Continuous Emulsion Polymerization of Vinyl Acetate. II Operation in a Single Couette–Taylor Vortex Flow Reactor using Sodium Lauryl Sulfate as Emulsifier

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ABSTRACT: Continuous emulsion polymerizations of vinyl acetate were conducted at 50°C in a single continuous Couette–Taylor vortex flow reactor (CCTVFR) using sodium lauryl sulfate as emulsifier and potassium persulfate as initiator. The polymerization can be carried out very smoothly and stably, but the steady-state monomer conversion attained in a CCTVFR is not as high as that in a plug flow reactor (PFR), but only slightly higher than that in a continuous stirred tank reactor (CSTR), even if the Taylor number is adjusted to an optimum value. Also, the effects of operating variables, such as the emulsifier, initiator, and monomer concentrations in the feed and the mean residence time on the kinetic behaviors were almost the same as those observed in a CSTR. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2755–2762, 2002

Key words: colloids; kinetics; radical polymerizaton; emulsion polymerization

INTRODUCTION

Continuous emulsion polymerization is important for economical production of commercial synthetic polymer latexes. Although large-scale production of synthetic polymer latexes is, at present, usually carried out with a continuous stirred tank reactor (CSTR) system, application of a tubular reactor (TR) to continuous emulsion polymerization is desirable because the reactor efficiency of a TR with plug flow is much higher than that of a CSTR with perfectly mixed flow. In addition, oscillations in monomer conversion, particle number, and polymer molecular weight can be suppressed.[1,2] However, long-term stable operation of continuous emulsion polymerization in a TR is not necessarily easy because of plugging of reactor tubes due to the deposition of flocculated polymer particles onto the reactor wall.[3]

As an alternative to a TR, we proposed using a continuous flow reactor with a Couette–Taylor vortex flow, called a continuous Couette–Taylor vortex flow reactor (CCTVFR),[4,5] because (1) the flow pattern in this reactor can be made very close to plug flow by decreasing the rotational speed of the inner cylinder (Taylor number) and (2) it is anticipated that shear-induced coagulation of polymer latexes can be minimized with this reactor because a weak shear field can be realized in the reaction mixture. To demonstrate these attributes of CCTVFR, we carried out the continuous seeded and unseeded emulsion polymerization of styrene (St), a sparingly water-soluble monomer, in a CCTVFR at 50°C.[4,5] We found that this reactor system is certainly suitable for continuous production of polymer latexes with a considerably narrower particle size distribution,[4] and that the continuous unseeded emulsion polymerization of St could be operated very smoothly without any oscillatory behavior and with much higher efficiency than that of a CSTR.[5] Kataoka et al.[6] conducted the continuous emulsion polymerization of St in a CCTVFR. Moritz et al.[7] also carried out the continuous emulsion polymerization of n-butyl methacrylate in a CCTVFR with the same objectives as ours. Thus, we concluded from our experimental observations that a CCTVFR is suitable, for example, as the seeding reactor (pre-reactor) for a continuous unseeded emulsion polymerization reactor system with CSTRs connected in series.

The emulsion polymerization of VAC, a moderately water-soluble monomer, follow very different kinetics from that of the emulsion polymerization of St, a sparingly water-soluble monomer.[8–10] Therefore, it is interesting to compare the kinetic behavior of the continuous emulsion polymerization of VAC in a CCTVFR with that of the continuous emulsion polymerization of St in a CCTVFR.[5] Moreover, it is interesting to know whether the performance of a CCTVFR is much better than that of a CSTR in the continuous emulsion polymerization of VAC and whether coagulation of polymer latexes and oscillations in monomer conversion, particle number and polymer molecular

weight, which are usually observed in the continuous emulsion polymerization of VAC in a CSTR,[2,11,12] can be reduced or suppressed with a CCTVFR. With these objectives, we carried out the continuous emulsion polymerization of VAC at 50°C in a single CCTVFR.

EXPERIMENTAL

Flow characteristics of CCTVFR

A typical flow pattern caused by rotation of the inner of the two concentric cylinders is shown in Figure 1. The flow pattern is well known to be governed by the dimensionless number called the Taylor number, T_a, which is defined as

$$T_a = \left(\frac{\omega b R_i}{v}\right)\left(\frac{b}{R_i}\right)^{1/2} \tag{1}$$

where R_i is the inner cylinder radius (cm), b is the radial clearance between concentric cylinders (cm), v is the kinematic viscosity (cm^2/s), and ω is the angular velocity of inner cylinder (1/s).

