Pseudosteady States in Semicontinuous Emulsion Copolymerization

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Synopsis

The appearance of pseudo-steady states in semicontinuous emulsion copolymerization is studied. Different correlations between the monomer feed rate and the polymerization reaction rate proposed in the literature for homopolymerization systems can be derived from a unified view as presented in this work. The theoretical analysis for copolymerization systems predicts that the individual consumption rates of both monomers involved assume a constant value if the monomer addition rates are kept constant. Different cases for either fixed radical concentration or seeded polymerization with water-soluble or sparingly water-soluble monomers are considered. The assumptions and results of the analysis are tested against experimental data from the seeded copolymerization of vinyl acetate/n-butyl acrylate.

INTRODUCTION

It has been observed experimentally, for semicontinuous emulsion copolymerization processes with constant monomer addition rate, that if the total number of particles, N, remains constant, the rate of polymerization takes on a constant value. If the monomer addition flow rate is large enough to maintain the saturation value of monomer concentration [M^p] in the latex particles, the rate of polymerization is independent of the addition rate (*flooded region*). If [M^p] falls below this value, the polymerization rate approaches a constant value which depends on the monomer addition rate (*controlled region–monomer starved conditions*). This behavior has been observed for styrene and methyl acrylate,[1] vinyl acetate,[2] the copolymerizations of styrene with butyl acrylate,[3] butyl methacrylate with butyl acrylate,[4] acrylonitrile with butyl acrylate, and acrylonitrile with styrene.[5]

Wessling[6] showed that for homopolymerization systems that follow the Smith–Ewart mechanism, the polymerization rate approaches a "steady-state" dependent on the monomer addition rate. Above a critical value of monomer addition rate, the particles become saturated with monomer and the polymerization rate remains constant and independent of the monomer addition rate. This analysis was tested against the Gerrens data on styrene, a monomer known to follow Smith–Ewart kinetics. Gerrens[1] reported similar results working with the copolymerization of styrene and methyl acrylate. The Smith–Ewart theory was taken as a basis for calculation. Bataille et al.[2] studied the behavior of vinyl acetate, a monomer with much higher solubility in water than styrene,

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and the results were analyzed kinetically using both the ideal case of $\bar{n} = 0.5$ and the nonideal one where $\bar{n}$ is much greater than 0.5. Their conclusions confirmed the general theory of Wessling.[6]

Although the general conclusions of the above cited works are in good agreement, several different observations were reported. Wessling's treatment predicted that at the "steady-state" conditions the rate of polymerization R (mol/s) and the monomer feed rate F (mol/s) will follow the relationship

$$1/R = G + 1/F$$

where G is a constant. In the case of fixed radical concentration, Wessling's treatment predicted that $R = F$. Gerrens' results indicated in general that $R = \sigma F$ with $\sigma = 1$. In 1973, Wessling and Gibbs[7] reported the same results with $\sigma = 0.91$ and Snuparek and Krska[3] with $\sigma = 1$ (styrene/butyl acrylate). Bataille et al.[2] confirmed the reciprocal relationship proposed by Wessling.[6]

Snuparek was the first to report results on the behavior of the individual monomer consumption rates for a copolymerization system (butyl methacrylate/butyl acrylate). His results indicated that the individual monomer consumption rates at steady state were equal to the feed rate of each monomer.

Due to the transient nature of semicontinuous processes, the state at which a constant value of the polymerization rate is established is not, strictly speaking, a steady state, though some variables behave like being at a steady state. This state is referred to as a pseudo-steady state (PSS). Though this pseudo-steady state has been observed by many investigators in different semicontinuous polymerization systems, there is still no rigorous analysis to investigate such a behavior. An extension to Wessling's theoretical development is presented here for copolymerization systems and our findings are compared with experimental data collected for the seeded copolymerization of vinyl acetate (VAc)/n-butyl acrylate (BuA). The choice of this particular comonomer system provided the possibility of studying the behavior of a system involving a monomer of a relatively high water solubility (VAc, 2.4 wt %) and another of much lower water solubility in water (BuA, 0.16 wt %).

THE THEORETICAL PREDICTION OF PSEUDO-STEADY STATES

In semicontinuous emulsion polymerization the feed can be either a neat monomer stream or a preemulsified one. In the following analysis neat monomer feeds are assumed. Reactor component balances for each monomer and a reactor volume balance for the semicontinuous process can be derived as follows:

$$F_1 - R_{p1}V_R = \frac{d[\mathrm{M}_1^R]}{dt} V_R + \frac{dV_R}{dt} [\mathrm{M}_1^R] \qquad (1)$$

$$F_2 - R_{p2}V_R = \frac{d[\mathrm{M}_2^R]}{dt} V_R + \frac{dV_R}{dt} [\mathrm{M}_2^R] \qquad (2)$$

$$\frac{dV_R}{dt} = \frac{F_1 MW_1}{d_1} + \frac{F_2 MW_2}{d_2}$$
$$- \left[R_{p1}MW_1\left(\frac{1}{d_1} - \frac{1}{d_p}\right) + R_{p2}MW_2\left(\frac{1}{d_2} - \frac{1}{d_p}\right) \right]V_R \qquad (3)$$

