

Continuous Flow Operation in Emulsion Polymerization of Styrene

MAMORU NOMURA, HIDEKI KOJIMA,* MAKOTO HARADA,†
WATARU EGUCHI,† and SHINJI NAGATA, *Department of Chemical
Engineering, Kyoto University, Kyoto, Japan*

Synopsis

The kinetics of continuous emulsion polymerization of styrene were studied theoretically on the basis of the authors' batch reaction model, and a new reaction model was proposed for continuous operation. The validity of the model was tested by experiments conducted with stirred tank reactors in series. The characteristics of the first reactor used to generate polymer particles were studied in particular detail. It was found that there was an optimum residence time for the first reactor, the value of which was quantitatively predictable from the operating variables. The most suitable combinations of several types of reactors for continuous emulsion polymerization are also discussed.

INTRODUCTION

Although both batch- and flow-type reactors are widely used for emulsion polymerization, continuous reactors are becoming more and more important for the mass production of polymers of consistent quality.

Continuous emulsion polymerization is widely used in industry. However, the reactor type and operating conditions are mostly determined by experience and hence are not always the most suitable from the standpoint of the reaction mechanism.

In contrast to batch kinetics, the kinetics of continuous emulsion polymerization have received scant attention in the literature, only a few papers having been presented since the appearance of the experimental study of Wall and co-workers.¹ The kinetics of the continuous emulsion polymerization of styrene have been studied theoretically and experimentally by Gershberg,² applying the Smith and Ewart theory,³ and also theoretically by Sato and Taniyama.⁴

Research to date has mainly concentrated on studies of the number of polymer particles and the degree of conversion of monomer at steady state. Therefore, it has not yet been considered which types of reactor and operating conditions are the most suitable for continuous emulsion polymerization. One of the authors⁵ of this paper has already discussed the optimum

* Present address: Mitsubishi Rayon Company, Otake, Japan.

† Present address: Engineering Research Institute, Kyoto University, Uji, Japan.

type of reactor for continuous emulsion polymerization. Recently, Omi⁶ has reported a theoretical treatment on this subject, applying the Gershberg model.

In this paper, the authors aim to clarify the reaction kinetics for continuous emulsion polymerization using the batch reaction model reported previously,⁷ and to propose a guide for the design of suitable reactors and operation of continuous emulsion polymerization of highly water-insoluble monomers.

THEORY

Derivation of the Basic Equations

Consider the case where the emulsion polymerization mechanism shown in Table I takes place in a series of continuous stirred tank reactors as

TABLE I
Elementary Reactions of Emulsion Polymerization and Their Rates

Reaction	Reaction type	Reaction rate
Initiation of radicals	$I \rightarrow 2R^*$	$r_i = 2k_d I$ (A)
Initiation of particle from micelle	$R^* + m_s \rightarrow N^*$	$k_1 m_s R^*$ (B)
Initiation	$R^* + N \rightarrow N^*$	$k_2 N R^*$ (C)
Termination	$R^* + N^* \rightarrow N$	$k_3 N^* R^*$ (D)
Propagation in particle	$P^*_j + M \rightarrow P^*_{j+1}$ ^a	$k_p M_p N^*$ (E)
Transfer to monomer	$P^*_j + M \rightarrow M^* + P_j$	$k_{m_j} M_p N^*$ (F)
Transfer to transfer agent	$P^*_j + T \rightarrow T^* + P_j$	$k_{T_j} T_p N^*$ (G)

^a P^*_j is a polymer radical containing j monomer units in an active particle N^*_j .

shown in Figure 1. The following assumptions may be made: (1) each reactor is uniformly mixed; (2) the density change of the reaction mixture is negligible, regardless of the degree of polymerization; (3) each polymer particle contains not more than one polymerizing radical; (4) no polymerization occurs between stages.

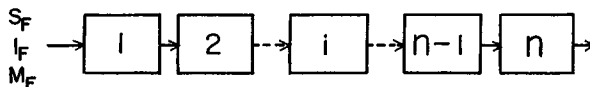


Fig. 1. Schematic diagram of reactors in series.

Thus, the following differential equations can be established for the respective substances in the i th reactor stage, using the reaction rate equations shown in Table I and the batch reaction model reported previously.⁷

(i) Initiator concentration, I :

$$\theta_i \frac{dI_i}{dt} = I_{i-1} - I_i - k_d I_i \theta_i \quad (1)$$

where θ_i is a mean residence time of the i th reactor.