When the value of T_a exceeds a certain value around 50, called the critical Taylor number, T_{ac}, a transition takes places from pure Couette flow to a flow pattern where toroidal vortices are regularly spaced in an annular space along the axis of the cylinders, as shown in Figure 1. The flow can be seen as an train of clearly separated vortex pairs, each consisting of two counter-rotating vortices. This flow is called laminar vortex flow. It is well known that the intermixing between two adjacent vortices is comparatively limited, but the
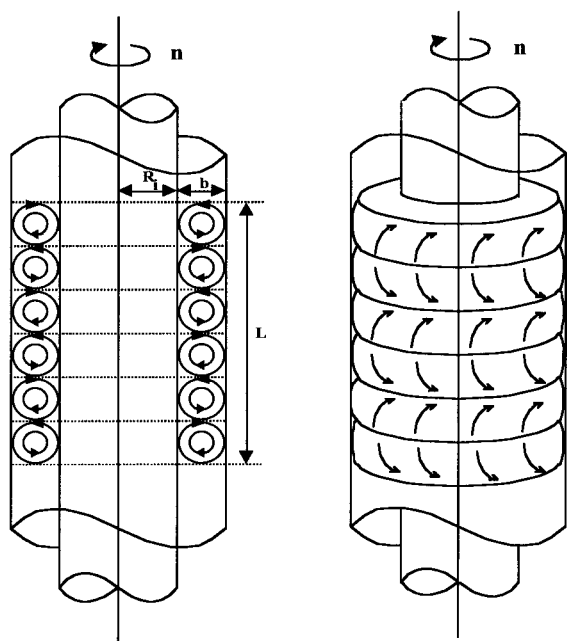

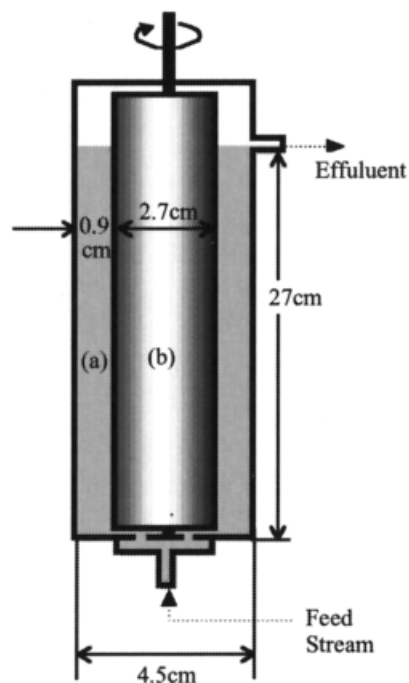**Figure 1** Schematic diagram of Couette–Taylor vortex flow.

Figure 2 Schematic diagram of Couette–Taylor vortex flow reactor and its dimensions: (a) annular space of two concentric cylinders, (b) inner cylinder.

mixing inside each vortex is fairly good. Furthermore, if a small constant axial flow is added to this laminar vortex, each vortex moves with a velocity equal to the average velocity of the axial flow, holding its original shape. Therefore, we can assume that a CCTVFR with laminar vortex flow has locally ideal stirred-tank behavior, but overall plug flow behavior.

The detailed configuration of the reactor used in this study is shown in Figure 2.[4,5] The annular space is used as a reaction vessel. The inner circular cylinder is made of stainless steel and the outer circular cylinder made of glass with a water jacket, as shown in Figure 3. The outside diameter of the inner cylinder is 27 mm, and the inside diameter of the outer cylinder is 45 mm. The length of the reactor and the total volume of annular space are 270 mm and 292.2 cm^3, respectively. The mixing characteristics of the reactor were examined by the stimulus-response method, and the results are reported in the previous papers.[4,5]

Polymerization experiments

Materials and experimental set-up

The VAC monomer supplied by Kuraray Company without inhibitor was stored in a refrigerator and distilled under vacuum (40°C, 290 mmHg) just before use. Potassium persulfate (KPS) and sodium lauryl sulfate (NaLS) of extra pure grade were used as received as the initiator and the emulsifier, respectively. All water was distilled and deionized (DDI). The sche-
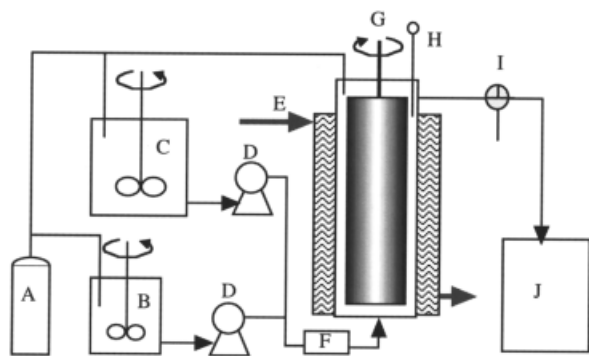
Figure 3 Schematic diagram of experimental apparatus: (A) high purity nitrogen tank, (B) storage tank for aqueous initiator solution, (C) storage tank for styrene emulsion, (D) metering pumps, (E) cooling water, (F) thermostated water bath, (G) rotational inner cylinder, (H) thermometer, (I) sampling cock, and (J) storage tank for waste emulsion.

matic diagram of the experimental apparatus used is illustrated in Figure 3. VAC monomer emulsion and aqueous initiator solution were held separately in glass-made tanks, B and C, respectively.

