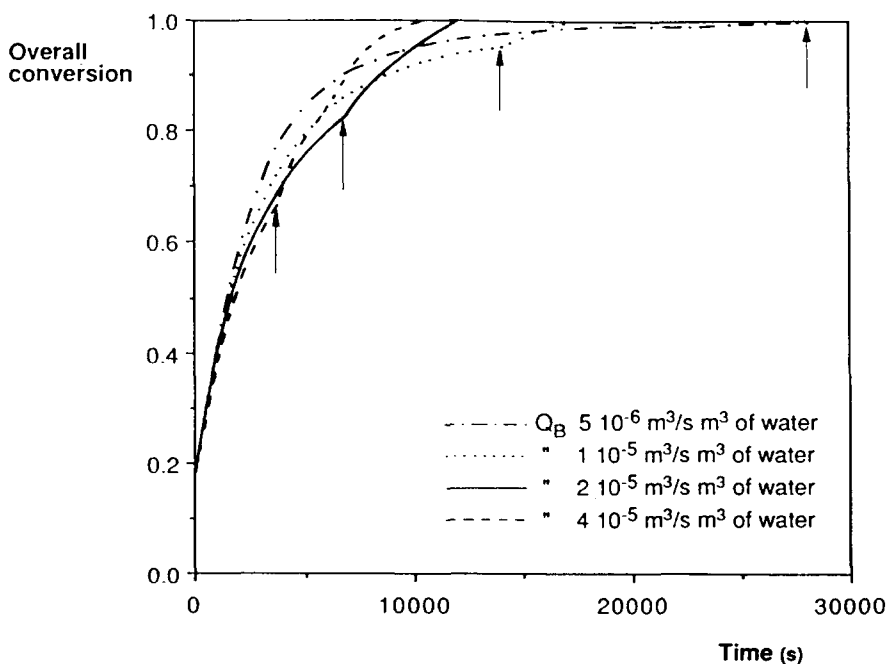

Fig. 4. Effect of the monomer B feed rate on the overall conversion during the semistarved process with a constant feed rate. A_0 = 1,937 mol/m^3 of water; B_0 = 234 mol/m^3 of water. Total amount of monomer B = 1,937 mol/m^3 of water; N = $5 \cdot 10^{20}$ part/m^3 of water. The arrows indicate the end of the monomer addition period.

where I_2 and A are the number of moles of initiator and monomer A per m^3 of water, respectively.

The average number of radicals per particle can be calculated using the equation derived by Ugelstad and Hansen[6] coupled with the balance of radicals in the aqueous phase, as shown in Appendix I.

Equations (24) and (25) can be solved through a standard Runge-Kutta algorithm. The amount of the monomer B converted to copolymer at any time is

$$P_B = (A_0 - A)/K1 \qquad (26)$$

where A_0 is the number of moles of monomer A in the initial charge per m^3 of water.

The total volume of monomer B added into the reactor at any time is given by

$$V_{BT} = V_B + \frac{(A_0 - A)P_{mB}}{K1\rho_B} \qquad (27)$$

where Pm_B is the molecular weight of monomer B and ρ_B its density.

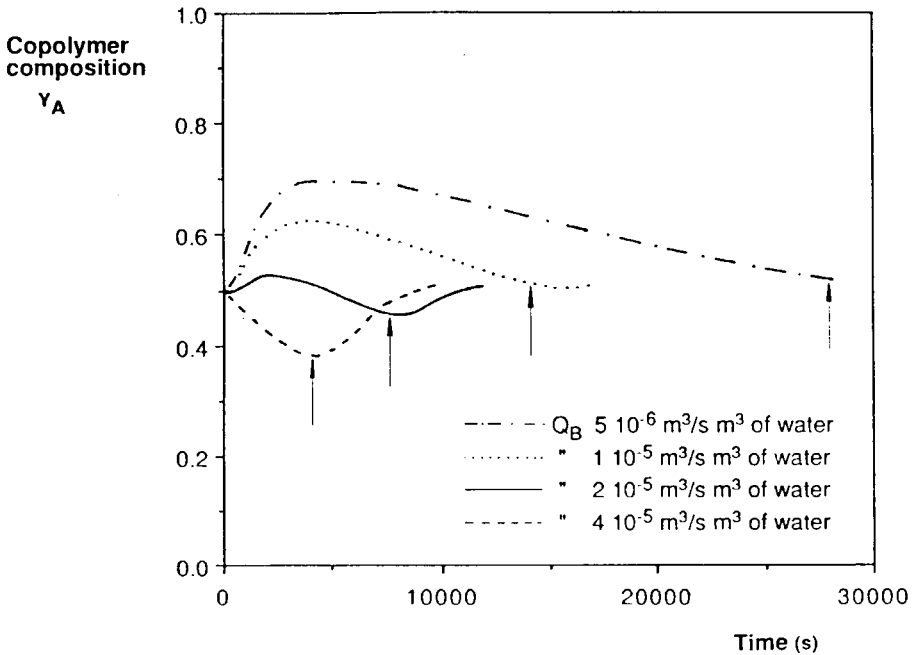Fig. 5.   Influence of the monomer B feed rate on the copolymer composition for the semi-starved process with a constant feed rate. $A_0 = 1{,}937$ mol/m^3 of water; $B_0 = 234$ mol/m^3 of water; $N = 5 \cdot 10^{20}$ part/m^3 of water. The arrows indicate the end of the monomer addition period.