Introducing the long chain approximation, one can easily derive the well-known expressions for the monomer consumption rates as applied to emulsion polymerization systems[8]:

$$R_{p1} = \frac{N_p \bar{n} k_{p11} k_{p22}}{N_A} \cdot \frac{r_1 [M_1^p]^2 + [M_1^p][M_2^p]}{k_{p22} r_1 [M_1^p] + k_{p11} r_2 [M_2^p]} \tag{4}$$

$$R_{p2} = \frac{N_p \bar{n} k_{p11} k_{p22}}{N_A} \cdot \frac{r_2 [M_2^p]^2 + [M_1^p][M_2^p]}{k_{p22} r_1 [M_1^p] + k_{p11} r_2 [M_2^p]} \tag{5}$$

These expressions provide the monomer consumption rates per unit volume of the latex in the reactor. The volume of the latex is the sum of all phase volumes, i.e., aqueous phase, polymer phase, and monomer droplets (if they exist). The term $N_p \bar{n}/N_A$ represents the average radical concentration in the reactor for a compartmentalized free-radical polymerization such as emulsion polymerization.

To account for monomer partitioning between the polymer and aqueous phase, we define the monomer partition coefficients as follows: $a_1 = \phi_1^p/\phi_1^a$ and $a_2 = \phi_2^p/\phi_2^a$. Volume fractions ϕ_i^q are directly related to concentrations through the relation $[M_i^q] = \rho_i \phi_i^q$. The following balances can be derived for the polymer and aqueous phases, and total reactor volume:

$$\phi_1^p + \phi_2^p + \phi_p^p = 1 \tag{6}$$

$$\phi_1^a + \phi_2^a + \phi_w^a = 1 \tag{7}$$

$$V_p = V_R - \frac{V_w^a}{1 - \phi_1^a - \phi_2^a} \tag{8}$$

Implicit in the above equations is the assumption that no polymer is dissolved in the aqueous phase nor water in the polymer particles. The polymer phase volume includes the volume of the pure polymer as well as the volume of the monomer in the monomer-swollen polymer particles.

Note that since

$$a_i = \frac{\phi_i^p}{\phi_i^a} = \frac{\phi_i^p \rho_i}{\phi_i^a \rho_i} = \frac{[M_i^p]}{[M_i^a]} \tag{9}$$

component balances over the two phases (defining an average reactor monomer concentration) lead to

$$[M_i^R] = \left(\frac{V_p}{V_R} + \frac{1}{a_i} \frac{V_a}{V_R} \right)[M_i^p] \tag{10}$$

and using equations (8), (9), we obtain

$$[M_i^R] = \left[\frac{V_p}{V_R} \left(1 - \frac{1}{a_i} \right) + \frac{1}{a_i} \right][M_i^p] \tag{11}$$

$$V_p = V_R - \frac{V_w^a}{1 - ([M_1^p]/\rho_2 a_1) - ([M_2^p]/\rho_2 a_2)} \tag{12}$$

For a seeded emulsion polymerization process the number of particles N will be fixed so that the product $N_p V_R$ will be constant and the rate terms $R_i = R_{pi} V_R$ will not be functions of V_R. Using this general modeling framework, one can predict theoretically the PSS conditions discussed earlier.

From eq. (11) we can define

$$f_i = \frac{V_p}{V_R} \left(1 - \frac{1}{a_i} \right) + \frac{1}{a_i} \tag{13}$$

so that

$$f_i = \frac{[M_i^R]}{[M_i^p]}$$

The model equations (1) and (2) can be now written in general as

$$F_i - R_i = \frac{d(f_i[M_i^p]V_R)}{dt} \tag{14}$$

Introducing the transformation $[M_1^p] = m[M_2^p]$ the reaction rates (mol/s) can be expressed as

$$R_i = KN\bar{n}b_i[M_i^p] \tag{15}$$

where

$$b_1 = \frac{r_1 m + 1}{k_{p22} r_1 m + k_{p11} r_2} \tag{16}$$

$$b_2 = \frac{r_2 + m}{k_{p22} r_1 m + k_{p11} r_2} \tag{17}$$

$$K = \frac{k_{p11} k_{p22}}{N_A} \tag{18}$$

Solving for $[M_i^p]$ and substituting back into eq. (14), one obtains

$$F_i - R_i = \frac{d}{dt} \left(\frac{f_i R_i V_R}{KN\bar{n}b_i} \right) \tag{19}$$

A necessary condition to obtain PSS behavior for both monomer consumption rates is that the ratio m of the monomer concentrations in the polymer phase assume a constant value. It is clear from eqs. (15), (16), and (17) that if R_i is constant, then the ratio R_1/R_2 is constant, and therefore m should be constant since the term $b_1[M_1^p]/b_2[M_2^p]$ is only a function of m.

Therefore, from eq. (19) we finally have

$$R_i = F_i \left/ \left[1 + \frac{1}{Kb_i} \cdot \frac{d}{dt} \left(\frac{f_i V_R}{N\bar{n}} \right) \right] \right.$$ (20)

From this general expression the dependence of the PSS reaction rate on the monomer addition rate is demonstrated. Several other parameters are involved such as the total number of particles in the system, the average number of radicals per particle, propagation constants, etc. Under certain conditions and related assumptions, this expression can provide more insight on the factors affecting the PSS reaction rate. To simplify the mathematics involved, in the following we will neglect the volume change due to the monomer to polymer transformation the contribution of which is minor.