(ii) The concentration of initiator radicals in the water phase, R^*_i :

$$\theta_i \frac{dR^*_i}{dt} = r_{i,t}\theta_i - k_1 m_{s,i} R^*_i \theta_i - k_2 N_{T,i} R^*_i \theta_i + R^*_{i-1} - R^*_i \quad (2)$$

$$r_{i,t} = 2k_d f I_i \quad (2')$$

(iii) The total number of polymer particles, $N_{T,i}$:

$$\theta_i \frac{dN_{T,i}}{dt} = k_1 m_{s,i} R^*_i \theta_i + N_{T,i-1} - N_{T,i} \quad (3)$$

(iv) The number of active polymer particles containing a polymerizing radical of j monomer units, $N_{j,i}$:

$$\begin{aligned} \theta_i \frac{dN^*_{1,i}}{dt} = & k_1 m_{s,i} R^*_i \theta_i + (k_{m,i} M_{p,i} + k_{T,i} T_{p,i}) N^*_{1,i} \theta_i + k_2 N_i R^*_i \theta_i \\ & - (k_p M_{p,i} + k_{m,i} M_{p,i} + k_{T,i} T_{p,i} + k_2 R^*_i) N^*_{1,i} \theta_i + N^*_{1,i-1} - N^*_{1,i} \quad (4) \end{aligned}$$

$$\begin{aligned} \theta_i \frac{dN^*_{j,i}}{dt} = & k_p M_{p,i} N^*_{j-1,i} \theta_i - (k_p M_{p,i} + k_{m,i} M_{p,i} + k_{T,i} T_{p,i} + k_2 R^*_i) N^*_{j,i} \theta_i \\ & + N^*_{j,i-1} - N^*_{j,i} \quad (5) \end{aligned}$$

Thus, for the total number of active polymer particles, N^*_i :

$$\theta_i \frac{dN^*_i}{dt} = k_1 m_{s,i} R^*_i \theta_i + k_2 N_i R^*_i \theta_i - k_2 N^*_i R^*_i \theta_i + N^*_{i-1} - N^*_i \quad (6)$$

where

$$N^*_i = \sum_{j=1}^{\infty} N^*_{j,i} \quad (7)$$

$$N_{T,i} = N_i + N^*_i \quad (8)$$

(v) Monomer concentration, M :

$$\theta_i \frac{dM_i}{dt} = M_{i-1} - M_i - \left[\frac{k_p M_{p,i} M_w}{N_A} \right] N^*_i \theta_i \quad (9)$$

(vi) The concentration of dead polymer containing j -monomer units, P_j :

$$\theta_i \frac{dP_{j,i}}{dt} = (k_2 R^*_i + k_{m,i} M_{p,i} + k_{T,i} T_{p,i}) N^*_{j,i} \theta_i + P_{j,i-1} - P_{j,i} \quad (10)$$

(vii) The concentration of total emulsifier molecules, S . The depletion of emulsifier micelles occurs because they break up and their molecules are adsorbed onto the surface of growing polymer particles. This situation may be represented by the following equations:

$$\theta_i \frac{dS_i}{dt} = S_{i-1} - S_i \quad (11)$$

$$S_i = S_{m,i} + (36\pi/a_s^3)^{1/3} \bar{v}_i^{2/3} N_{T,i} \quad (12)$$

where S_{mi} is the concentration of emulsifier in micellar form and \bar{v}_i is the average volume of the monomer-swollen particles in the i th reactor. The second term of the right-hand side of eq. (12) represents the amount of emulsifier adsorbed as a monomolecular layer on the surfaces of polymer particles. In eq. (12), if $(36\pi/a_s^3)^{1/2}\bar{v}_i^{2/3}N_T \geq S_i$ is fulfilled, let $S_{mi} = 0$. This means that all the emulsifier molecules present are adsorbed onto the surface of polymer particles and no more emulsifier micelles exist.

(viii) The concentration of the transfer agents, T :

$$\theta_i \frac{dT_i}{dt} = T_{i-1} - T_i - \left[\frac{k_{TR}T_{pi}M_T}{N_A} \right] N^* \theta_i \quad (13)$$

where M_T denotes the molecular weight of the transfer agents.

Application of Basic Equations

The basic eqs. (1) to (13) may be simplified as follows, applying a stationary state method to the initiator radicals. It will be reasonable to assume a constant rate of radical formation $r_{i,i} = r_i = 2k_{df}I_F$ in any stage, since the half-life of the decomposition of the potassium persulfate initiator is sufficiently long compared with the total mean residence time in this experiment:

$$R^*_{i} = \frac{r_i}{k_1[m_{si} + (k_2N_{Ti}/k_1)]} = \frac{r_i}{k_1m_{si}[1 + (\epsilon N_{Ti}/S_{mi})]} \quad (14)$$

where $\epsilon = (k_2/k_1)M_m$.

As reported previously⁷ the parameter ϵ is very important in describing the generating process of polymer particles.