The feed rate of the more reactive monomer is

$$Q_B = \frac{dV_{BT}}{dt} \tag{28}$$

The model was applied to the copolymerization of two monomers of very different reactivity ratios: vinyl acetate ($r_A = 0.1$) and methyl acrylate ($r_B = 9$). Simulations were carried out using the values of the parameters given in Table I.

Figure 2 presents the results obtained when the polymerization of a latex with a solids content of 25% and $Y_A = 0.5$ was simulated and shows the evolution of the volume of methyl acrylate monomer (per m^3 of water), V_B, and copolymer, V_{Bpol}, up to a fractional conversion of 0.99. The addition of these two values gave the total amount of monomer B, V_{BT}, that should have been fed into the reactor at a given time to obtain a copolymer of constant composition 50/50. From Figure 2, the feed rate profile was calculated using Eq. (28). Figure 3 shows the feed rate profiles obtained for varying number of particles in the seed. The initial increase shown in all the curves corresponds to the stage in which monomer droplets are present in the reactor. In this interval, the concentration of VAc, as well as the average number of radicals in the polymer particles, increased as a result of the increasing particle size.
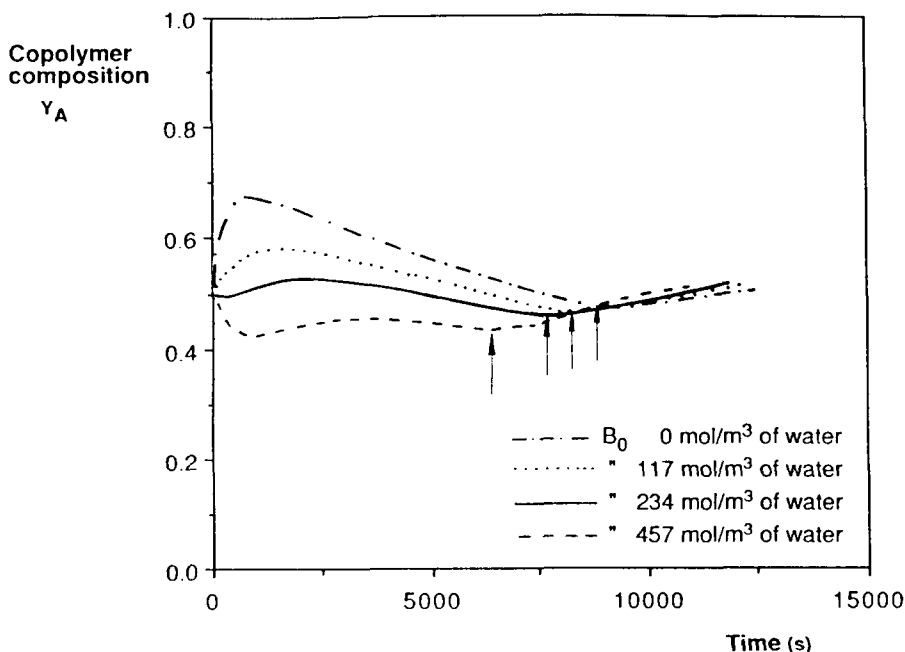

Fig. 6. Effect of the amount of monomer B initially charged into the reactor on the copolymer composition for the semistarved process with constant feed rate. $A_0 = 1{,}937$ mol/m^3 of water. Total amount of monomer B $= 1{,}937$ mol/m^3 of water; N $= 5 \cdot 10^{20}$ part/m^3 of water; Monomer B addition rate $= 0.22$ mol/s m^3 of water. The arrows indicate the end of the monomer addition period.

