Continuous Emulsion Polymerization of Vinyl Acetate. I. Operation in a Single Continuous Stirred Tank Reactor using Sodium Lauryl Sulfate as Emulsifier

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ABSTRACT: Continuous emulsion polymerizations of vinyl acetate were carried out at 50 °C in a single continuous stirred-tank reactor using sodium lauryl sulfate as emulsifier and potassium persulfate as initiator. It was found that (1) the so-called limit cycles could take place in monomer conversion, the number of polymer particles and the molecular weight of polymers produced under certain operating conditions, (2) the time-average steady-state monomer conversion was proportional to the 0.31 power of the emulsifier concentration in the feed, to the 0.50 power of the initiator concentration, to the -1.0 power of the monomer concentration, and to the 0.90 power of the mean residence time, and (3) the time-average steady-state number of polymer particles produced was proportional to the 2.1 power of the emulsifier concentration in the feed, to the -0.80 power of the initiator concentration, to the 0 power of the monomer concentration, and to the -0.92 power of mean residence time. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2748–2754, 2002

Key words: continuous emulsion polymerization; continuously stirred tank reactor; vinyl acetate; emulsion polymerization

INTRODUCTION

Continuous emulsion polymerization processes are at presently employed on a large scale in the production of synthetic rubber latex. However, these processes are also becoming more and more important for the production of other synthetic latexes. Vinyl acetate (VAC) homo- and co-polymer latexes are very important because, among other things, of the increasing demand due to environmental problems as paints, coatings, adhesives, and so on. Therefore, it is anticipated that in the future a considerable part of these latex products will be produced commercially with continuous emulsion polymerization processes.

In spite of enormous importance for the production of VAC homo- and co-polymer latexes by continuous emulsion polymerization processes, only a few published papers are available at present.[1,2] From these reports, however, we do not necessarily understand the details of the effects of operating variables on the kinetic behavior of the continuous emulsion polymerization of VAC in a continuously stirred tank reactor (CSTR). Several modeling papers, without extensive experimental data, have also been published to date,

their purpose being mainly to explain quantitatively the oscillatory behaviors in the monomer conversion and the number of polymer particles produced.[3–7]

The purpose of this study is, therefore, to experimentally elucidate in more detail the kinetic behavior of the continuous emulsion polymerization of VAC operated in a single CSTR using sodium lauryl sulfate (NaLS) as emulsifier and potassium persulfate (KPS) as initiator. In the succeeding paper, the results are compared with that of the continuous emulsion polymerization of VAC carried out in a single continuous Couette–Taylor vortex flow reactor (CCTVFR) using NaLS as emulsifier and KPS as initiator.
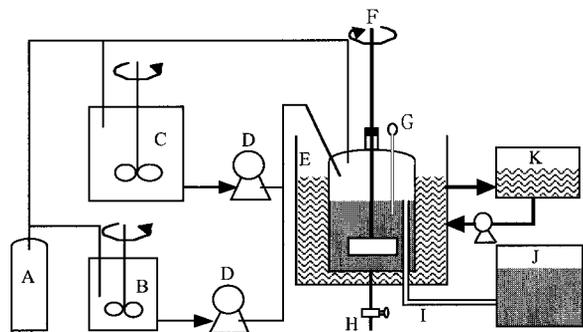
EXPERIMENTAL

To enable the comparison of the kinetic data obtained in continuous emulsion polymerization with those obtained in batch emulsion polymerization, the procedures and the methods for purification of reagents used and for measurements of the average degree of polymerization of polymer produced, the monomer conversion, and the number of polymer particles produced were made basically the same as those employed earlier in batch emulsion polymerization experiments.[8,9]

Experimental apparatus

Continuous emulsion polymerization of VAC was carried out in a single glass-made CSTR. The schematic

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Figure 1 Schematic diagram of experimental apparatus: (A) high purity nitrogen tank, (B) storage tank for aqueous initiator solution, (C) storage tank for VAC emulsion, (D) metering pumps, (E) thermostated water bath, (F) four-bladed paddle-type impeller, (G) thermometer, (H) sampling stopcock, (I) overflow pipe for effluent waste emulsion, (J) storage tank for waste emulsion, (K) temperature controller.

diagram of the experimental apparatus is shown in Figure 1. The geometry and the dimensions of the reactor, impeller, and buffle plates were the same as those used in batch experiments.[8,9]