Substituting eq. (14) into eqs. (3) and (6) gives

$$\theta_i \frac{dN_{Ti}}{dt} = r_i \theta_i \frac{1}{1 + (\epsilon N_{Ti}/S_{mi})} + N_{T_{i-1}} - N_{Ti} \quad (15)$$

$$\theta_i \frac{dN^*_{i}}{dt} = r_i \theta_i \left(1 - \frac{2N^*_{i}/N_{Ti}}{1 + [1/(\epsilon N_{Ti}/S_{mi})]} \right) + N^*_{i-1} - N^*_{i} \quad (16)$$

If the total amount of monomer and polymer in each stage remains constant throughout the operation from the start, eq. (9) can be rewritten in terms of the monomer conversion X_{Mi} and applied to the following two situations:

(a) At the reaction stage where monomer droplets exist ($X_{Mi} \leq X_{MC2}$ and in case of styrene, $X_{MC2} = 0.43$), eq. (9) becomes

$$\theta_i \frac{dX_{Mi}}{dt} = X_{M_{i-1}} - X_{Mi} + KN^*_{i} \theta_i \quad (17)$$

where

$$K = \frac{k_p M_{pc} M_w}{M_0 N_A} = \frac{k_p M_{pc} M_w}{M_r N_A}$$

(b) At the reaction stage where monomer droplets disappear ($X_{Mi} \geq X_{MC2}$), eq. (9) becomes

$$\theta_i \frac{dX_{Mi}}{dt} = X_{Mi-1} - X_{Mi} + \left(\frac{1 - X_{Mi}}{1 - X_{MC2}} \right) K\theta_i N_i^* \quad (18)$$

because the monomer concentration in the polymer particles M_{pi} may be represented by $M_{pc} \left(\frac{1 - X_{Mi}}{1 - X_{MC2}} \right)$, at $X_{Mi} \geq X_{MC2}$.

If the initially charged concentrations of initiator, emulsifier, and monomer in each stage are made exactly the same as those in the feed streams and if the initial volume of reaction mixture is equalized to that at steady-state operation, eq. (11) can be simplified. Thus, at the reaction stage (a) where monomer droplets exist ($X_{Mi} \leq X_{MC2}$),

$$S_i = S_{mi} + k_v (M_F X_{Mi})^{2/3} N_{Ti}^{1/3} \quad (19)$$

where $k_v = (36\pi / [(1 - \varphi_c)^2 a_s^3 \rho^2])^{1/3}$ and φ_c , a_s , and ρ , respectively, denote the monomer weight fraction in the polymer particles at $X_{Mi} \leq X_{MC2}$, the surface area occupied by an emulsifier molecule, and the density of the monomer-swollen polymer particles. At the reaction stage (b) where monomer droplets disappear ($X_{Mi} \geq X_{MC2}$), one obtains

$$S_i = S_{mi} + k_v (M_F X_{MC2})^{2/3} N_{Ti}^{1/3} \quad (20)$$

because as long as the density change of monomer-swollen particles is neglected, no more volume change occurs in the polymer particles.

Consideration of Steady-State Operation

The Number of Polymer Particles

Let us consider the number of polymer particles produced in the first stage of the reactor. At steady state, the derivatives of the left-hand side of eqs. (15) to (17) can be equated to zero. Combining these equations with eq. (19), the general expression for the number of polymer particles formed in the first stage of the reactor is obtained:

$$\frac{\epsilon N_{T1}^2}{r_i \theta_1 - N_{T1}} = S_F - k_v \left(\frac{M_F K}{2} \right)^{2/3} \left[\frac{r_i \theta_1}{r_i \theta_1 - (N_{T1}/2)} \right]^{2/3} N_{T1} \theta^{2/3}. \quad (21)$$

The reason why eqs. (17) and (19) were used instead of eqs. (18) and (20) in deriving eq. (21) is that monomer droplets and emulsifier micelles always coexist in the first reactor under usual operating conditions. Since the inequality $\epsilon N_{Ti} / S_{mi} \gg 1$ also holds approximately for continuous operation, the following relation may be applicable with reasonable accuracy:

$$r_i \theta_1 = N_{T1} (1 + \epsilon N_{T1} / S_{mi}) \gg N_{T1}. \quad (22)$$

Then, the number of polymer particles N_{T1} can be calculated easily from eq. (21), neglecting the terms $N_{T1}/2$ in the last bracket of the right-hand side and N_{T1} in the denominator of the left-hand side:

$$N_{T1} = \frac{1}{2} \left\{ \left[\left(\frac{r_i k_v}{\epsilon} \right)^2 \left(\frac{M_F K}{2} \right)^{4/3} \theta_1^{10/3} + \left(\frac{4r_i S_F \theta_1}{\epsilon} \right) \right]^{1/2} - \left(\frac{r_i k_v}{\epsilon} \right) \left(\frac{M_F K}{2} \right)^{2/3} \theta_1^{5/3} \right\} \quad (23)$$

Equation (23) reduces to:

$$N_{T1} = k_v^{-1} \left(\frac{M_F K}{2} \right)^{-2/3} S_F \theta_1^{-2/3} \quad (24)$$

when

$$\theta_1 \gg \left\{ \frac{4S_F \epsilon}{k_v^2 r_i [(M_F K/2)^{4/3}]} \right\}^{3/7} \quad (25)$$