Sparingly Water-Soluble Monomers

In the case of sparingly water-soluble monomers, one can argue that almost all the monomer resides in the monomer-swollen polymer particles, e.g., $\phi_i^a = 0$. Thus, $f_i = V_p/V_R$ and the rate expression becomes

$$R_i = F_i \left/ \left[1 + \frac{1}{Kb_i} \cdot \frac{d}{dt} \left(\frac{V_p}{N\bar{n}} \right) \right] \right.$$ (21)

Fixed Radical Concentration

As the particle size increases, the radical concentration must increase. Eventually, a point is reached where more than one radical is present per particle. In this situation, the radical concentration is more likely to be constant. The system will, therefore, behave more or less like continuous addition bulk or solution polymerization with constant radical concentration. In this case we have

$$N\bar{n}/V_p = \text{const}$$ (22)

Then from eq. (21) we obtain

$$R_i = F_i$$

It should be mentioned here that the particle size needed to achieve conditions of fixed radical concentration might be out of the range usually encountered in emulsion systems. However, there is no evidence excluding this possibility.

Seeded Systems

If the system is seeded, we expect that the total number of particles N will be constant. In the limiting case II of the Smith–Ewart model $\bar{n} = 0.5$. Under these conditions or conditions where $\bar{n}$ is constant, the particle growth rate will be constant. Then from eq. (21) we obtain

$$R_i = F_i \bigg/ \left(1 + \frac{1}{Kb_i N\bar{n}} \cdot \frac{dV_p}{dt}\right) \tag{23}$$

From eq. (8) we can write

$$\frac{dV_p}{dt} = \frac{dV_R}{dt}$$

because the volume of the water in the aqueous phase V_w^a does not change and $\phi_i^a = 0$. If we define the monomer feed rates ratio as $\mu = F_1/F_2$, from eq. (3) the growth rate of the reactor volume is given as

$$\frac{dV_R}{dt} = F_1 \cdot \left(\frac{MW_1}{d_1} + \frac{MW_2}{\mu d_2}\right) \tag{24}$$

or

$$\frac{dV_R}{dt} = F_2 \cdot \left(\frac{\mu MW_1}{d_1} + \frac{MW_2}{d_2}\right) \tag{25}$$

Then the expressions for the PSS become

$$R_1 = F_1 \bigg/ \left[1 + \frac{1}{Kb_1 N\bar{n}} \cdot \left(\frac{MW_1}{d_1} + \frac{MW_2}{\mu d_2}\right) \cdot F_1\right] \tag{26}$$

$$R_2 = F_2 \bigg/ \left[1 + \frac{1}{Kb_2 N\bar{n}} \cdot \left(\frac{\mu MW_1}{d_1} + \frac{MW_2}{d_2}\right) \cdot F_2\right] \tag{27}$$

These relationships can be rearranged in reciprocal form:

$$1/R_i = G_i + 1/F_i \tag{28}$$

where

$$G_1 = \frac{1}{Kb_1 N\bar{n}} \cdot \left(\frac{MW_1}{d_1} + \frac{MW_2}{\mu d_2}\right) \tag{29}$$

$$G_2 = \frac{1}{Kb_2 N\bar{n}} \cdot \left(\frac{\mu MW_1}{d_1} + \frac{MW_2}{d_2}\right) \tag{30}$$

Again, as in the case of fixed radical concentration, the dependence of the PSS reaction rate on the monomer addition rate is linear with a slope of unity.

Water-Soluble Monomers

For water-soluble monomers eq. (13) yields

$$f_i V_R = V_p \left(1 - \frac{1}{a_i}\right) + \frac{V_R}{a_i} \tag{31}$$

In the case of fixed radical concentration the problem is more complex than that with the sparingly water-soluble monomers. The condition of fixed radical concentration is not sufficient to obtain a constant reaction rate. However, if the partition coefficients are proportional to the volume ratio of the aqueous phase to the polymer phase, then a PSS is predicted. In this case

$$V_a / V_p a_i = \text{const} \tag{32}$$

By differentiation of eq. (31) and because of eqs. (22) and (32) we have

$$\frac{d}{dt}\left(\frac{f_i V_R}{N\bar{n}}\right) = \frac{d}{dt}\left(\frac{V_p}{N\bar{n}} + \frac{V_a}{a_i N\bar{n}}\right) = \frac{d}{dt}\left(\frac{V_p}{N\bar{n}}\right) + \frac{d}{dt}\left(\frac{V_a}{V_p a_i} \cdot \frac{V_p}{N\bar{n}}\right) = 0 \tag{33}$$

Then $R_i = F_i$ again, as in the case of sparingly water-soluble monomers. From the definition of the partition coefficients, the condition (32) means that the ratio of the total moles of monomer in the polymer phase over the total moles of monomer in the water phase is constant. However, since $R_i = F_i$ the overall amount of monomer (mol) in the reactor remains constant. Thus, this condition basically suggests that the amount of monomer in each phase does not change at the PSS.