Experimental procedure

Prior to start-up, oxygen remaining in the storage tanks (B and C) was purged by bubbling high-purity nitrogen gas (purity > 99.995%) for ~ 1.5 h. The oxygen remaining in the whole reactor system was also removed by bubbling the high-purity nitrogen gas from the reactor inlet attached at the bottom of the reactor for ~0.5 h. Then, the polymerization was started by feeding both the monomer emulsion and the aqueous initiator solution into the empty reactor by turning on each metering pump (D). The reaction temperature was kept constant within $50 \pm 0.5°C$ by circulating cooling water (E) from a thermostated water bath through the reactor jacket. Polymerization experiments were normally conducted for longer than 12 times the mean residence time. Effluent reaction mixture from the outlet attached at the top of the reactor was regularly collected and was subjected to the measurements of the monomer conversion and the number of polymer particles produced. The monomer conversion and the number of polymer particles produced was determined by the same methods as employed in previous work.[10,13]

RESULTS AND DISCUSSION

Effect of Taylor number (rotational speed of the inner cylinder)

It is known that the flow pattern in a CCTVFR can be changed from perfectly mixed flow to a flow pattern close to plug flow by decreasing the rotational speed of the inner cylinder (n_s); that is, by decreasing the

Taylor number (T_a).[4,5] Therefore, the effect of T_a value on the monomer conversion, X_M, versus reaction time (dimensionless reaction time, t/θ) was examined by varying the rotational speed of the inner cylinder, n_S, from 20 to 290 rpm. The emulsifier and monomer concentrations in the emulsion tank (C) and the initiator concentration in the aqueous initiator solution tank (B) were adjusted so that the emulsifier, monomer, and initiator concentrations in the merged feed stream just entering the reactor are $S_F = 2.0$ g/dm³ water, $M_F = 0.2$ g/cm³ water, and $I_F = 1.25$ g/dm³ water, respectively. The mean residence time was fixed at $\theta = 20$ min. Because the viscosity of the reaction mixture comprising a heterogeneous phase varies with the progress of polymerization, it is very difficult to calculate the exact T_a value from eq. 1. When the value of T_a was calculated, therefore, the viscosity of water at 50°C was employed as an approximate value for the viscosity of the reaction mixture because the volume fraction of the dispersed monomer droplet and polymer particle phases in the reaction mixture was comparatively lower (<20%). For example, when the rotational speed of the inner cylinder changed from 20 to 290 rpm, the corresponding T_a value changed roughly from 375 to 5447. In this study, therefore, we exclusively used the rotational speed of the inner cylinder as a substitute for the Taylor number.

The effect of the rotational speed of the inner cylinder, n_s on the monomer conversion versus time curve is shown in Figure 4. The monomer conversion oscillates cyclically, independent of the value of n_s, and does not reach a steady-state value at least by the time of 13 times the mean residence time. It is not clear at present, however, whether this oscillatory response is a sustained oscillation (the so-called limit cycle) that continues permanently. Moreover, the monomer con-
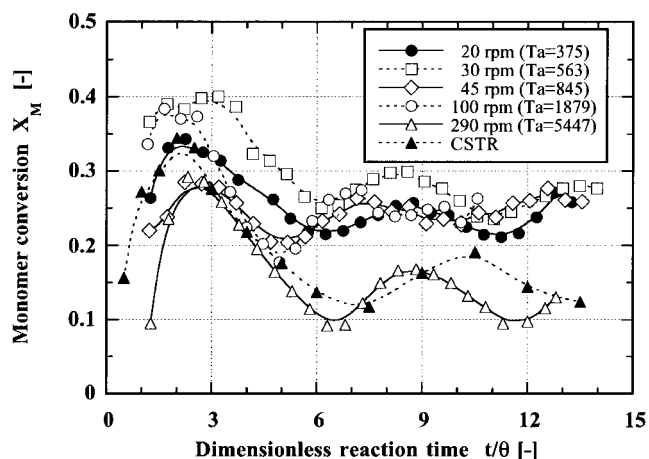

Figure 4 Effect of rotational speed of inner cylinder on the monomer conversion versus reaction time. (Reaction conditions: $S_F = 2.0$ g/dm³ water, $I_F = 1.25$ g/dm³ water, $M_F = 0.2$ g/cm³ water, and $\theta = 20$ min.)

version did not change so much even if the value of n_s was changed between 20 and 100 rpm, although the monomer conversion observed at the stirring speed of 20–100 rpm was somewhat higher than that observed at $n_s = 290$ rpm, and that in a CSTR operated with the same conditions as in this study.[13] Considering that the monomer conversion versus time curve observed at $n_s = 290$ rpm is almost the same as that observed in a CSTR, we can consider that the flow pattern in the CCTVFR operated at $n_s = 290$ rpm must be very close to perfectly mixed flow.