Equation (24) is the same as that obtained by Gershberg³ and Taniyama.⁴ When the second-stage residence time, θ_2 , fulfills the condition (26), no new particles will be formed at any stage after the first, since all the micellar emulsifier molecules have been adsorbed onto the surfaces of growing polymer particles:

$$\theta_2 \geq \frac{S_F^{3/2}}{k_v^{3/2} N_{T1}^{3/2} (M_F K/2)} - \theta_1. \quad (26)$$

The inequality (26) is usually satisfied as long as the first-stage residence time is not much shorter than that of the second stage. Then, the number of polymer particles in any stage i is

$$N_{Ti} = N_{Tn} = N_{T1}. \quad (27)$$

Further, the number of active polymer particles containing a radical in the i th stage is related to that of the $(i - 1)$ th stage, applying eqs. (15) and (16) at steady state:

$$N^*_{i1} = \frac{r_i \theta_1 N_{T1}}{2r_i \theta_1 - N_{T1}} \quad (28)$$

$$N^*_{ii} = \frac{r_i \theta_i N_{Ti}}{2r_i \theta_i - N_{Ti} + 2N_{Ti-1}} + \left(\frac{N_{Ti}}{2r_i \theta_i - N_{Ti} + 2N_{Ti-1}} \right) N^*_{i-1}. \quad (29)$$

Combining eqs. (22) and (27) with eqs. (28) and (29), the total number of active polymer particles, N^*_i is approximated by the following simple formula, which is the same conclusion as that obtained for batch operation:

$$N^*_i = \frac{N_{T1}}{2}. \quad (30)$$

Monomer Conversion

In the first stage, the steady-state conversion is given by

$$X_{M1} = KN^* \theta_1 = K \theta_1 \frac{r_i \theta_1 N_{T1}}{2r_i \theta_1 - N_{T1}} \cong \frac{KN_{T1}}{2} \theta_1 \quad (31)$$

because $r_i \theta_1 \gg N_{T1}$ (see inequality (22) above). Supposing that the monomer droplets disappear in the $(h + 1)$ th reactor stage, monomer conversion at the i th stage is approximated by

$$X_{Mi} = \frac{KN_{T1}}{2} \sum_{k=1}^i \theta_k \quad i \leq h \quad (32)$$

$$X_{Mi} = 1 - (1 - X_{Mh}) \prod_{k=h+1}^i \left[\frac{2(1 - X_{MC2})}{2(1 - X_{MC2}) + KN_{T1} \theta_k} \right] \quad i \leq h + 1. \quad (33)$$

Degree of Polymerization of Polymers Obtained Under Steady-State Operation

Applying a stationary-state method to eqs. (2), (4), (5), and (10), the molecular weight distribution or the average degree of polymerization of polymers can be evaluated approximately as follows, using eqs. (27) and (30): The concentration of dead polymers containing j monomer units flowing out of the i th reactor P_{ji} is

$$P_{ji} = \sum_{k=1}^i \left\{ \left[\frac{k_p M_{pk}}{k_p M_{pk} + k_{mf} M_{pk} + k_{tf} T_{pk} + (r_i/N_{T1})} \right]^j \times \left[\frac{r_i + (k_{mf} M_{pk} + k_{tf} T_{pk}) N_{T1}}{2k_p M_{pk} N_{T1}} \right]^2 \theta_k \right\}. \quad (34)$$

The viscosity-average degree of polymerization of such polymers is given by

$$\bar{P}_{\mu i} = (\Gamma(a + 2))^{1/a} \left\{ \frac{\sum_{k=1}^i (\theta_k \beta_k / \delta_k^{a+2})}{\sum_{k=1}^i (\theta_k \beta_k / \delta_k^2)} \right\}^{1/a} \quad (35)$$

where

$$\delta_k = \frac{k_{mf} M_{pk} + k_{tf} T_{pk} + (r_i/N_{T1})}{k_p M_{pk}} \quad (36)$$

$$\beta_k = \frac{\{r_i + (k_{mf} M_{pk} + k_{tf} T_{pk}) N_{T1}\}^2}{2k_p M_{pk} N_{T1}} \quad (37)$$

and a is the power number in the Mark-Houwink equation. Monomer concentration in polymer particles in the k th reactor M_{pk} is represented by the following equations:

$$M_{pk} = M_{pc} \text{ when } X_{Mk} \leq X_{MC2} \text{ and } M_{pk} = M_{pc} \left(\frac{1 - X_{Mk}}{1 - X_{MC2}} \right)$$

when $X_{Mk} > X_{MC2}$.

Experimental Apparatus and Procedure

Emulsion polymerizations were carried out in two or three tank reactors in series, as shown in Figure 2. Each reactor was a cylindrical glass vessel with a dished bottom, equipped with a four-bladed turbine-type impeller, four baffle plates, sampling cock, thermometer, etc. The geometry of the reactors, impellers, and baffle plates is shown in Figure 3. The first reactor was geometrically similar to the succeeding reactors, but the size of the reactor was varied according to the experimental conditions. Except for the first stage, the tank diameter T was 75 mm.