Materials

Sodium lauryl sulfate (NaLS) and potassium persulfate (KPS) of extra pure grade were used as emulsifier and initiator, respectively, without further purification. VAC monomer was distilled twice under reduced pressure in a nitrogen atmosphere, stored in a refrigerator kept at −20 °C, and distilled again just before use. All water used in the polymerization experiments was purified by distillation in the presence of alkaline potassium permanganate.[8,9]

Experimental procedures

The experimental setup used is shown in Figure 1. The experimental procedure was almost the same as that employed in the continuous emulsion polymerization of styrene.[10] The polymerization was started by the following procedure: Aqueous initiator solution and monomer emulsion were separately held in individual glass-made tanks (B and C), with the oxygen remaining in these tanks purged by bubbling high-purity nitrogen gas (purity > 99.995%) (A) for 1.5 h. The reactor was initially charged with the feed concentration of all materials except the initiator. Any oxygen remaining in the whole reactor system was purged by bubbling the high-purity nitrogen gas from the sampling stop-cock (H) for ~0.5 h. Then, a necessary amount of aqueous initiator solution, which had been previously deoxygenated by the same method, was quickly injected into the reactor to begin the polymerization, and at the same time, the feed pumps (D) were

started. The reaction temperature was kept within 50 ± 0.5 °C with a thermostated water bath (E). Monomer conversion was followed gravimetrically using aqueous NaCl solution as precipitant for poly(vinyl acetate) latex, and the viscosity-average degree of polymerization of polymer produced was determined by the viscosity-in-benzene-solution method employing the Mark–Howink Equation given by Nakajima:[11]

$$[\eta] = 5.36 \times 10^{-4} \bar{M}_\eta^{0.62} \tag{1}$$

where $\bar{M}_\eta$ is the viscosity-average molecular weight.

The number of polymer particles produced was determined by electron micrography using the following equations:

$$\bar{d}_p^3 = \sum_i n_i d_{pi}^3 / \sum_i n_i \tag{2}$$

$$N_T = 6 M_F X_M / \pi \bar{d}_p^3 \rho_p \tag{3}$$

where ρ_p is the density of polymer, M_F is the initial monomer concentration,, and X_M is the monomer conversion where the sample was taken.

RESULTS AND DISCUSSION

Typical examples of the course of continuous emulsion polymerization of vac

A typical example, shown in Figure 2, demonstrates that under certain conditions, the monomer conversion and the viscosity-average degree of polymerization of polymer produced both oscillate cyclically and do not reach steady-state values. The polymerizations were carried out with the emulsifier, initiator, and
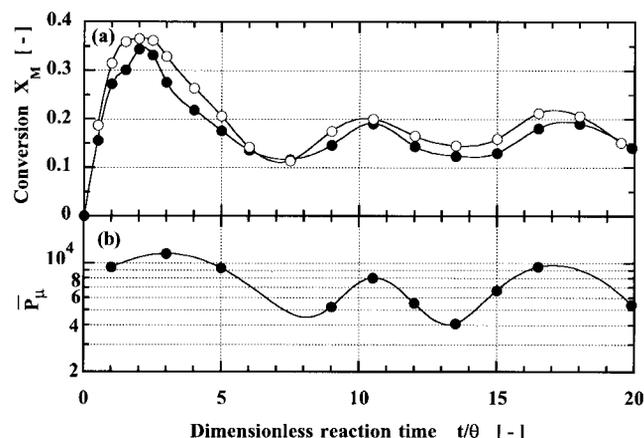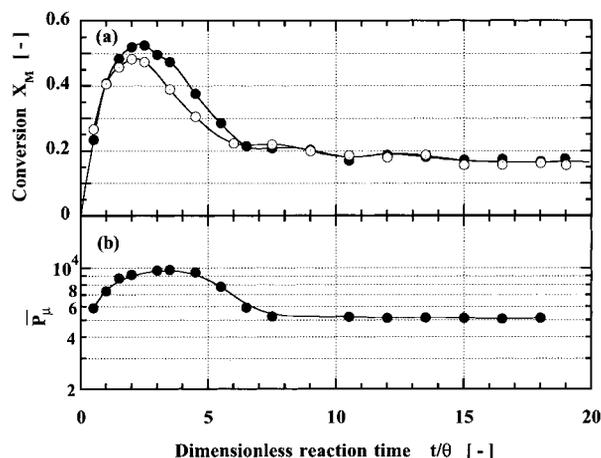