For a seeded system with constant $\bar{n}$ and partition coefficients, we have from eq. (20):

$$R_i = F_i \left/ \left[1 + \frac{1}{Kb_i N\bar{n}} \cdot \frac{d(f_i V_R)}{dt} \right] \right. \tag{34}$$

and

$$\frac{d(f_i V_R)}{dt} = \left(1 - \frac{1}{a_i}\right) \cdot \frac{dV_p}{dt} + \frac{1}{a_i} \cdot \frac{dV_R}{dt} \tag{35}$$

Since the reaction rates assume constant values and $\bar{n}$ is assumed constant, the monomer concentrations in the polymer phase are constant, i.e., $[M_i^p]$ is constant. The partition coefficients are also assumed constant; thus $[M_i^a]$ is constant and, consequently, ϕ_i^a is constant. Thus, again from eq. (8) we obtain

$$\frac{dV_p}{dt} = \frac{dV_R}{dt}$$

The PSS reaction rate expressions are then

$$R_1 = F_1 \left/ \left[1 + \frac{1}{Kb_1 N\bar{n}} \cdot \left(\frac{MW_1}{d_1} + \frac{MW_2}{\mu d_2}\right) \cdot F_1 \right] \right. \tag{36}$$

$$R_2 = F_2 \left/ \left[1 + \frac{1}{Kb_2 N\bar{n}} \cdot \left(\frac{\mu MW_1}{d_1} + \frac{MW_2}{d_2}\right) \cdot F_2 \right] \right. \tag{37}$$

These expressions are exactly the same as eqs. (26) and (27) for the case of sparingly water-soluble monomers.

For the cases studied here the expressions and assumptions for water-soluble monomers are, of course, more strong than those for sparingly water-soluble monomers. The latter can be easily derived from the water-soluble monomer expressions.

In the case of fixed radical concentration the final expression is the same. For water-soluble monomers the assumption made was that the monomer amount in each phase is constant at the PSS. For sparingly water-soluble monomers this is true.

In the case of a seeded system with constant $\bar{n}$ the assumption made for water-soluble monomers was that the partition coefficients are constant. For sparingly water-soluble monomers this is again true.

Continuous Addition Emulsion Homopolymerization

From the above PSS reaction rate expressions for a general copolymerization system, one can obtain the corresponding expressions for homopolymerization. Because of its simplicity, the homopolymer case has been studied in the literature and similar analyses produced the same expressions as ours.

The analysis and the results for sparingly water-soluble monomers and fixed radical concentration are exactly the same.

In the case of sparingly water-soluble monomers and seeded reaction, by setting $\mu = 0$, $m = 0$, and dropping the subscripts we obtain from equation (27):

$$R = F \left/ \left[1 + \frac{N_A}{k_p N \bar{n}} \cdot \left(\frac{MW}{d} \right) \cdot F \right] \right. \tag{38}$$

Wessling[6] studied the kinetics of continuous addition homopolymerization. He came up with the same conclusions but his treatment was based on material balances over the polymer phase and the assumption that all the monomer diffuses instantaneously into the polymer particles. However, no analysis was provided for the case of water-soluble monomers and in the presence of monomer partitioning between the different phases.

Low Addition Rates and a Unified View

From the cases studied in the preceding sections a general result is that under certain assumptions the relationship between the monomer consumption rates and the monomer feed rates is the same for both soluble and insoluble monomers. Depending on the specific process conditions, this relationship is either $R_i = F_i$ (fixed radical concentration) or $1/R_i = G_i + 1/F_i$ (seeded system with constant $\bar{n}$). However, the results reported in the literature for different systems, as discussed earlier in this work, are in support of either one of the two relationships for the same process conditions. The monomer consumption rate was found to be directly proportional to monomer feed rate (e.g., $R_i = F_i$) both in seeded[1,7] and nonseeded polymerizations.[4,5] The reciprocal relationship was again observed both in seeded[6] and nonseeded[2] systems. This, of course,

suggests that, under specific underlying conditions, both of the relationships are practically valid.

A key parameter affecting the PSS conditions is the total number of particles in the system. Assuming that the feed rates are in the range of monomer starved conditions, increasing the number of particles will result in a lower value for the constant appearing in the denominator of eq. (20). This means that the PSS reaction rate is approaching the magnitude of the monomer feed rate. In the limit, as N grows unbounded, $R_i = F_i$. In this limit all the cases studied before are unified without any assumptions. However, this limiting case of unbounded N is not a realistic one.

The most probable condition to be realistic is the semicontinuous operation under extremely low monomer feed rates. In this case, if the reciprocal formula derived for seeded systems is put in the form

$$R_i = F_i / (1 + F_i G_i) \tag{39}$$

then the term $F_i G_i$ becomes very small relative to unity and at the PSS the system seems to follow the relationship $R_i = F_i$. In all works cited before, the monomer feed rates were indeed extremely small to allow for this apparent duality. This conclusion is also in good agreement with the well-established fact that the resulting copolymer composition is very close to the comonomer feed composition if the semicontinuous copolymerization is carried out with very low feed rates. This can be achieved only if the monomer consumption rates assume the value of the corresponding monomer feed rates. This has been observed in both seeded and nonseeded systems. The preceding analysis is confirmed by our experimental data in the following.

EXPERIMENTAL PROCEDURES

Emulsion copolymerizations of vinyl acetate (VAc)/n-butyl acrylate (BuA) were carried out in a 1000 mL jacketed glass resin reactor flask under nitrogen blanket and atmospheric pressure. Several considerations were taken into account to avoid coagulation problems. FMI positive displacement pumps were employed for precise control of very small liquid flow rates and used for the monomer delivery into the reactor. The reaction was carried out at 60°C. Reactor temperature was controlled by an internal cooling coil connected to another pump which delivered cold water at rates decided by a computer-based temperature controller. An analog open bath immersion circulator was used for maintaining the jacket temperature at the same value as the reaction mixture temperature, and so acting as insulation to the reactor. The inlet/outlet temperatures of the coil and the jacket, and the reactor temperature were continuously monitored by T-type thermocouples.