The materials used were purified in the same way as described in the previous paper.⁷ Polymerizations were carried out under the conditions

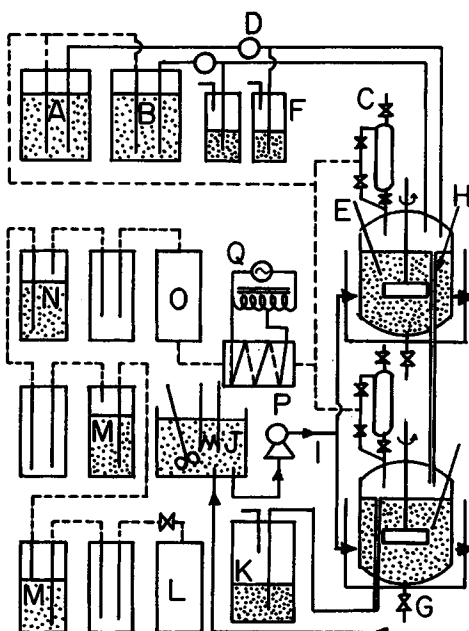


Fig. 2. Schematic diagram of experimental apparatus: (A) head tank for styrene monomer; (B) head tank for aqueous initiator and emulsifier solution; (C) feeder for initiator; (D) flow meter; (E) thermometer; (F) holding tank for preparatory run; (G) sampling cock; (H) level controller; (I) hot water line; (J) hot water bath; (K) holding tank for waste liquor; (L) N_2 gas cylinder; (M) pyrogallol solution; (N) H_2SO_4 ; (O) $CaCl_2$; (P) electric furnace; (Q) voltage regulator.

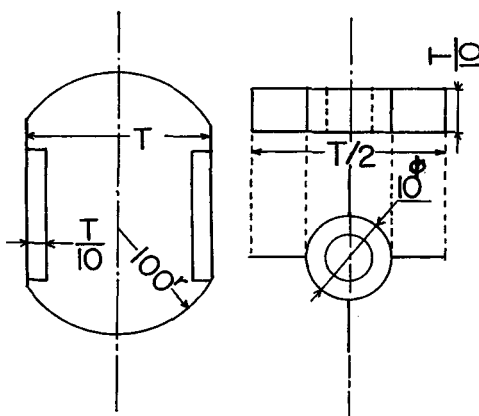


Fig. 3. Details of reactor and impeller.

presented in Table II, and only the mean residence times of stages were varied by changing the feed rate. Polymerizations were started by the following procedure. Styrene monomer and an aqueous solution of emulsifier and initiator were stored in constant head tanks, (A) and (B), respectively, as shown in Figure 2.

Initially, each reactor was charged with all the required raw materials except the initiator, and their concentrations were made equal to those in the feed stream at the moment when the aqueous initiator solution in the feeder C (Fig. 2) was poured into the reactor to start the polymerization. The volume of reaction mixture in each reactor was made equal to the steady-state value.

Prior to start-up, trace oxygen in the reaction mixture and in the gas phase above it was removed by bubbling purified nitrogen through the mixture for about 1 hr. Polymerization was started by feeding raw material from the storage tanks into the first stage and by injecting the aqueous initiator solution in the feeder C into each reactor. Monomer conversion, the number of polymer particles, and the average degree of polymerization were determined by the same methods as reported previously.⁷ The amount of emulsifier remaining in micellar form was determined by the soap back-titration method, while the emulsifier necessary to cover the unadsorbed surfaces of the polymer particles as a monomolecular layer was determined directly by the soap titration method.

TABLE II
Experimental Conditions^a

Initial charge	Feed	Material
Emulsifier $S_0 = 12.50$, g/l. water	$S_F = 12.50$	sodium lauryl sulfate
Initiator $I_0 = 1.25$, g/l. water	$I_F = 1.25$	potassium persulfate
Monomer $M_0 = 0.50$, g/g-water	$M_F = 0.50$	styrene

^a Reaction temperature, 50°C; mean residence time of each stage, various.

Experimental Results

Typical Course of a Continuous Emulsion Polymerization

Figure 4 represents a typical course of emulsion polymerization started in the way described in the previous section. The solid lines were those calculated using eqs. (14) to (20) with a digital computer under the conditions shown in Table II, the constants having the following values⁷:

$$\begin{aligned}
 K &= 4.0 \times 10^{-19} \text{ (in cc water/sec molecule), } k_v = 2.70 \times 10^{15} \\
 r_t &= 3.70 \times 10^{12} \text{ (in molecules/cc water sec), } \bullet = 1.28 \times 10^6 \\
 a_s &= 3.50 \times 10^{-15} \text{ (in cm}^2\text{/molecule), } X_{MC2} = 0.43
 \end{aligned}$$

The dotted lines were calculated under the same operating conditions and with the values given above, assuming the reaction mechanism reported by Smith and Ewart,³ the only difference being that the generating rate of polymer particles in eq. (15) was replaced by a rate expression, $r_{t,i} \theta_i \left(\frac{S_{mi}}{S_p} \right)$.