Figure 2 Typical example of the course of continuous emulsion polymerization of VAC: (a) monomer conversion versus reaction time, and (b) the viscosity-average degree of polymerization of polymer produced versus reaction time. (Reaction conditions: 50 °C, S_F = 2.0 g/dm³ water, I_F = 1.25 g/dm³ water, M_F = 0.20 g/cm³ water, and θ = 20 min.)
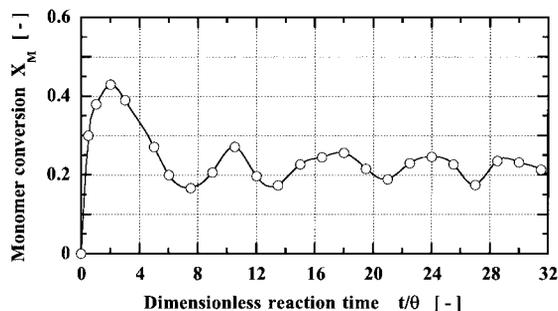
Figure 3 Typical example of limit cycle in monomer conversion in the continuous emulsion polymerization of VAC. (Reaction conditions: 50 °C, S_F = 2.0 g/dm³ water, I_F = 1.25 g/dm³ water, M_F = 0.20 g/cm³ water, and θ = 23 min.)

Figure 4 Typical example of the course of continuous emulsion polymerization of VAC without oscillatory responses: (a) monomer conversion versus reaction time, and (b) the viscosity-average degree of polymerization of polymer produced versus reaction time. (Reaction conditions: 50 °C, S_F = 0.70 g/dm³ water, I_F = 2.50 g/dm³ water, M_F = 0.20 g/cm³ water, and θ = 20 min.)

monomer concentrations in the feed and the mean residence time fixed at S_F = 2.0 g/dm³ water, I_F = 1.25 g/dm³ water, M_F = 0.2 g/cm³ water, and θ = 20 min. As shown by the closed and open circles, good reproducibility was confirmed by carrying out the polymerization experiment twice. The period of the oscillation in the viscosity-average degree of polymerization of polymer produced is almost the same as that of the monomer conversion. As shown later, the reason for these oscillations can be ascribed to the oscillation in the number of polymer particles produced. However, there is some doubt that the oscillatory response seen in Figure 2 may only be a transient behavior on the way to a steady-state. Therefore, a long-term experiment was carried out to make sure that these cyclic oscillations could be sustained oscillations (the so-called limit cycle). The results of a long-term polymerization experiment are shown in Figure 3. It is seen that the cyclic oscillation continues with almost the same amplitude and period as those observed in the early stage of the polymerization, even after 32 times the mean residence time has elapsed since the start of polymerization. These experimental result suggest, therefore, that the cyclic oscillation observed in Figure 2 should be the so-called limit cycle. Under some different conditions, however, both the monomer conversion and the viscosity-average degree of polymerization of polymer produced could reach each real steady-state very smoothly without any oscillatory response, as shown in Figure 4. Good reproducibility was also confirmed by carrying out two experiments with the same reaction conditions. Moreover, it must be noted here that we often observe the case, as shown in Figure 5, where the monomer conversion finally reaches a steady-state with an initial monomer conversion overshoot followed by a long period of damped oscillations.

A typical example that indicates that the number of polymer particles produced also oscillates cyclically with reaction time when cyclic oscillations in the monomer conversion take place is shown in Figure 6.