In the case of St, contrary to the case of VAC, the monomer conversion did not oscillate with reaction time and approached a steady-state value very smoothly in less than twice the mean residence time.[5] Furthermore, when the T_a value was decreased to T_{ac}, the critical Taylor number, the steady-state monomer conversion approached the value observed in batch emulsion polymerization.[5] This result is because the flow pattern in the reactor approached plug flow with decreasing T_a value and, accordingly, the number of polymer particles produced increased up to that produced in a batch reactor. As already stated, the kinetic behavior of the continuous emulsion polymerization of VAC in a CCTVFR is very different from that of St. This difference mainly comes from the difference in the kinetics of particle formation and growth. It is known that in the batch emulsion polymerization of VAC, the particle growth rate (the rate of polymerization) is proportional to the 0.16 (1/6) power of the number of polymer particle produced because of a very high rate of radical desorption from the polymer particles.[10] Therefore, even if the number of polymer particles produced is increased twice, for example, by changing T_a value, the rate of polymerization increases only by 10%. Thus, the change in the number of polymer particles does not affect the monomer conversion as much in the case of VAC emulsion polymerization. The reason for the oscillatory response seems to be that the reactor behaves almost like a CSTR, possibly because of the appreciable axial back mixing, regardless of T_a value. In the case of the continuous emulsion polymerization of St with a CCTVFR, the flow pattern in the reactor could be made very close to plug flow by decreasing the T_a value to near the T_{ac} value.[5] Therefore, the reason why the axial back mixing is so dominant in the case of continuous VAC emulsion polymerization in a CCTVFR is not clear at present.

We define here the time-average steady-state monomer conversion, $\bar{X}_{MS}$ by the following expression:[12]

$$\bar{X}_{MS} = \frac{\int_{(t/\theta)_1}^{(t/\theta)_2} X_M dX_M}{(t/\theta)_2 - (t/\theta)_1} \qquad (2)$$
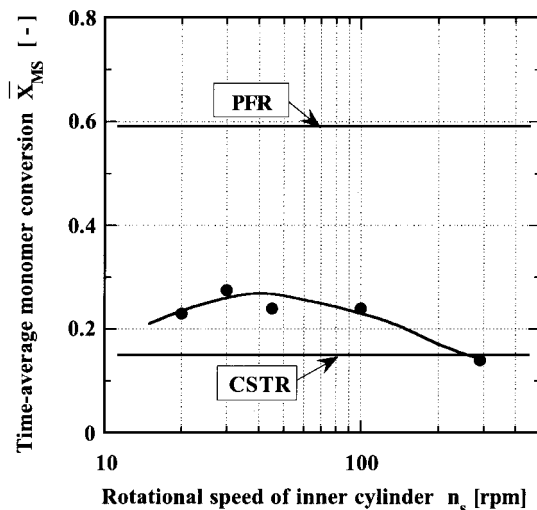

Figure 5 Effect of rotational speed of inner cylinder on the time-average steady-state monomer conversion in Figure 4 and its comparison with that attained in a PFR and in a CSTR.

where t/θ is the dimensionless reaction time, and $(t/\theta)_1$ is an appropriate time after ample time is elapsed following the decay of the initial conversion overshoot.

We calculated the time-average steady-state monomer conversions, $\bar{X}_{MS}$, from the data in Figure 4 and plotted them against the rotational speed of the inner cylinder, n_s in Figure 5. In this case, the time-average steady-state monomer conversion was calculated between about $(t/\theta)_1 = 6$ and $(t/\theta)_2 = 12$. With decreasing the value of n_s from 290 rpm, the value of $\bar{X}_{MS}$ increases from that attained in a CSTR, reaches a maximum at ~30 rpm, and then begins to decrease. It is clear that this tendency is almost the same as that observed in the continuous emulsion polymerization of St in a CCTVFR,[5] but the maximum value of $\bar{X}_{MS}$ is far less than the value that would be attained in a PFR.[10]