Therefore, the rate of consumption of VAc increased and more MA was required in order to maintain a constant copolymer composition. Once the monomer droplets disappeared, the concentration of VAc in the polymer particles decreased continuously, and consequently the addition rate of MA decreased. When the number of particles of the seed increased, the maximum of the curves (the point where monomer droplets disappeared) shifted to shorter process times. Figure 3 also shows that the greater the number of particles, the shorter the time needed for the completion of the polymerization.

SEMISTARVED PROCESS WITH CONSTANT FEED RATE

From a practical point of view, it is easier to use a constant feed rate instead of the time-dependent feed rate profiles obtained in the previous section. A model for the constant feed rate semistarved process was developed to compare this process with the one described previously. The model includes Eqs. (24) and (25) with the addition of the material balance for monomer B

$$\frac{dB}{dt} = -\left(kp_{AB}P_A^p + kp_{AA}P_B^p\right)[B]_p \bar{n} N/N_A + F_B \qquad (29)$$

where B is the number of moles of monomer B per m^3 of water and F_B the molar feed rate. The average number of radicals per particle was calculated as shown in Appendix I. During the integration, the concentrations of the
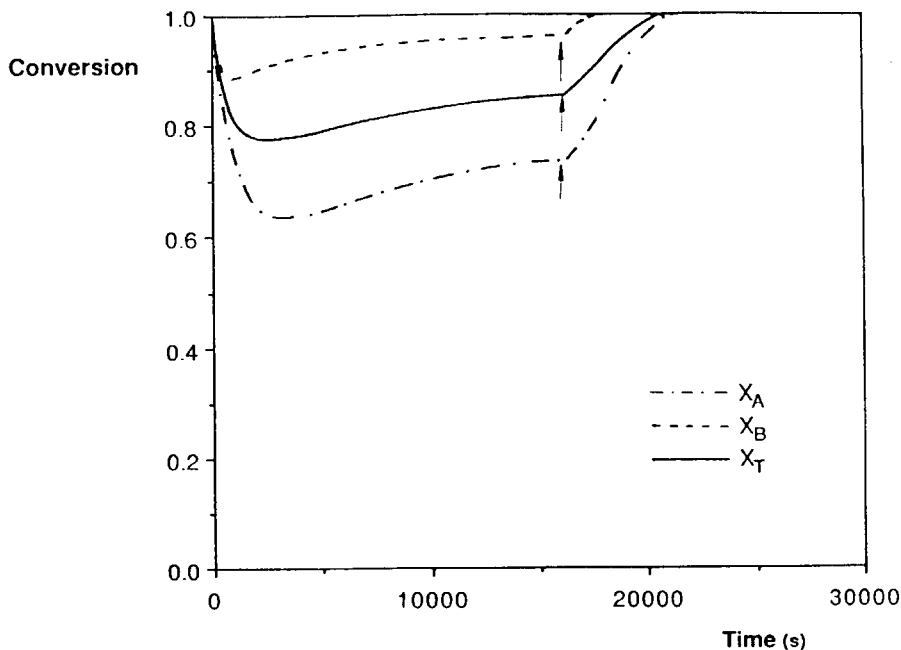

Fig. 7. Evolution of the overall conversion and the individual conversions of both monomers during the starved process. Feed rate of a 50/50 molar ratio monomer mixture: 0.219 mol/s m^3 of water; N = 5 · 10^{20} part/m^3 of water. The arrows indicate the end of the monomer addition period.

monomers in the polymer particles were calculated using Eqs. (8) to (22) taking into account that during this process, the volume of monomer B, V_B, was a known quantity. However, the initial amount of monomer B to be charged into the reactor was calculated as in the previous case, namely, the amount of monomer B that ensured the production of a copolymer of the desired composition at the beginning of the process. Simulations were carried out by using the values of the parameters presented in Table I.