Monomers were purified to remove inhibitors before polymerization. Vinyl acetate (Badische-BASF) was distilled under highly purified nitrogen through a rectifying column. Butyl acrylate (USI Chemicals) was washed with 5% (wt) solution of sodium hydroxide and then with distilled water until its pH became neutral. After it was dried over anhydrous sodium sulfate, it was distilled under vacuum and nitrogen atmosphere. Monomer purity was checked by gas chro-

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TABLE I
Semicontinuous Emulsion Copolymerization Recipe

Ingredient	Parts by[a] weight (%)	1000 mL reactor (g)
Seed latex (80 : 20 wt %, VAc : BuA)		
Total comonomer	2.667	20
Deionized water	66.667	500
Triton X-165	0.400	3
Aerosol MA-80	0.133	1
Aerosol OT 75%	0.133	1
Ammonium persulfate	0.267	2
Sodium bicarbonate	0.133	1
Semicontinuous stage		
Comonomer added	30.667	230

[a] Based on water plus comonomer mixture.

matography before use. Emulsifiers, buffer, and initiator were used as provided by the suppliers.

The recipe[9] used in making the seed latex, as well as for the semicontinuous emulsion copolymerization is given in Table I. Both batch and semicontinuous runs were conducted. The batch copolymerization experiments were useful in specifying the upper limit of the semicontinuous reaction rates and confirming the operation under monomer starved conditions. During the semicontinuous experiments the monomer addition rates were held constant for a specified period of time. Different addition rates were used and the addition period was specified so that the total monomer added at the end of this period was the same for every run. The ratio of the two monomer feed rates was held constant for all the runs (VAc : BuA = 4 : 1, in g/min) to study the copolymerization of 80 : 20 VAc/BuA system. The monomer feed rates are shown in Table II.

TABLE II
Semicontinuous Runs: Monomer Feed Rates[a]

Run	Vinyl acetate	Butyl acrylate
	g/min (mol/s $\times 10^4$)	
Flooded region		
SEMF1	4.0538 (7.848)	0.9586 (1.247)
SEMF2	3.2851 (6.359)	0.8205 (1.067)
Controlled region		
SEMC1	1.2876 (2.493)	0.3047 (0.396)
SEMC2	0.7652 (1.481)	0.1651 (0.215)
SEMC3	0.4888 (0.946)	0.1186 (0.154)

[a] Correction due to pump variability applied.

RESULTS AND DISCUSSION

In semibatch processes there is no standard way of defining conversion. For these processes several definitions of conversion are given in the literature (i.e., overall conversion, instantaneous conversion, conversion at time t, etc.). In our treatment the so-called *overall conversion* was used. This is defined as the ratio of the amount of monomer converted into polymer (including the monomer for seeding) to the total amount of monomer used in the recipe. Conversion was followed by gravimetric analysis.

When the feed rates exceeded the maximum values for starved conditions (flooded region), the conversion–time curves overlapped with the batch test curves, confirming the fact that the batch polymerization rate is the maximum rate which can be achieved (Fig. 1). Figure 2 shows that, in the controlled region, the conversion time curves were slightly sigmoidal and dependent on the feed rates. Curves became almost linear shortly after the beginning of monomer feeding and remained so until its end. It is clear that the conversion (and the overall polymerization rate) increased with increasing feed rates, i.e., the rate of polymerization was controlled by the availability of the monomer in the system, as expected for monomer starved conditions. The rate of polymerization during the semibatch runs in the controlled region was obviously slower than that of the corresponding batch run. These observations are in agreement with Wessling's analysis of the kinetics of continuous addition emulsion polymerization.[6] The linear part of the conversion curves corresponds to a constant *overall* reaction rate. Data of the residual monomer concentrations (collected by gas chromatography) were used to calculate the individual con-
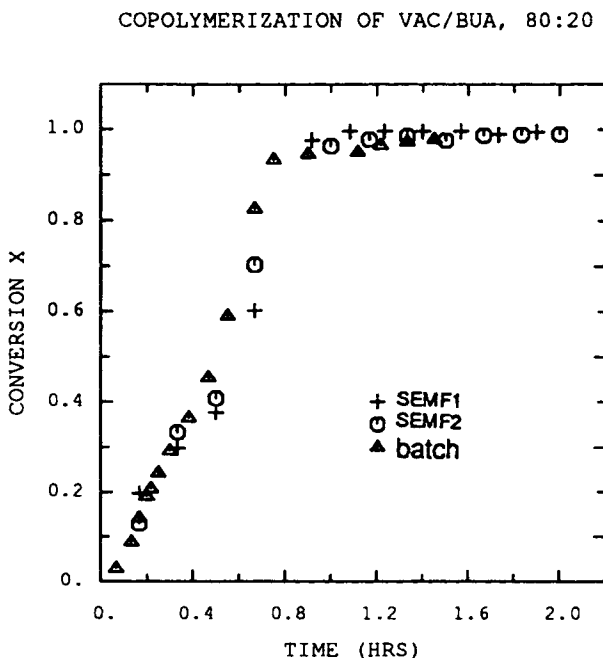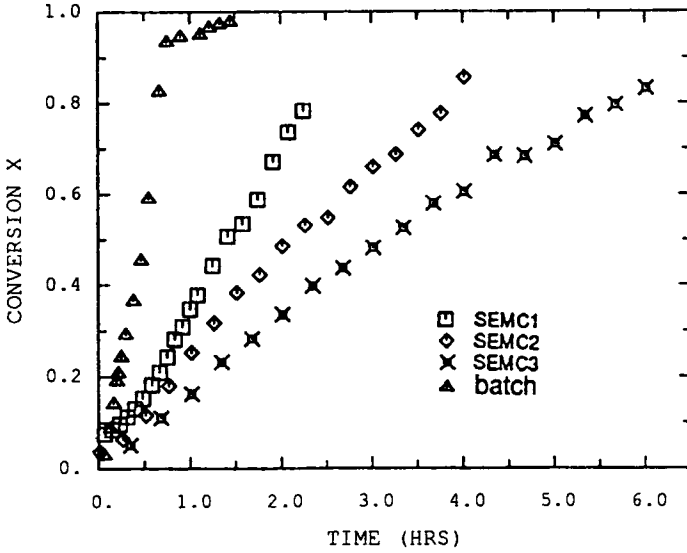
COPOLYMERIZATION OF VAC/BUA, 80:20