Effect of emulsifier concentration in the feed

The effect of the emulsifier concentration in the feed just entering the reactor (S_F) on the monomer conversion versus time curve observed when the value of S_F is varied from 0.7 to 8.0 g/dm³ water and the monomer and initiator concentrations in the feed are fixed at $M_F = 0.2$ g/cm³ water and $I_F = 1.25$ g/dm³ water, respectively, is shown in Figure 6. The rotational speed of the inner cylinder and the mean residence time were kept constant at $n_S = 45$ rpm ($T_a = 845$) and $\theta = 20$ min, respectively. It is clear that the higher the initial emulsifier concentration, the higher the monomer conversion. When the initial emulsifier concentration is lower, for example, $S_F = 0.7$ g/dm³ water, the oscillatory behavior in monomer conversion is not so
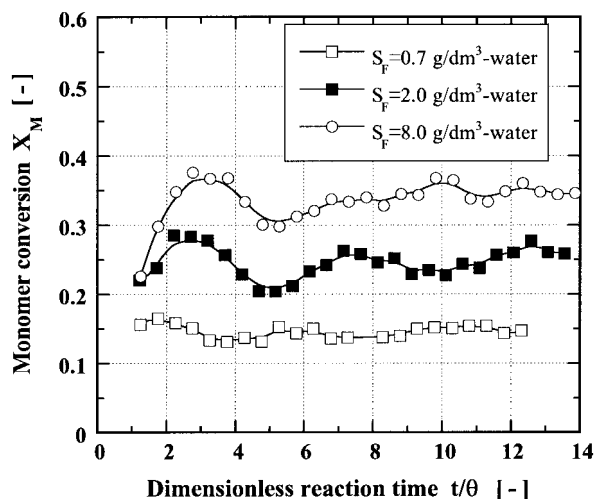
Figure 6 Effect of emulsifier concentration in the feed on the monomer conversion versus reaction time. (Reaction conditions: $I_F = 1.25$ g/dm^3 water, $M_F = 0.2$ g/cm^3 water, $\theta = 20$ min, and $n_s = 45$ rpm.)

appreciable. However, with increasing emulsifier concentration, the monomer conversion varies widely in the beginning of polymerization, but gradually reaches a value around the time-average steady-state value, $\bar{X}_{MS}$, showing a small but irregular variation with reaction time. The observed $\bar{X}_{MS}$ is plotted against the value of S_F in Figure 7 and is compared with that observed in a CSTR.[12] The time-average steady-state monomer conversion increases in proportion to the 0.3 power of the emulsifier concentration in the feed, which is almost the same result as that observed in a CSTR, and the time-average steady-state monomer conversion is slightly higher than that observed in a CSTR under these reaction conditions.[13] This latter result indicates that the number of polymer
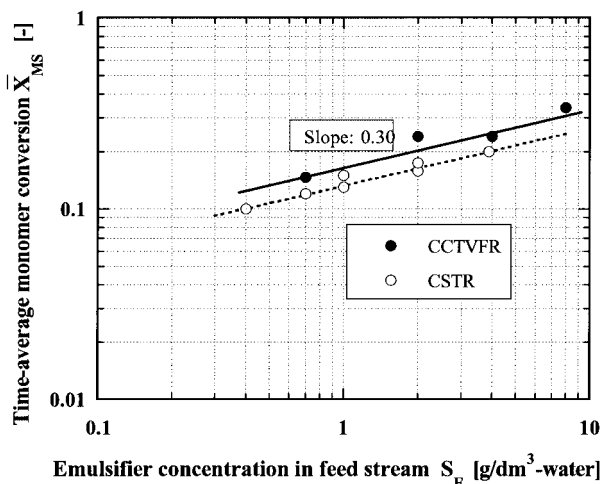

Figure 7 Effect of rotational speed of inner cylinder on the time-average steady-state monomer conversion, corresponding to Figure 6.
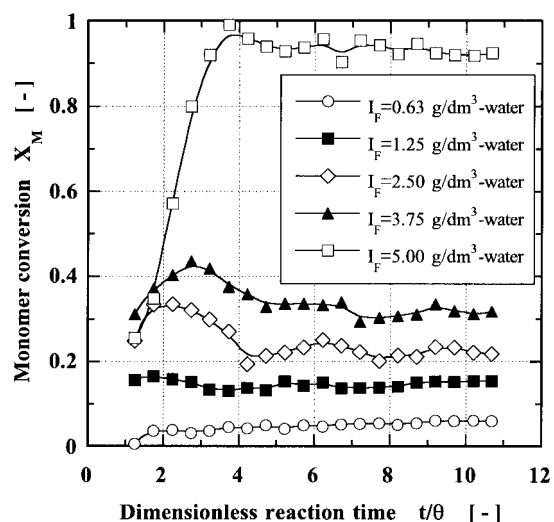

Figure 8 Effect of initiator concentration in the feed on the monomer conversion versus reaction time. (Reaction conditions: $S_F = 0.7$ g/dm^3 water, $M_F = 0.2$ g/cm^3 water, $\theta = 20$ min, and $n_s = 45$ rpm.)

particles produced in a CCTVFR is also somewhat higher than that produced in a CSTR, although not shown here.