Figures 4 and 5 present the effect of the feed rate on the overall conversion and on the cumulative copolymer composition, respectively. In these figures, the arrows indicate the time at which the MA had been fed into the reactor. The polymerization subsequently continued as a batch reaction, during which period simulations were carried out by integrating Eqs. (24), (25), and (29) with F_B equal to zero. Figure 4 shows an increase in the polymerization rate soon after the addition of MA ended and that the higher the MA feed rate the more pronounced the increase of the polymerization rate. The region of high polymerization rate corresponds to the homopolymerization of VAc after the complete polymerization of MA in the reactor. The larger the MA feed rate the sooner MA polymerized and the larger the amount of unreacted VAc in the reactor when MA disappeared completely. This resulted in a higher polymerization rate. Figure 5 shows that high feed flow rates of monomer B led to an initial enrichment of the copolymer with monomer B, in agreement with the experimental results reported by Arzamendi[1] (see Fig. 1). On the other hand, low monomer B feed rates gave a copolymer in which the initial
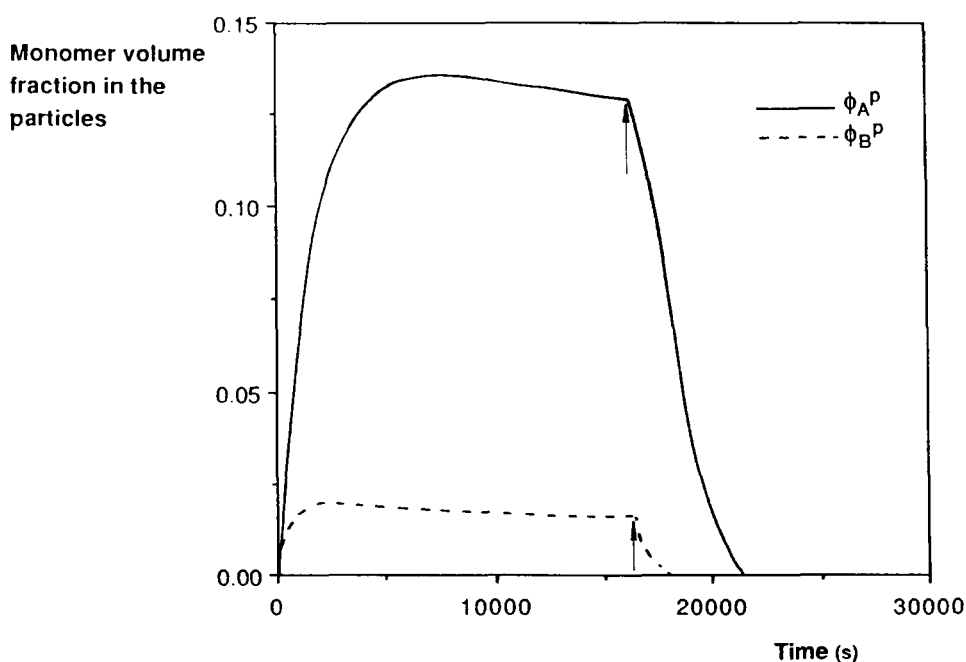

Fig. 8. Monomer volume fractions in the polymer particles against the process time for the starved process. Feed rate of a 50/50 molar ratio monomer mixture: 0.219 mol/s m³ of water; $N = 5 \cdot 10^{20}$ part/m³ of water. The arrows indicate the end of the monomer addition period.

monomer A content was higher than desired. However, when an intermediate feed flow rate, namely 2×10^{-5} m^3/s m^3 of water, was used, a roughly uniform copolymer composition was obtained with a process time that was half of that needed for the variable feed rate process. It should be pointed out that Figure 5 presents cumulative copolymer compositions and hence, the final approach of the curves to a composition 50/50 only means that all of the monomer in the reactor polymerized irrespective of the composition of the copolymer formed. As a matter of fact, the copolymer formed after the end of the addition of MA reacted in a batch process, giving a nonuniform copolymer that in some cases (large MA feed rates) can be a homopolymer of VAc.

The effect of the amount of monomer B initially charged into the reactor on the evolution of the cumulative copolymer composition is presented in Figure 6. This shows that the smaller the amount of monomer B initially charged into the reactor, the higher the monomer A content of the copolymer formed at the beginning of the process. Also, it was found that the use of initial amounts of monomer B different from that which ensures the production of a copolymer of the desired composition at the beginning of the process resulted in an increase in the heterogeneity of the copolymer.