This situation is conceptually similar to the Gershberg model.² In Figure 4b, the positive ordinate represents the amount of emulsifier existing in

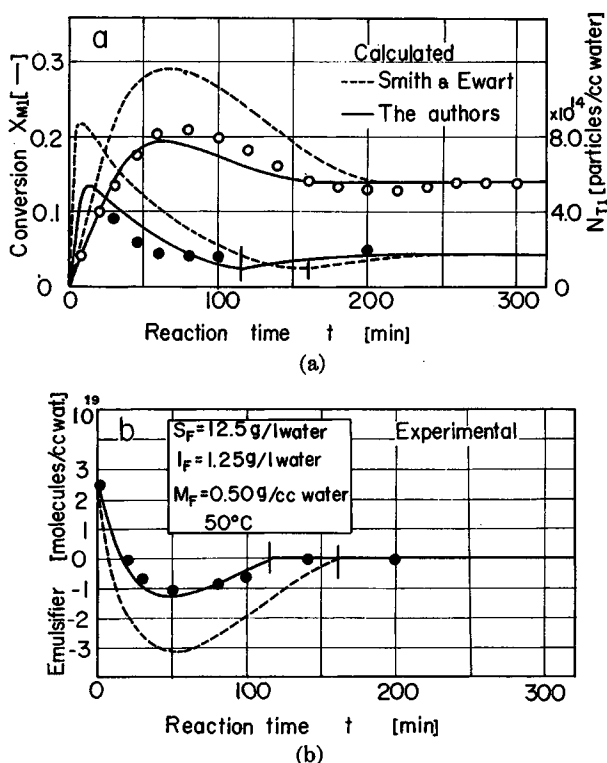


Fig. 4. Typical course of a continuous emulsion polymerization of styrene. (a): (O) conversion; (●) number of particles. (b) (●) emulsifier.

micellar form, and the negative ordinate represents the emulsifier necessary to cover the unadsorbed surface of the polymer particles as a monomolecular layer. In both our and the Gershberg models, the conversion of monomer and the number of polymer particles pass through a maximum and then level off to a steady-state value. Though the shape of the curves predicted by the two models are similar, there is a great difference in magnitude between the solid and dotted lines, especially during the transient period.

The data points in Figure 4a and 4b show the results of an experiment which was conducted under the same conditions and starting procedure as those assumed in the above calculation. As can be seen in Figure 4, the experimental results may be explained by our model, even during the transient period.

The monomer conversion and the number of polymer particles predicted theoretically by the Gershberg model are higher than the observed values during the transient period. This is due to the fact that the radicals generated in the water phase enter the polymer particles in preference to the micelles, as pointed out in the previous paper.⁷ The definite fluctuation of conversion observed by Gershberg² could not be observed in these experiments.

It is concluded that our batch reaction model is applicable to continuous operation with good accuracy, except in the situation where the auto-acceleration effect is dominant. Our reaction model is very useful for the automatic control of the continuous operation of emulsion polymerization because it covers even the transient or nonsteady-state region.

Number of Polymer Particles and Monomer Conversion at Steady State

Let us now consider the properties of emulsion polymerization at steady state. All experiments were conducted at the operating conditions shown in Table II and by the starting procedure described previously. The numbers of polymer particles observed in the latex leaving the first and the second reactor stages are shown in Figure 5. The numbers of polymer particles in the first and the second reactor stages are in agreement with each other within an experimental error. Thus it can be concluded that an appreciable number of particles could not be formed after the first stage if the operating variables in these experiments fulfill the inequality (26). In Figure 5, the solid line represents the exact solution of the basic eqs. (14) to (20), and the dotted line shows the approximate prediction by eq. (23). Both methods correctly predict the effect of the operating variables upon the number of particles at steady state. On the other hand, the broken line which represents the results of the Gershberg model is considerably in error when the residence time of the first reactor stage is small.

The comparison of experimental polymerization rates with those calculated at steady state was made in Figure 6, where all experimental data was obtained in the operating region where monomer droplets existed.

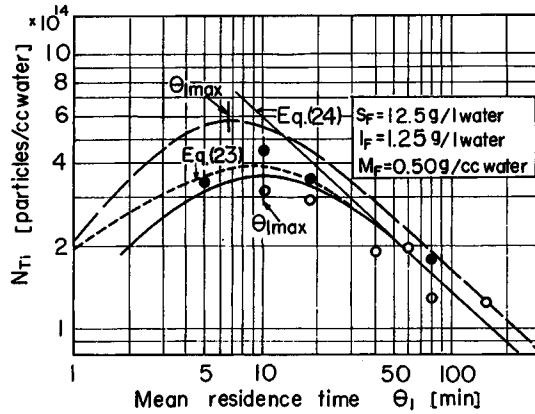


Fig. 5. Relationship between N_{T1} and θ_1 . Experimental: (O) 1st stage; (●) 2nd stage. Calculated (exact soln.): (—) Gershberg²; (---) this study.