Fig. 1. Overall conversion vs. time data for the batch and semibatch runs with different monomer feed rates (see Table II) of the emulsion copolymerization of VAc/BuA, 80 : 20. Flooded region.

COPOLYMERIZATION OF VAC/BUA, 80:20

Fig. 2.   Overall conversion vs. time data for the batch and semibatch runs with different monomer feed rates (see Table II) of the emulsion copolymerization of VAc/BuA, 80 : 20. Controlled region.

sumption rates of the two monomers from eqs. (1) and (2). In Figures 3 and 4 the monomer consumption rates are shown to assume a constant value in the very early stages of the process.
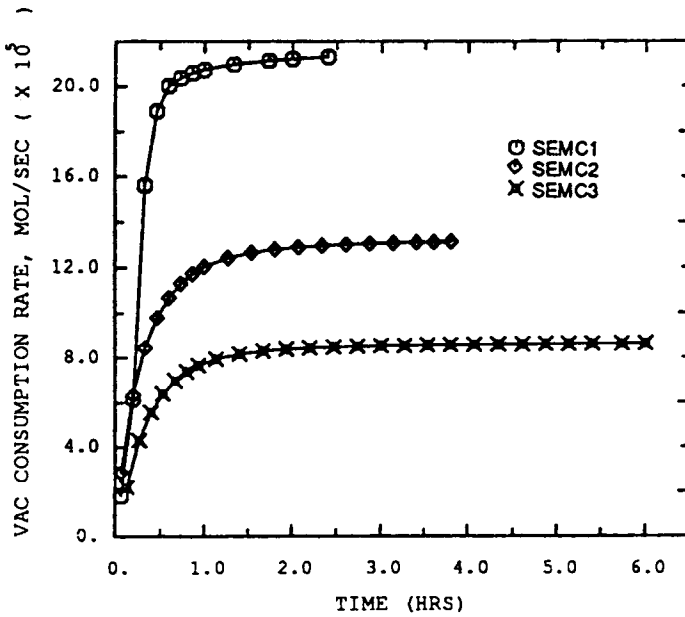
COPOLYMERIZATION OF VAC/BUA, 80:20

Fig. 3.   VAc consumption rate vs. time of the 80 : 20, VAc/BuA semibatch copolymerization for various monomer feed rates (see Table II).
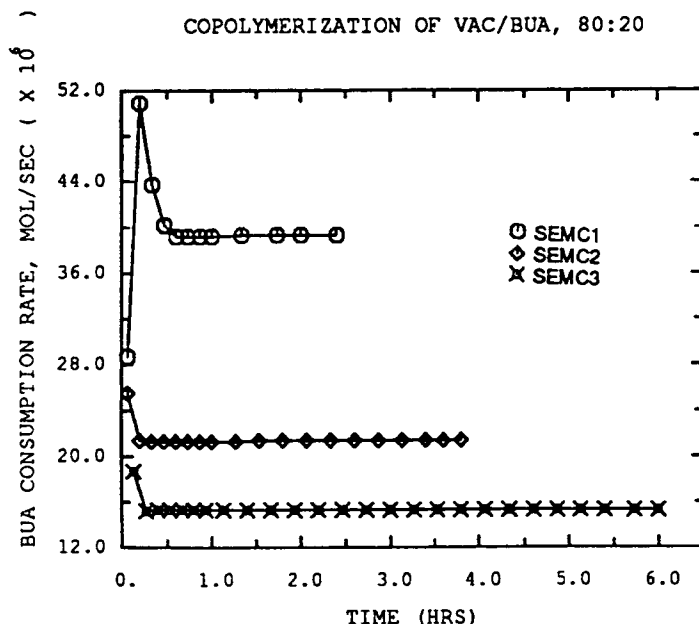
Fig. 4.   BuA consumption rate vs. time of the 80 : 20, VAc/BuA semibatch copolymerization for various monomer feed rates (see Table II).

Figures 5 and 6 demonstrate the linear relationship $R_i = \sigma F_i$ between the individual monomer consumption rates at the PSS and the corresponding monomer addition rate. The proportionality constant between the reaction rate and the addition rate was found to be equal to 0.82 for VAc and 0.99 for BuA.