STARVED PROCESS

In this process, the reactor was initially charged with the seed and all the water and initiator. Polymerization was begun when a stream containing both monomers was fed into the reactor. The composition of the feed, as well as its
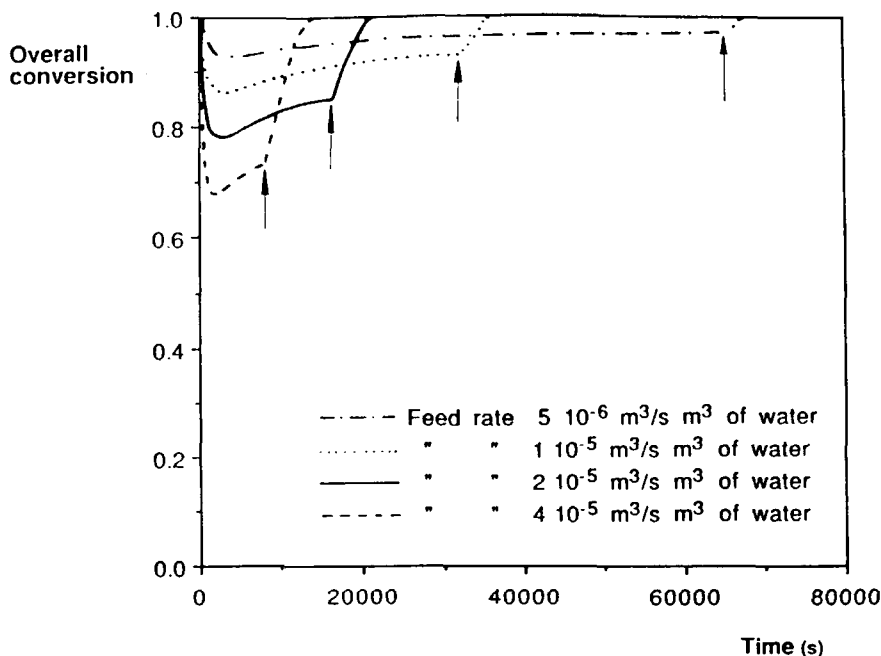

Fig. 9. Effect of the monomer feed rates on the overall conversion for the starved process. Molar monomer ratio in the feed: 50/50; $N = 5 \cdot 10^{20}$ part/m^3 of water. The arrows indicate the end of the monomer addition period.

flow rate, were kept constant during the process. The material balances for the monomer are

$$\frac{dA}{dt} = -(kp_{AA}P_A^p + kp_{BA}P_B^p)[A]_p\bar{n}N/N_A + F_A \tag{30}$$

$$\frac{dB}{dt} = -(kp_{AB}P_A^p + kp_{BB}P_B^p)[B]_p\bar{n}N/N_A + F_B \tag{31}$$

The concentrations of the monomers in the polymer particles were calculated as in the semistarved process with constant feed rate. When $t = 0$, no monomer is in the reactor, therefore $A_0 = B_0 = 0$. Simulations were carried out by using the parameters in Table I.

Figure 7 shows the evolution of the overall conversion and the conversions of both monomers when a 50/50 molar ratio of the monomers in the feed was used. It can be seen that monomers, particularly the less reactive one, continuously accumulated in the reactor. Figure 8 presents the volume fractions of the monomers in the polymer particles. It can be seen that there was an initial increase in the concentrations of both monomers in the particles. This increase was more pronounced for the less reactive monomer. After some time, the ratio of the concentrations of the monomers in the polymer particles nearly reached a constant value, namely, the ratio of the consumption rates of both monomers was the same as their molar concentration ratio in the feed. Therefore, the copolymer formed thereafter and up to the end of the monomer addition had the same composition as the feed. The final decrease of the
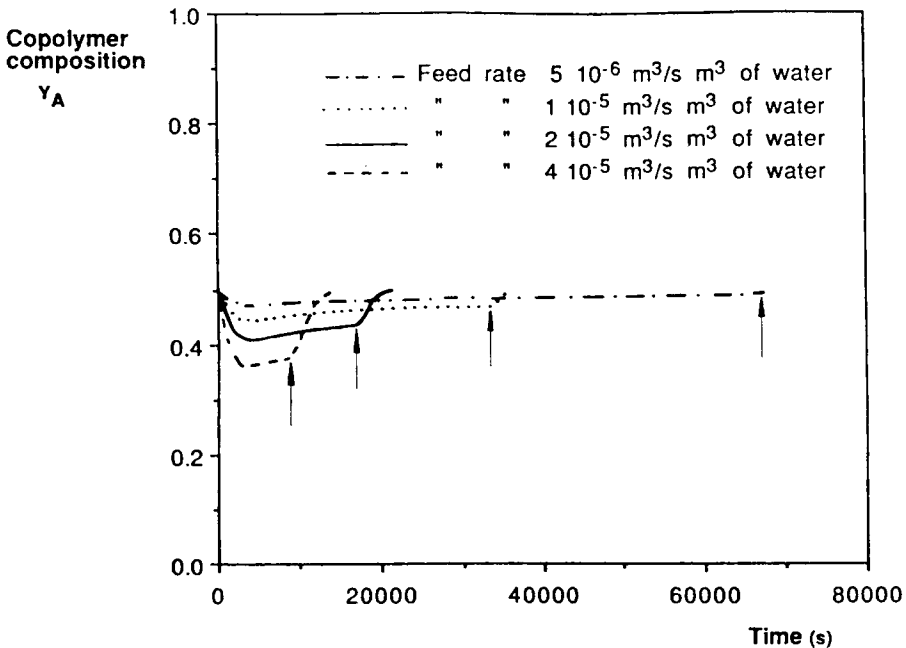
Fig. 10. Influence of the monomer feed rates on the copolymer composition for the starved process. Molar monomer ratio in the feed: 50/50; $N = 5 \cdot 10^{20}$ part/m^3 of water. The arrows indicate the end of the monomer addition period.