Effect of initiator concentration in the feed

The effect of initiator concentration on the monomer conversion versus time curve obtained by varying the initiator concentration in the feed (I_F) from 0.63 to 5.0 g/dm^3 water, while keeping the monomer and emulsifier concentrations in the feed fixed at $M_F = 0.2$ g/cm^3 water and $S_F = 0.7$ g/dm^3 water, respectively, is shown in Figure 8. The rotational speed of the inner cylinder and the mean residence time were kept constant at $n_S = 45$ rpm and $\theta = 20$ min, respectively. When the value of S_F is in the vicinity of the critical micellar concentration, S_{CMC} ($S_{CMC} \approx 0.5$ g/dm^3 water[14]), the oscillations in monomer conversion are not necessarily appreciable. However, it is interesting to note that when the initiator concentration in the feed was only slightly increased from 3.75 to 5.0 g/dm^3 water, the monomer conversion abruptly jumped from a lower steady-state value near 30% to a higher steady-state value near 90% conversion. Gerrens et al.[15] demonstrated that this phenomenon can be possible when the emulsion polymerization of monomers with a strong gel effect is carried out in a CSTR. According to Gerrens et al.,[15] there could be two (lower and upper) stable steady-states and one unstable steady-state between these "lower" and "upper" stable steady-states when certain reaction conditions are satisfied. If the initial monomer conversion overshoot is beyond the unstable steady-state, the monomer conversion will reach, if any, the "upper" stable steady-state in high monomer conversion range. Be-
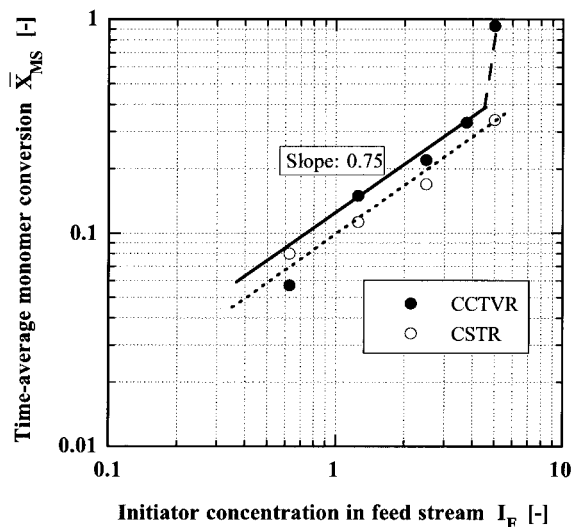
Figure 9 Effect of initiator concentration in the feed on the time-average steady-state monomer conversion, corresponding to Figure 8.

Figure 10 Effect of monomer concentration in the feed on the monomer conversion versus reaction time. (Reaction conditions: $S_F = 0.7$ g/dm^3 water, $I_F = 1.25$ g/cm^3 water, $\theta = 20$ min, and $n_s = 45$ rpm.)

cause the CCTVFR in this case behaves almost like a CSTR, one can consider that the steady-state monomer conversion around 90% must be the "upper" stable steady-state that would be observed in a CSTR. According to Figure 9, one can estimate that the "lower" stable steady-state will be around 40% conversion.

The time-average steady-state monomer conversion calculated from Figure 8 is plotted against the corresponding initiator concentration in the feed in Figure 9 and is compared also with that observed in a CSTR.[13] The time-average steady-state monomer conversion varies in proportion to the 0.75 power of the initiator concentration in the feed, which is almost the same as that observed in a CSTR.[13] However, the time-average steady-state monomer conversion attained in a CCTVFR is slightly higher than that observed in a CSTR.