It is important to observe that only the behavior of VAc deviates from the mechanism proposed by Gerrens. The 0.99 proportionality coefficient of BuA is very close to the theoretical one and the difference is definitely within experimental error. The deviation of VAc behavior can be attributed to the different degree of solubility of VAc as compared to BuA. In Table III several key variables affecting the course of polymerization are listed. All of them were calculated at the PSS conditions of run SEMC3. One observation to be made from the data in this table is the fact that even at the PSS almost 5–6% of the total VAc present in the system resides in the water phase. On the other hand, BuA in the water phase is always less than 1% of its total amount in the system. The ratio of the monomer concentrations in the polymer phase m remains fairly constant as assumed earlier. The total number of particles in the system was calculated by TEM and remained constant throughout the run at a value of 5.14×10^{16} particles. Thus, the analysis for the case of seeded systems applies to our experimental data. It is important, though, that the copolymer system studied does by no means follow Smith–Ewart kinetics II. The average number of radicals per particle is much larger than 1 as shown in Table III. A slight increase in $\bar{n}$ is observed. At first glance, this seems to be a problem to apply correctly the analysis for seeded systems presented earlier, because a major assumption made was that $\bar{n}$ is constant. However, a more careful examination of the $\bar{n}$ variation reveals that its magnitude is really too small to result in a significant change of the reaction rate value at the PSS. The reaction rate
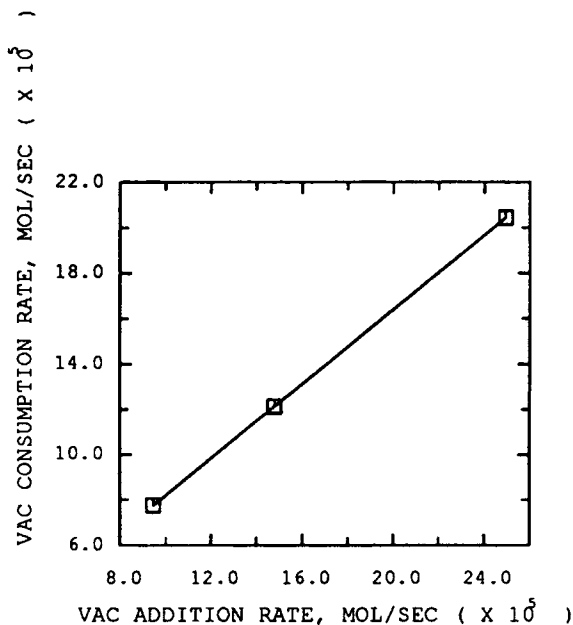
Fig. 5. VAc consumption rate at the pseudo-steady state vs. VAc addition rate for various monomer feed rates.

change at the PSS caused by $\bar{n}$ variation can be obtained by expanding the rate in Taylor series as follows:

$$R_i = R_{i,pss} + \frac{dR_i}{d\bar{n}}\bigg|_{pss} \cdot (\bar{n} - \bar{n}_{pss}) + \cdots + (\text{higher order terms}) \quad (40)$$

This expression can be transformed in dimensionless form by performing a division by R_{pss} and by using eq. (15) we obtain

$$\frac{R_i}{R_{i,pss}} = 1 + \frac{1}{\bar{n}_{pss}} \cdot (\bar{n} - \bar{n}_{pss}) + \cdots + (\text{higher order terms}) \quad (41)$$

Using the data in Table III, the second order term in eq. (41) is found to be of order 10^{-2} and thus its contribution can be neglected as small relative to unity. Therefore, with this order-of-magnitude analysis the $\bar{n}$ variation can be neglected and $\bar{n}$ can be considered as constant for all practical purposes.

Another assumption to be validated concerns the behavior of the partition coefficient for the water-soluble monomer (VAc). From Table III again, a_1 reaches an almost constant value as assumed in the analysis for water-soluble monomers. Thus, the analysis for sparingly water-soluble monomers applies to BuA and that for water-soluble monomers to VAc and consequently our data should fit a reciprocal relationship of the form:
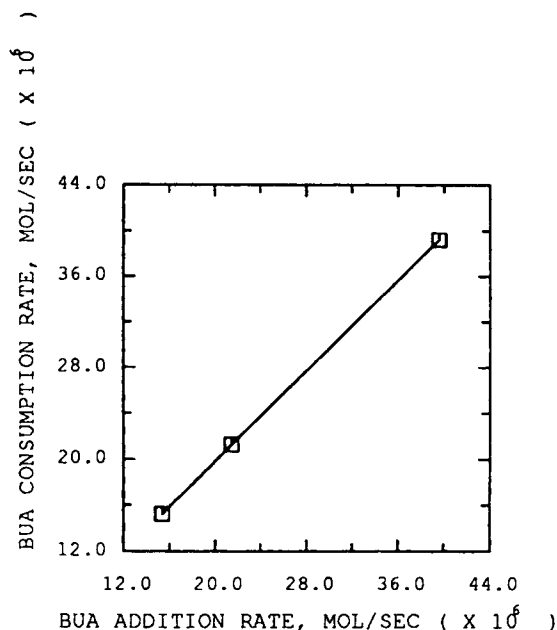
$$1/R_p = G + K/F \quad (42)$$