monomer concentration in the polymer particles corresponds to the batch process.

Figures 9 and 10 present the effect of the feed flow rate on the overall conversion and the copolymer composition, respectively. In Figure 9, it can be seen that the conversion-time behavior showed a minimum which decreased when the addition rate was increased. Furthermore, the conversion reached at
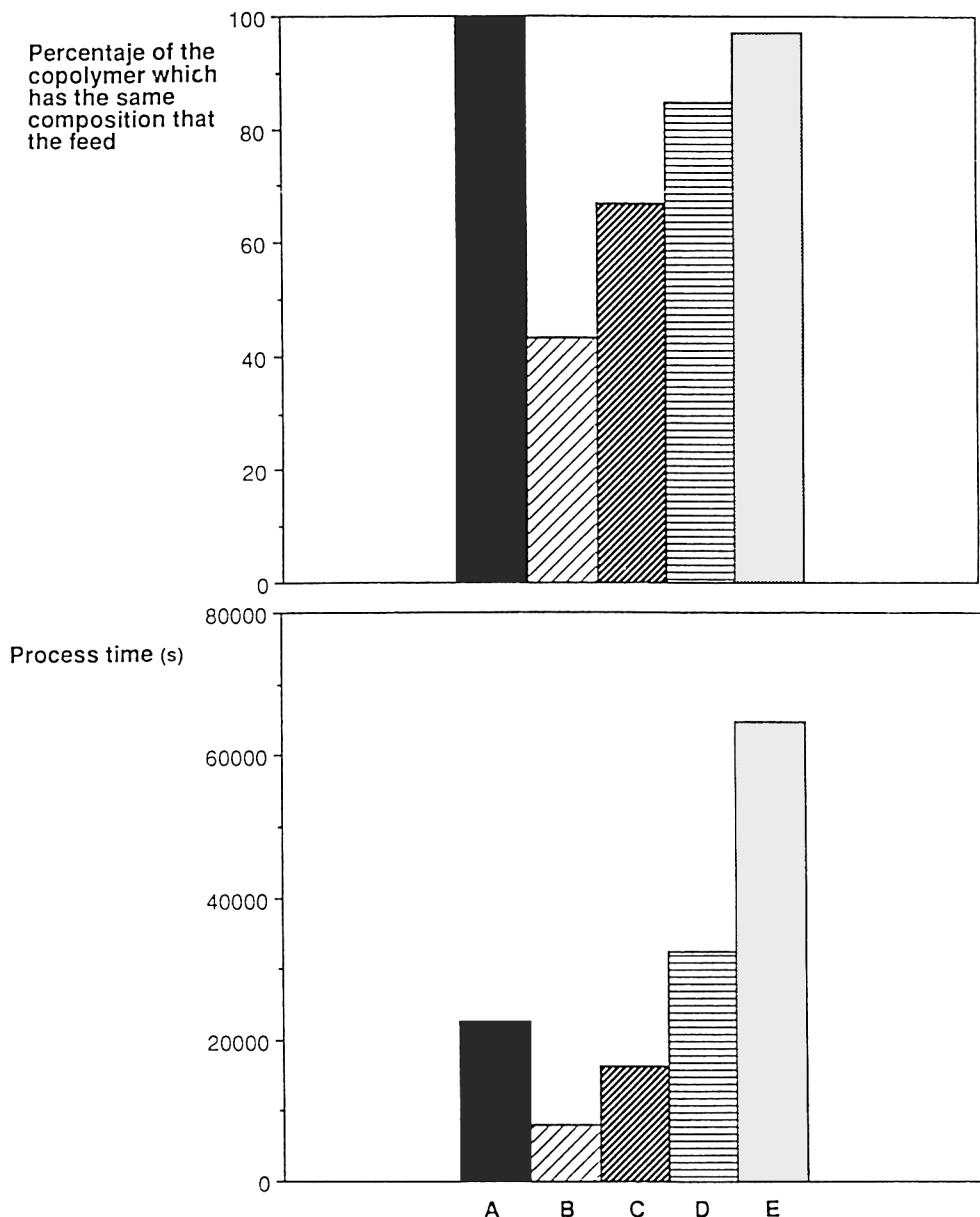
Fig. 11. Comparison of the process time and copolymer quality of the semistarved process with variable feed rate, A, with the starved process at different feeding rates, $B = 4 \cdot 10^{-5}$ m^3/s m^3 of water, $C = 2 \cdot 10^{-5}$ m^3/s m^3 of water, $D = 1 \cdot 10^{-5}$ ml^3/s m^3 of water, $E = 0.5 \cdot 10^{-5}$ m^3/s m^3 of water. Feed monomer molar ratio = 50/50. For all the simulations $N = 5 \cdot 10^{20}$ part/m^3 of water.