The electron micrographs of polymer particles taken in the experiment shown in Figure 6 are shown in Figure 7. The pictures, numbered P1 to P6, correspond to those taken at the points indicated by P1 to P6 in Figure 6(b). In pictures P1 and P2, almost no very fine particles exist that have just nucleated. However, a lot of very fine particles start to appear in picture P3. This result suggests that the second particle nucleation stage has just begun somewhere between P2 and P3. In picture P5, on the other hand, very fine particles have again disappeared. This result implies that the second particle nucleation stage has stopped somewhere between P4 and P5. From these considerations, we can conclude that the number of polymer particles produced oscillates cyclically with reaction time, as shown by the solid line. Moreover, each maximum in the number of polymer particles produced seems to appear somewhat ahead of the corresponding maxi-
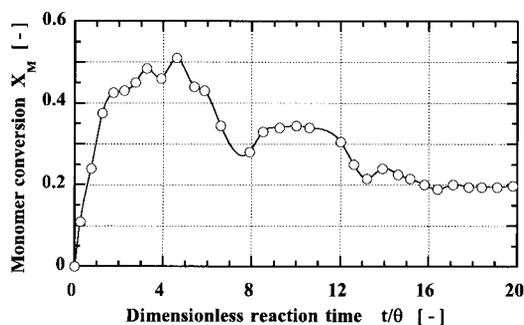
Figure 5 Typical example of the course of continuous emulsion polymerization of VAC with damped oscillation in monomer conversion. (Reaction conditions: 50 °C, S_F = 2.0 g/dm³ water, I_F = 0.313 g/dm³ water, M_F = 0.20 g/cm³ water, and θ = 45 min.)
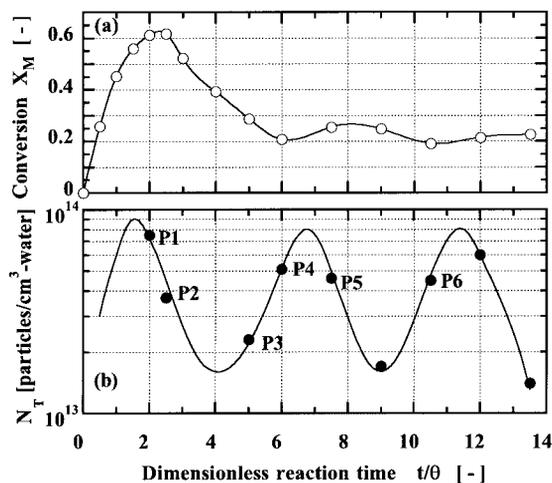
Figure 6 Typical example of the course of continuous emulsion polymerization of VAC with cyclic oscillation in monomer conversion and the number of polymer particles produced. (Reaction conditions: 50 °C, S_F = 0.70 g/dm^3 water, I_F = 1.25 g/dm^3 water, M_F = 0.10 g/cm^3 water, and θ = 20 min.)

mum in the monomer conversion. This result directly demonstrates that the intermittent particle nucleation in the continuous emulsion polymerization of VAC in a CSTR is the reason for the oscillations in the monomer conversion, the number of polymer particles produced, and the average molecular weight of the produced polymer.

Effects of operating variables on the course of polymerization

We denote the instantaneous values of the monomer conversion and the number of polymer particles as X_M and N_T, respectively. When sustained oscillation takes place, the monomer conversion and the number of polymer particles produced oscillate around each time-average value with reaction time; therefore, we distinguish between their true and time-average steady-state values. The true steady-state values of these parameters are denoted X_{MS} and N_{TS}, respectively, and their time-average steady-state values are denoted $\bar{X}_{MS}$ and $\bar{N}_{TS}$, respectively. For example, the time-average steady-state monomer conversion, $\bar{X}_{MS}$, is defined by the following expression:

$$\bar{X}_{MS} = \frac{\int_{(t/\theta)_1}^{(t/\theta)_2} X_M dX_M}{(t/\theta)_2 - (t/\theta)_1} \qquad (4)$$

where t/θ is the nondimensional reaction time, and $(t/\theta)_1$ is the appropriate time after ample time has elapsed after decay of the initial conversion overshoot.[6]
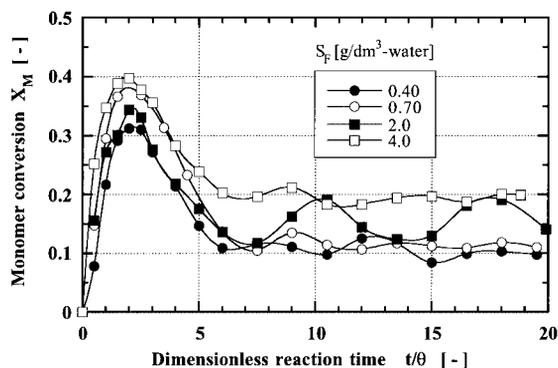
Effect of emulsifier concentration in the feed