Fig. 6. BuA consumption rate at the pseudo-steady state vs. BuA addition rate for various monomer feed rates.

where G and K are constant coefficients. K was found to be equal to 1.0464 for VAc and 1.0057 for BuA. This is in excellent agreement with our treatment where the theoretical value of K is 1. The value of G depends on many parameters such as the number of particles in the system, the average number of radicals per particle, the monomer feed rate ratio, propagation constants, etc.; so it varies from run to run. However, the linear dependence of both monomers reaction rate on the corresponding monomer feed rate confirms the analysis presented earlier in this work. An interesting observation discussed in the preceding demonstrates how the available data can fit also the relationship $R_i = \sigma_i F_i$. For the run SEMC3 the values of G were: $G_1 = 1955.6$ s/mol and $G_2 = 554.2$ s/mol. The kinetic constants used were at 60°C: $r_1 = 0.04$, $r_2 = 5.5$, $k_{p11} = 3700$ L/mol s[10], $k_{p22} = 66$ L/mol s.[11-13] Thus, for the feed rates of run

TABLE III
PSS Variables for Run SEMC3

X	$\bar{n}$	a_1	a_2	% VAc	% BuA	m
				In pol. phase		
0.61	9.91	39.90	324.65	93.25	99.09	121.59
0.68	10.26	39.89	320.99	93.85	99.16	121.83
0.71	10.42	39.88	319.37	94.11	99.20	121.93
0.77	10.66	39.88	317.16	94.46	99.24	122.07
0.79	10.77	39.87	316.14	94.61	99.26	122.13
0.83	10.91	39.87	314.87	94.82	99.29	122.21

SEMC3, we obtain that $1 + F_1G_1 = 1.185$ and $1 + F_2G_2 = 1.0085$. Then from eq. (39) the proportionality constant is found to be $\sigma_1 = 0.84$ and $\sigma_2 = 0.99$ as earlier calculated in this section by fitting the PSS data.

As pointed out by Wessling's treatment, the time required to reach the PSS for both monomers depended on the rate of addition. Increasing the monomer addition rate extends the time it takes to get to the PSS. BuA, as expected, reaches this PSS faster and its consumption rate drops down to zero almost instantaneously when monomer feeding is stopped. VAc behaves slower and its consumption rate is nonzero for a while after the end of the monomer addition period. For the entire monomer addition time the monomer reaction rates were less than the rate of monomer addition, indicating that the level of unreacted monomer in the reactor builds up during the run. This fact was experimentally confirmed by an independent measurement of the reactor concentrations by gas chromatography.

CONCLUSIONS

The theoretical development presented indicates that in semicontinuous emulsion copolymerization or homopolymerization, with constant monomer addition rates and starved conditions, the system reaches a pseudo-steady state at which the individual monomer consumption rates assume a constant value. The PSS monomer consumption rate depends linearly with the monomer addition rate. The slope of the linear function is unity. In the case of fixed radical concentration the relationship is $R_i = F_i$, while in the case of seeded systems and constant number of particles it is of the form $1/R_i = G_i + 1/F_i$. The result is the same for both cases either when dealing with water-soluble or sparingly water-soluble monomers. However, the conditions for assuming the PSS are different. For seeded systems a constant or slowly varying $\bar{n}$ is the only requirement for sparingly water-soluble monomers. In addition to this, constant or slowly varying partition coefficients are required for water-soluble monomers. Depending on the magnitude of the monomer feed rate the relationship $R_i = F_i$ can be applicable for seeded systems also. The analysis presented unifies the different experimentally observed and reported in the literature relationships between R_i and F_i. The final PSS may depend on a variety of factors not accounted for in the preceding analysis. However, for all practical purposes the assumptions made and the predicted results for water-soluble and insoluble monomers were confirmed experimentally for the seeded copolymerization of VAc/BuA.

APPENDIX: NOMENCLATURE

a_i partition coefficient
d_i monomer density (kg/m^3)
d_p polymer density (kg/m^3)
F_i monomer feed rate ($kmol/s$)
k_{pii} propagation rate constant ($m^3/kmol\ s$)
$[M_i^q]$ unreacted monomer i concentration in phase q ($kmol/m^3$ phase q)
$[M_i^R]$ unreacted monomer i concentration in reactor ($kmol/m^3$ latex)
MW_i monomer molecular weight

m ratio of monomer concentration $[M_1^p]$ over $[M_2^p]$

N total number of particles

N_p number of particles per unit volume of latex $(1/m^3)$

N_A Avogadro's constant

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

R_i polymerization reaction rate $(kmol/s)$

R_{pi} polymerization reaction rate per unit volume of latex $(kmol/s\ m^3)$

r_i reactivity ratio

V_q total volume of phase q (m^3)

V_R total volume of latex in the reactor (m^3)

V_w^a water volume in aqueous phase (m^3)

Greek Symbols

ρ_i molar monomer density (mol/m^3)

σ_i proportionality constant between R_i and F_i

ϕ_i^q volume fraction of monomer i in phase q

ϕ_p^p volume fraction of polymer in polymer phase

ϕ_w^a volume fraction of water in aqueous phase

Subscripts

$i = 1$, for VAc

$i = 2$, for BuA

$q = a$, for aqueous phase

$q = p$, for polymer particles

Superscripts

$q = a$, for aqueous phase

$q = p$, for polymer particles

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