the end of monomer addition decreased and hence, the amount of monomer that reacted in a batch way increased with increasing feed rate. The form of the composition curves in Figure 10 may be explained by recalling the results presented in Figure 8. At the beginning of the process, monomer B reacted faster (accumulated less) than monomer A and therefore, copolymer rich in monomer B was produced. As a result, the cumulative copolymer composition shifted from a value of 0.5, corresponding to the seed, to values indicating lower monomer A contents. However, once the ratio of the concentrations of the monomers in the polymer particles reached a constant value, a copolymer of composition 0.5 was produced and the cumulative copolymer composition approached 0.5. The abrupt change in composition during the batch process was due to the polymerization of the remaining VAc-rich monomer mixture.

Figure 11 presents a comparison of the process time and copolymer quality of the varying feed rate semistarved process with the results obtained in the starved process at different constant feed rates. It can be seen that, to obtain a copolymer of similar quality, the time needed for the starved process was four times greater than the one corresponding to the semistarved process using feed rate profiles.

CONCLUSIONS

It has been shown that the semistarved process with variable addition rate of the more reactive monomer calculated is the only monomer addition policy that ensures the production of a copolymer of constant composition during the copolymerization of two monomers of widely different reactivity ratios.

A nearly constant copolymer composition was obtained under starved conditions, provided that slow monomer feed rates were used. However, that approach led to a much higher process time than the semistarved process with variable addition rates. When high monomer feed rates were used, significant amounts of the copolymer initially became enriched with the more reactive monomer and together with the copolymer formed in the batch process at the end of the reaction, this led to a heterogeneous copolymer.

When deviations of the copolymer composition from the desired one are allowed, the semistarved process with a constant addition rate of the more reactive monomer might be a good alternative to the process with varying feeding rates because of the shorter process times and the advantage of working with a constant feed rate.

APPENDIX I

The average number of radicals per particle is given by[6]

$$\bar{n} = \cfrac{a^2/8}{m + \cfrac{a^2/4}{m + 1 + \cfrac{a^2/4}{m + 2 + \cdots}}} \tag{32}$$

where

$$a = \left(8k_{abs} N_A [R_T]_{aq} v_p / kt^p \right)^{1/2} \tag{33}$$

$$m = k_d N_A v_p / kt^p \tag{34}$$

k_{abs} and k_d are the rate coefficients for radical absorption and desorption, respectively, v_p is the volume of one polymer particle, kt^p is the average termination constant in the polymer particles, and $[R_T]_{aq}$ the concentration of free radicals in the aqueous phase. $[R_T]_{aq}$ is an unknown variable, requiring an additional equation. This equation is the balance of radicals in the aqueous phase.

$$k_{abs}[R_T]_{aq}N = k_d \bar{n}N + 2fK_I I_2 N_A - 2kt^{aq}[R_T]_{aq}^2 N_A V_{aq} \tag{35}$$

where kt^{aq} is the average termination constant in the aqueous phase.

The absorption of radicals was assumed to be reversible and occur by diffusion. The rate coefficient for radical absorption is

$$k_{abs} = 4\pi r_p FD_W N_A \tag{36}$$

where F is the radical capture efficiency, r_p the polymer particle radius, and D_W the diffusion coefficient of the radicals in the aqueous phase.