The effect of emulsifier concentration in the feed (S_F) on the monomer conversion versus time curves observed when S_F is varied from 0.4 to 4.0 g/dm^3 water with the monomer and initiator concentrations in the feed and the mean residence time fixed at M_F = 0.2 g/cm^3 water, I_F = 1.25 g/dm^3 water, and θ = 20 min, respectively, is shown in Figure 8. Except for the case with S_F = 2.0 g/dm^3 water, oscillatory response, if any, is not so remarkable. The effect of emulsifier concentration on the feed on the time-average steady-state monomer conversion and number of polymer particles produced is shown in Figure 9. In this case, the time-average steady-state monomer conversion and number of polymer particles produced are proportional to the 0.31 power and the 2.1 power of the emulsifier concentration in the feed, respectively. According to the mass balance of monomer in the reactor, the rate of emulsion polymerization at steady-state, R_{ps} is expressed by

$$R_{ps} = \frac{M_F X_{MS}}{\theta} \quad \text{or} \quad \left(= \frac{M_F \bar{X}_{MS}}{\theta} \right) \qquad (5)$$

where θ is the mean residence time.
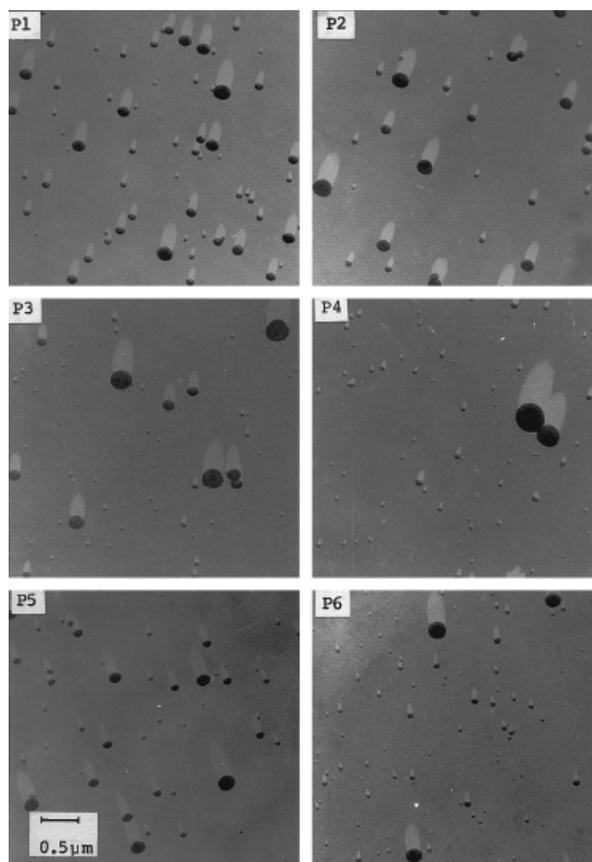
Figure 7 Electron micrographs of polymer particles corresponding to the experiment shown in Figure 6 Photos P1–P6 correspond to the figures P1–P6 in Figure 6b.

Figure 8 Effect of emulsifier concentration in the feed on the monomer conversion versus reaction time. (Reaction conditions: 50 °C, S_F = varied, I_F = 1.25 g/dm^3 water, M_F = 0.20 g/cm^3 water, and θ = 20 min.)

Using eq. 5 and the observed relationships, $\bar{X}_{MS} \propto S_F^{0.31}$ and $\bar{N}_{TS} \propto S_F^{2.1}$, we get

$$R_{ps} \propto \bar{N}_{TS}^{0.14} \tag{6}$$

This result corresponds roughly to that obtained in the batch emulsion polymerization of VAC[9,10] and also agrees approximately with the theoretical prediction, $R_P \propto N_T^{1/6}$, which was derived for the batch emulsion polymerization of VAC with the assumption that radial desorption from the polymer particles is dominant.[8,9,12,13]