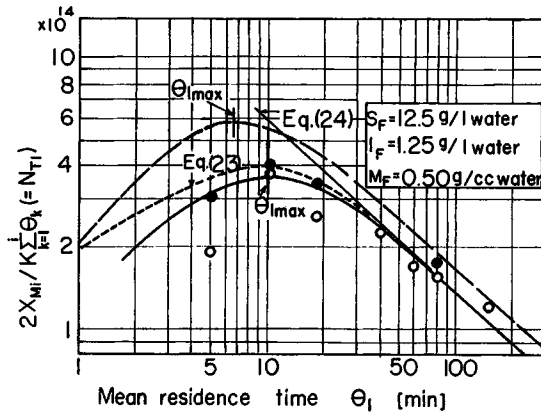


Fig. 6. Relationship between $\left(2X_{M_i}/K \sum_{k=1}^i \theta_k, i \leq h\right)$ and θ_1 . Experimental: (O) 1st stage; (●) 2nd stage. Calculated (exact soln.): (—) Gershberg²; (---) this study.

Under this condition, monomer conversion will be represented by eq. (32), and therefore the relation $\left(2X_{M_i}/K \sum_{k=1}^i \theta_k\right)$ versus θ_1 should be the same as N_{T1} versus θ_1 . The experimental data are in comparatively good agreement with the predicted values. Hence, one can estimate the steady-state conversion with reasonable accuracy by eqs. (23), (31), (32), and (33).

The viscosity-average degree of polymerization of the polymers leaving the first reactor was compared with that calculated by eq. (35) in Figure 7. It can be seen that the theoretical values are higher than the observed ones, but the longer the mean residence time of the first reactor, the closer the experimental values come to the theoretical values. One possible reason why the discrepancy between the theoretical and experimental molecular

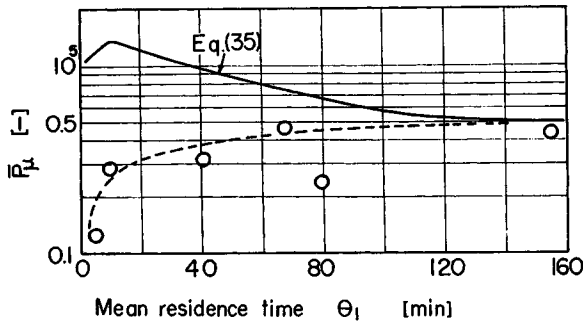


Fig. 7. Relationship between \bar{P}_μ and θ_1 .

weights is large at shorter residence times might be that the concentration of trace impurities is higher than it is at longer residence times, so the influence of impurities upon \bar{P}_μ is stronger at shorter residence times.

Optimum Reactor Type for Continuous Flow Emulsion Polymerization

As mentioned above, the formation of polymer particles usually occurs only in the first reactor. In order to maximize the volumetric efficiency of the reactor and the degree of polymerization, it is desirable to set conditions in the first reactor to produce the maximum number of polymer particles. This is the so-called “prereactor” concept, and it has been shown quantitatively by us⁵ and Omi and co-workers⁶ that this principle is very useful.

Now let us derive the optimum mean residence time for the first reactor so that it can produce the maximum number of polymer particles.

Differentiation of eq. (23) by θ yields $\theta_{1 \max}$, which is the first-stage residence time required to produce the maximum number of polymer particles, $N_{T1 \max}$:

$$\theta_{1 \max} = 0.956k_p^{-6/7} \left(\frac{r_t}{\epsilon}\right)^{-2/7} S_F^{3/7} \left(\frac{M_F K}{2}\right)^{-4/7} \tag{38}$$

$\theta_{1 \max}$ has the following relation with t_{c1} , which is the disappearance time of emulsifier micelles in batch operation carried out at the same operating conditions as in continuous operation:

$$\theta_{1 \max} = 0.831t_{c1} \tag{39}$$

This shows that in the system where polymer particles are generated from emulsifier micelles, one could estimate the optimum residence time for the first reactor just by measuring t_{c1} in a batch experiment. The maximum number of polymer particles formed in this case is given by

$$N_{T1 \max} = 0.619k_p^{-2/7} \left(\frac{r_t}{\epsilon}\right)^{2/7} S_F^{3/7} \left(\frac{M_F K}{2}\right)^{-2/7} \tag{40}$$

On the other hand, the number of polymer particles produced in batch operation, $N_{T \text{ batch}}$, is related by eq. (41) to $N_{T1 \text{ max}}$:

$$N_{T1 \text{ max}} = 0.577N_{T \text{ batch}} \quad (41)$$

This means that as long as the reactor is perfectly mixed, the maximum number of polymer particles produced in a continuous emulsion polymerization reactor is always 57.7% of that formed in batch operation at the same operating conditions.