Effect of monomer concentration in the feed

The effect of monomer concentration in the feed on the monomer conversion versus time curve observed when the monomer concentration in the feed was varied from $M_F = 0.1$ to 0.3 g/cm^3 water, while the emulsifier and initiator concentrations, the mean residence time, and the rotational speed of the inner cylinder were kept constant at $S_F = 0.7$ g/dm^3 water, $I_F = 1.25$ g/dm^3 water, $\theta = 20$ min, and $n_S = 45$ rpm, respectively, is shown in Figure 10. The observed monomer conversion is very scattered, especially when $M_F = 0.1$ g/cm^3 water. However, when the monomer concentration in the feed is increased to $M_F = 0.2$ and 0.3 g/cm^3 water, the monomer conversion approaches steady-state more steadily. The time-average steady-state monomer conversion calculated from
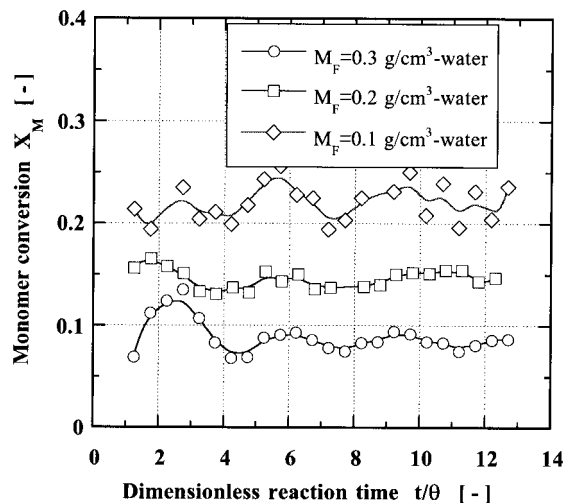
Figure 10 is plotted against the corresponding monomer concentration in Figure 11 and is compared with that observed in a CSTR.[13] The time-average steady-state monomer conversion obtained in a CCTVFR is slightly higher than that attained in a CSTR under these reaction conditions, and the time-average steady-state monomer conversions attained in both reactor systems varies in inverse proportion to the monomer concentration in the feed.

Effect of the mean residence time

The effect of the mean residence time, θ, on the monomer conversion versus time curve was examined by
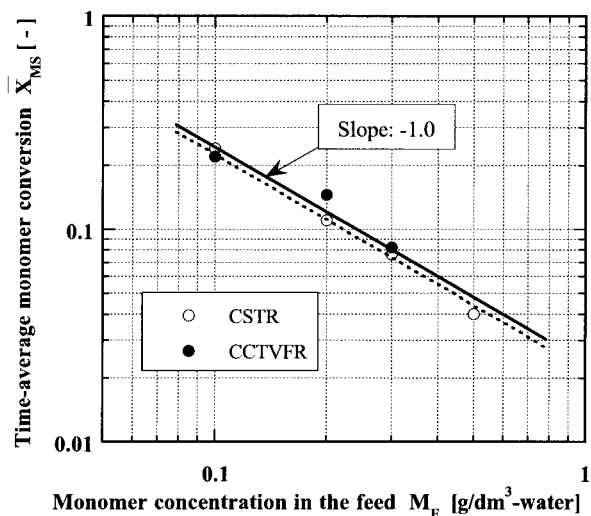

Figure 11 Effect of monomer concentration in the feed on the time-average steady-state monomer conversion, corresponding to
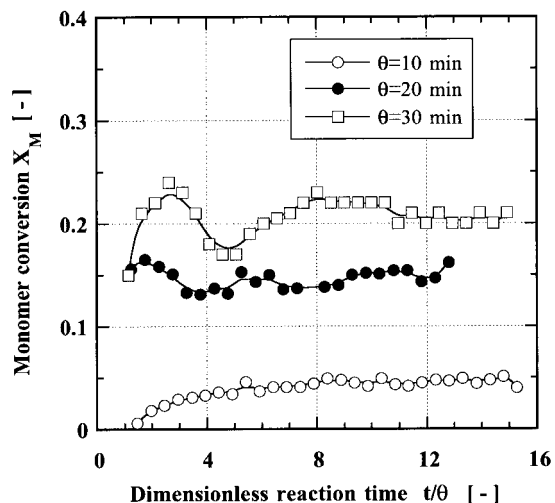
Figure 12 Effect of the mean residence time on the monomer conversion versus reaction time. (Reaction conditions: $S_F = 0.7$ g/dm^3 water, $I_F = 1.25$ g/cm^3 water, $M_F = 0.2$ f/cm^3 water, and $n_s = 45$ rpm.)

varying the value of θ from 10 to 30 min with other reaction conditions fixed at $S_F = 0.70$ g/dm^3 water, $I_F = 1.25$ g/dm^3 water, $M_F = 0.2$ g/cm^3 water, and $n_s = 45$ rpm, and the experimental results are shown in Figure 12. Although the oscillations in monomer conversion were appreciable in the very beginning of polymerization, the monomer conversion gradually reached a value around the time-average steady-state value with reaction time. The time-average steady-state monomer conversion versus the mean residence time is plotted in Figure 13. The steady-state monomer conversion increases roughly in proportion to the mean residence time in both CCTVFR and CSTR, the steady-state monomer conversion in a CCTVFR being
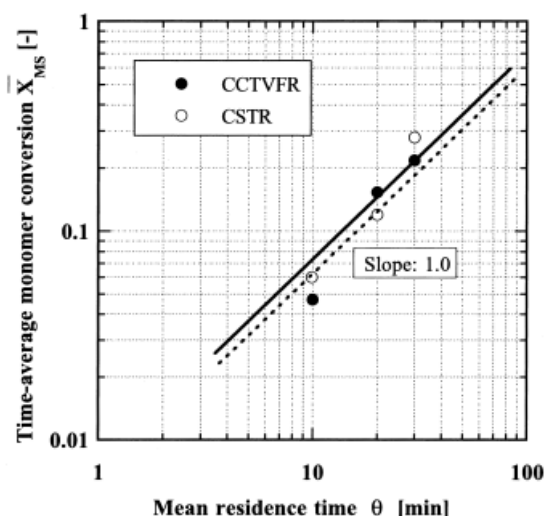