Effect of initiator concentration in the feed

The effect of initiator concentration in the feed (I_F) on the monomer conversion versus time curves, observed by varying I_F from 0.625 to 5.0 g/dm^3 water and with the emulsifier and monomer concentrations in the feed and the mean residence time fixed at S_F = 0.70 g/dm^3 water, M_F = 0.2 g/cm^3 water, and θ = 20 min, respectively, is shown in Figure 10. In the case with I_F = 5.0 g/dm^3 water, the polymerization started at 40 °C and then, the reaction temperature was switched to 50 °C at the time when the reaction time had reached six times the mean residence time since the start of polymerization. The reason for this is as follows: In continuous emulsion polymerization in a CSTR, it is known that there are three possible steady-states; they are, two stable (lower and upper) steady-states and one unstable steady-state between these "lower" and "upper" steady-states when certain reaction conditions are satisfied.[14] If an initial monomer conversion overshoot is beyond the unstable steady-state, the monomer conversion will reach, if any, the "upper" steady-state in the higher monomer conversion range. In the cases other than I_F = 5.0 g/dm^3 water, the monomer conversion seems to reach the "lower" steady-state in the lower monomer conversion range. For the monomer conversion to reach the "lower"
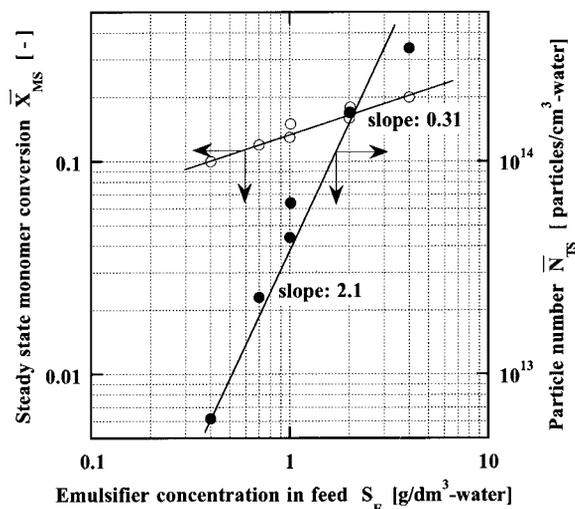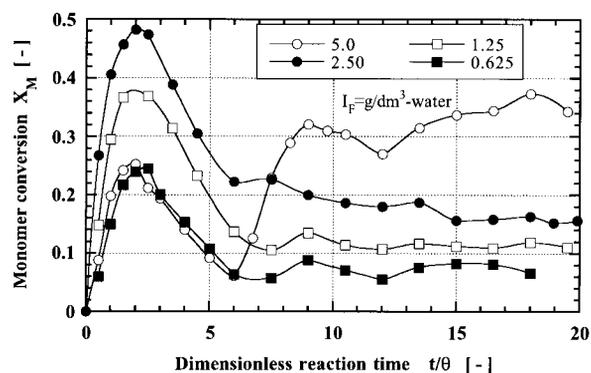

Figure 9 Effect of emulsifier concentration in the feed on the (time-average) steady-state monomer conversion and number of polymer particles produced corresponding to Figure 8.

steady-state by avoiding an excessive overshoot, therefore, we used the method of switching the reaction temperature from 40 to 50 °C around the time when an initial conversion overshoot was over.
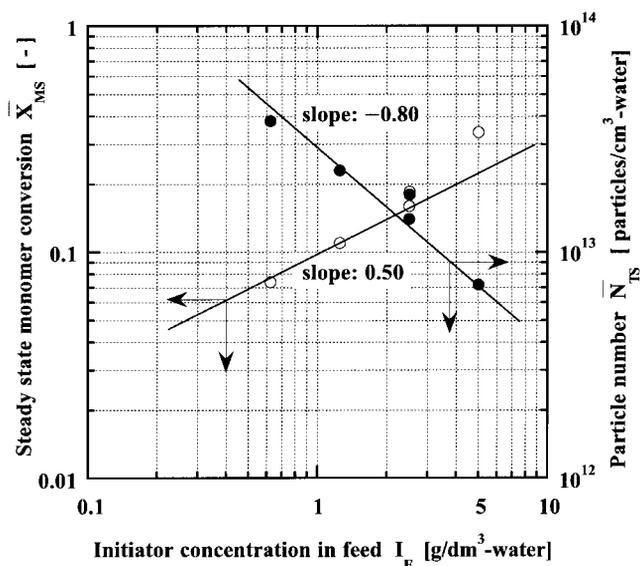
The effect of initiator concentration in the feed on the time-average steady-state monomer conversion and number of polymer particles produced is shown in Figure 11. The time-average steady-state monomer conversion and number of polymer particles produced are proportional to the 0.50 power and the −0.80 power of the initiator concentration in the feed, respectively.

Effect of monomer concentration in the feed

The effect of monomer concentration in the feed (M_F) on the monomer conversion versus time curves was examined by varying M_F from 0.1 to 0.5 g/cm^3 water and keeping the emulsifier and initiator concentra-