The average termination constants in the polymer particles and in the aqueous phase were calculated as follows

$$kt^p = kt_{AA}(P_A^p)^2 + kt_{BB}(P_B^p)^2 + 2kt_{AB}P_A^p P_B^p \tag{37}$$

$$kt^{aq} = kt_{AA}(P_A^{aq})^2 + kt_{BB}(P_B^{aq})^2 + 2kt_{AB}P_A^{aq} P_B^{aq} \tag{38}$$

where P_j^i is the time averaged probability of finding a free radical on a molecular unit of type j in phase i.

The rate constant for radical desorption was calculated by adding the desorption coefficients for radicals A and B.

$$kd = kd_A + kd_B \tag{39}$$

The individual desorption coefficients were calculated as the rate of monomer chain transfer multiplied by the probability of desorption of a single unit free radical

$$kd_i = (kf_{Ai}P_A^p + kf_{Bi}P_B^p)[i]_p \psi_i \tag{40}$$

Among the several equations proposed for these probabilities, in this work, the one developed by Friis and Nyhagen[7] was used

$$\psi_i = \frac{2D_p/r_p^2}{2D_p/r_p^2 + kp_{iA}[A]_p + kp_{iB}[B]_p} \tag{41}$$

NOMENCLATURE

a	Parameter given by Eq. (33)
A, B	Moles of monomers A and B, respectively (mol/m^3 of water)
A$_0$, B$_0$	Moles of monomers A and B initially charged into the reactor (mol)
$[A]_p$, $[B]_p$	Concentrations of monomers A and B in the polymer particles (mol/m^3)
D_W	Diffusion coefficient of the radicals in the aqueous phase (m^2/s)
D_p	Diffusion coefficient of the single-unit radicals in the swollen polymer particles (m^2/s)
F	Radical capture efficiency
F_A, F_B	Molar feed rate of monomers A and B, respectively (mol/s m^3 of water)
ΔG_j^i	Molar free energy of the compound j in the i phase (J/mol)

I_2 Moles of initiator (mol/m^3 of water)

k_{abs} Rate coefficient for radical absorption (s^{-1})

kd Rate coefficient for radical desorption (s^{-1})

kd_i Individual desorption coefficient (s^{-1})

kf_{ij} Monomer chain transfer constant (m^3/mol s)

K_I Rate constant for initiator decomposition (s^{-1})

kp_{ij} Propagation constant (m^3/mol s)

kt_{ij} Termination constant (m^3/mol s)

kt^j Average termination constant in phase j (m^3/mol s)

$K1$ Constant given by Eq. (1)

m Parameter given by Eq. (34)

$\bar{n}$ Average number of radicals per particle

N Number of particles per m^3 of water

N_A Number of Avogadro

P_B Moles of monomer B in the copolymer (mol)

P_i^j Time-averaged probability of finding a free radical on a molecular unit of type i in the phase j ($-$)

Q_B Volumetric feed rate of monomer B (m^3/s m^3 of water)

r_A Reactivity ratio of A; kp_{AA}/kp_{AB} ($-$)

r_B Reactivity ratio of B; kp_{BB}/kp_{BA} ($-$)

r_i Radius of the phase i (m)

R Gas constant (J/mol K)

Rp_i Rate of consumption of monomer i (mol/s m^3 of water)

$[R_T]_{aq}$ Concentration of free radicals in the aqueous phase (mol/m^3)

SC   Solid content of the latex (kg of polymer/kg of latex)

T Temperature (K)

v_i Molar volume of component i (m^3/mol)

v_p Volume of one swollen polymer particle (m^3)

V_A Volume of monomer A per m^3 of water

V_{aq} Volume of the aqueous phase per m^3 of water

V_B Volume of monomer B per m^3 of water

V_{Bpol} Volume of the monomer B which has entered in the copolymer (m^3/m^3 of water)

V_{BT} Total volume of monomer B added into the reactor at a given time (m^3/m^3 of water)

Y_A Copolymer composition (moles of monomer A in the copolymer chain/moles of monomers A and B in the copolymer chain)

Greek Symbols

ϕ_j^i Volume fraction of component j in the phase i ($-$)

ρ_B Density of monomer B (kg/m^3)

σ Interfacial tension (N/m)

χ_{ij} Interaction parameter ($-$)

ψ_i Probability of desorption of a single-unit radical of type i ($-$)

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