Figure 13 Effect of mean residence time on the time-average steady-state monomer conversion and comparison with that attained in a CSTR, corresponding to Figure 12.
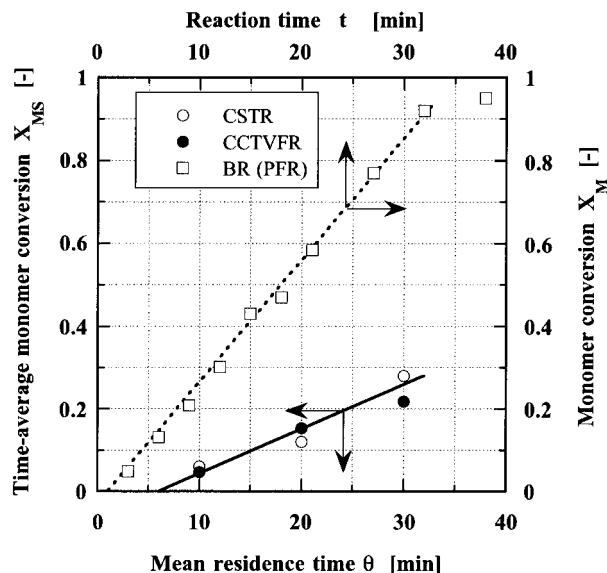

Figure 14 Comparison of the time-average monomer conversion attained in a CCTVFR with that attained in a PFR and in a CSTR, corresponding to Figure 12.

slightly higher than that in a CSTR. A comparison of the steady-state monomer conversion attained in a CCTVFR (closed circles) with that observed in a batch reactor (BR; open squares)[10] under the same conditions as employed in Figure 12 is shown in Figure 14. The dotted line indicates the relationship between the monomer conversion obtained in a BR and the reaction time. Also included in Figure 14 is the time-average steady-state monomer conversion observed in a CSTR (open circles) for reference.[13] It is well known that if a continuous flow reactor with plug flow (PFR) is operated at the mean residence time θ, the monomer conversion attained in a PFR would be the same as that obtained at the reaction time θ in a BR. Therefore, if the flow pattern in the CCTVFR employed in this study is close to plug flow, the plot of the time-average steady-state monomer conversion versus the mean residence time shown by the solid line should be close to the dotted line. However, the solid line is far below the dotted line. Moreover, the time-average steady-state monomer conversion observed in a CSTR[12] gathers around the solid line. These results suggest that the flow pattern in a CCTVFR is rather close to the perfectly mixed flow that is realized in a CSTR.

CONCLUSIONS

Continuous emulsion polymerization of VAC in a single CCTVFR was carried out using NaLS as the emulsifier and KPS as the initiator. Polymerization could be operated smoothly and stably without appreciable polymer deposition onto the reactor wall. Contrary to expectation, however, the oscillations in monomer

conversion could not be eliminated and the steady-state monomer conversion in a CCTVFR could not be as high as that attained in a PFR, but only slightly higher than that observed in a CSTR, even if the value of T_a was decreased to the vicinity of its critical value (T_{ac}). Also, the effects of operating variables such as the emulsifier, initiator, and monomer concentrations in the feed and the mean residence time on the steady-state monomer conversion are almost the same as those observed in a CSTR. These characteristics are very different from those observed in the continuous emulsion polymerization of St in a single CCTVFR[5] and are rather similar to those of the continuous emulsion polymerization of VAC in a CSTR. This result suggests that the flow pattern in a CCTVFR is rather close to perfectly mixed flow, which is realized in a CSTR,[13] almost independently of the Taylor number, although the reason for this is not clear at present. Considering these results, we can conclude that a CCTVFR is not necessarily very much superior to a CSTR in the continuous emulsion polymerization of VAC. For a CCTVFR to be applicable widely, it is essential to clarify the reason why the flow pattern in the CCTVFR applied to the continuous emulsion polymerization of VAC is very different from that observed in the continuous emulsion polymerization of St.

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