Figure 10 Effect of initiator concentration in the feed on the monomer conversion versus reaction time. (Reaction conditions: 50 °C, I_F = varied, S_F = 0.70 g/dm^3 water, M_F = 0.20 g/cm^3 water, and θ = 20 min.)
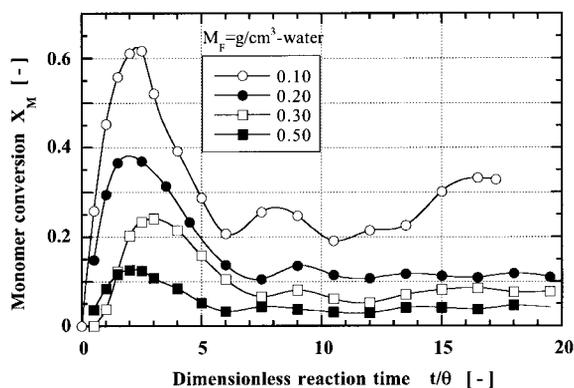
Figure 11 Effect of initiator concentration in the feed on the time-average steady-state monomer conversion and number of polymer particles produced corresponding to Figure 10.

tions in the feed and the mean residence time fixed at $S_F = 0.70$ g/dm^3 water, $I_F = 1.25$ g/dm^3 water, and $\theta = 20$ min, respectively. The experimental results are shown in Figure 12. Almost no appreciable oscillatory responses were observed under this recipe and conditions. On the other hand, the effect of monomer concentration in the feed on the time-average steady-state monomer conversion and num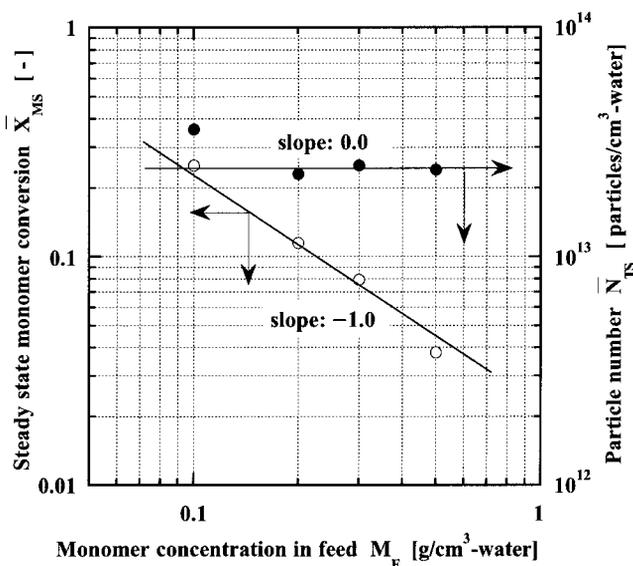ber of polymer particles produced, corresponding to Figure 12, is shown in Figure 13. It is evident that the time-average steady-state monomer conversion is inversely proportional to the monomer concentration, and that the monomer concentration does not affect the steady-state number of polymer particles produced.

Effect of mean residence time

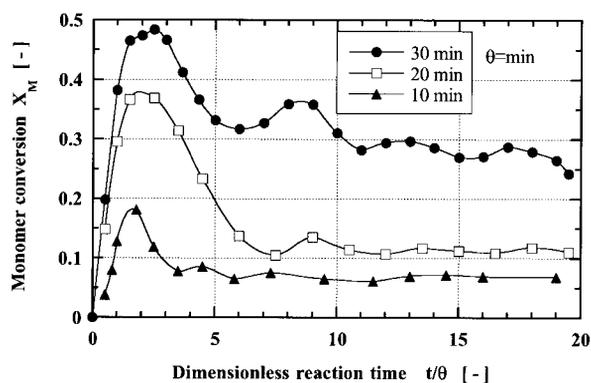The effect of the mean residence time (θ) on the monomer conversion versus time curves was examined by

Figure 12 Effect of monomer concentration in the feed on the monomer conversion versus reaction time. (Reaction conditions: 50 °C, M_F = varied, $S_F = 0.70$ g/dm^3 water, $I_F = 1.25$ g/dm^3 water, and $\theta = 20$ min.)
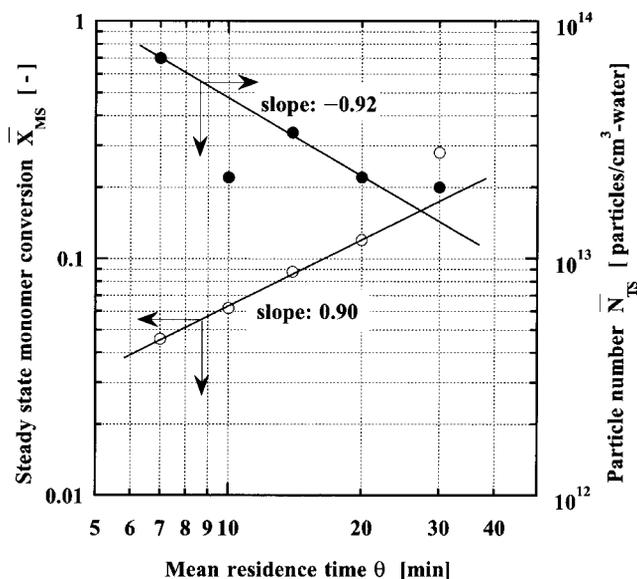

Figure 13 Effect of monomer concentration in the feed on the time-average steady-state monomer conversion and number of polymer particles produced corresponding to Figure 12.

varying θ from 7 to 30 min and keeping the emulsifier, initiator, and monomer concentrations fixed in the feed at $S_F = 0.70$ g/dm^3 water, $I_F = 1.25$ g/dm^3 water, and $M_F = 0.2$ g/cm^3 water, respectively. For simplicity, only the experimental results for $\theta = 10$, 20, and 30 min are shown in Figure 14. When $\theta = 10$ and 20 min, the monomer conversion did not oscillate appreciably and finally reached each steady-state. The case with $\theta = 30$ min is a typical example where the monomer conversion gradually reaches a steady-state with a long period of damped oscillations. It seems that the monomer conversion did not yet reach a steady-state even when the reaction time had elapsed over 20 times the mean residence time. Under this recipe and conditions, the time-average steady-state values of the monomer conversion and the number of polymer particles produced varied, as shown in Figure 15, in pro-

Figure 14 Effect of the mean residence time on the monomer conversion versus reaction time. (Reaction conditions: 50 °C, θ = varied, $M_F = 0.20$ g/cm^3 water, $S_F = 0.70$ g/dm^3 water, and $I_F = 1.25$ g/dm^3 water).

Figure 15 Effect of the mean residence time on the time-average steady-state monomer conversion and number of polymer particles produced corresponding to Figure 14.

portion to the 0.90 power and to the −0.92 power of the mean residence time, respectively.

CONCLUSIONS

The experimental results obtained in this study are summarized as follows:

$$\bar{X}_{MS} \propto S_F^{0.31} I_F^{0.50} M_F^{-1.0} \theta^{0.90} \tag{7}$$

$$\bar{N}_{TS} \propto S_F^{2.1} I_F^{-0.80} M_F^{0.0} \theta^{-0.92} \tag{8}$$

$$R_{ps} = \frac{M_F \bar{X}_{MS}}{\theta} \propto S_F^{0.31} I_F^{0.50} M_F^{0.0} \theta^{-0.12} \tag{9}$$

On the other hand, the experimental results reported by Green et al.[1, 15] are as follows:

$$R_{ps} = \frac{M_F \bar{X}_{MS}}{\theta} \propto S_F^{0.1} I_F^{0.1} \theta^{0.0} \tag{10}$$

$$N_{TS} \propto S_F^{0.99} I_F^{-1.75} \theta^{1.25} \tag{11}$$

Their experimental conditions are almost the same as those employed by us except that the reaction temperature used was 40 °C, ammonium persulfate was used as the initiator, and they did not report the effect of monomer concentration in the feed on the steady-state monomer conversion and number of polymer particles. Their experimental findings on the kinetics are not so different from those found in this study except that a completely reverse tendency was obtained of the effect of mean residence time on the number of polymer particles produced. Considering that the rate

of polymerization in batch emulsion polymerization of VAC is proportional to the 0.16 power of the number of polymer particles,[9] our experimental results seem to be rather reasonable.

The effects of the initial emulsifier, initiator, and monomer concentrations on the rate of polymerization and the number of polymer particles produced in the batch emulsion polymerization of VAC conducted at 50 °C using NaLS as emulsifier and KPS as initiator, respectively, are summarized as[9]

$$R_p \propto S_o^{0.15} I_o^{0.50} M_o^{0.38} \tag{12}$$

$$N_T \propto S_o^{0.92} I_o^{0.0} M_o^{0.0} \tag{13}$$

It is clear from the experimental results shown by eqs. 7–13 that the effects of operating variables on the kinetics of emulsion polymerization of VAC are very different between batch and continuous operations with a stirred-tank reactor. These characteristics are also very different from those of the emulsion polymerization of styrene to which the Smith–Ewart theory is applicable.[10, 15–19] These results suggest that the experimental data obtained in batch emulsion polymerization is not necessarily directly applicable to the design of the continuous flow operation of emulsion polymerization with a CSTR.

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