The validity of these expressions is clear from the results in Figure 6. The optimum mean residence time at which the first reactor could produce the maximum number of polymer particles is found to be 10.0 min by eq. (38) at the reaction conditions shown in Table II. The experimental data obtained at a first-stage residence time of 10.4 min correspond to the maximum number of polymer particles and is about 60% of that formed in batch operation. The observed disappearance time of micelles, t_{cl} , was 12.8 min in batch operation⁷ at the same operating conditions as shown in Figure 5. Thus, eqs. (39) and (41) are approximately valid.

On the other hand, according to the Gershberg model the variation of

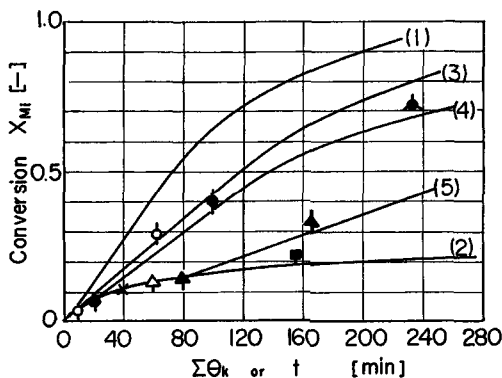


Fig. 8. Comparison of the progress of reaction in several reactor combinations.

Experimental data

	θ_1 , min	θ_2 , min	θ_3 , min	$\Sigma\theta_i$, min
Multistage	○ 10.4	○ 51.8	—	62.2
	● 20.0	● 80.0	▲ 131.0	231.0
	↑ 80.9	↑ 82.8	—	163.7
Single stage	○ ● ×	↑ ↑ ↑		

Calculated; (1) batch operation; (2) single stage continuous operation, $\theta_1 = \text{variable}$; (3) optimum reactor combination for continuous operation; (4) multistage operation, $\theta_1 = 20$, $\theta_2 = 80$, and $\theta_3 = \text{variable}$; (5) multistage operations; $\theta_1 = 80$ and $\theta_2 = \text{variable}$.

N_{T1} with θ_1 is much sharper than our model near $\theta_{1 \max}$, and $\theta_{1 \max}$ is underestimated while $N_{T1 \max}$ is overestimated.

Let us consider what type of reactor is most suitable for the succeeding stages. When monomer droplets still exist, it is desirable to select stirred tank reactors because the monomer should be dispersed finely enough so that monomer diffusion from the monomer droplets to the polymer particles does not become a rate-determining step.⁸ When the monomer droplets disappear, one should employ piston flow reactors to improve the volumetric efficiency of the reactor.

In Figure 8, the performance of various reactor combinations with continuous emulsion polymerization of styrene is compared. Curve (1) shows the progress of polymerization in batch operation, and curve (2) shows the course of reaction in single-stage continuous operation calculated by eqs. (23) and (31). The experimental results with a single stage lie along the calculated curve (2), and the volumetric efficiency of the single reactor is low because the value of N_{T1} decreases as the reactor volume increases.

Let us consider a multistage reactor system in which the first stage is a generator of polymer particles. The volumetric efficiency of the reactor system with $\theta_1 = 80.9$ min and $\theta_2 = 82.8$ min is comparatively low, but as the mean residence time of the first stage, θ_1 , approaches the value of $\theta_{1 \max} = 10.0$ min, the volumetric efficiency of the reactor system increases markedly and approaches curve (3), the calculated reaction path for the optimum reactor combination. This reaction path is defined as follows: A stirred tank reactor predicted by eq. (38) is used for the first stage, then an appropriate number of stirred tank reactors are used to bring monomer conversion up to X_{MC2} , and finally a piston flow reactor is used for conversion $X_M > X_{MC2}$. The experimentally observed progress of the reaction is also plotted in Figure 8 and is in good agreement with the calculated curve. If a piston flow reactor is used as a generator of polymer particles instead of a perfect mixed reactor, the course of polymerization in continuous operation is the same as that in batch operation.

Thus, the choice of the first reactor is the most important problem in continuous flow emulsion polymerization.

CONCLUSIONS

In the present paper, it has been shown that the theoretical equations derived from the batch reaction model could explain the course of continuous emulsion polymerization of styrene in any stage of a series of stirred tank reactors and that the Gershberg model based on the Smith and Ewart theory was inadequate for describing the continuous operation of styrene emulsion polymerization. The characteristics of the first reactor which generates the polymer particles were analyzed, and it was shown both theoretically and experimentally that there was an optimum residence time for the first reactor stage, at which the number of polymer particles was a maximum. Furthermore, a suitable reactor combination was proposed to maximize the volumetric efficiency.

Nomenclature

a	the power number in Mark-Houwink equation
a_s	surface area occupied by an emulsifier molecule, $\text{cm}^2/\text{molecule}$
f	initiator efficiency
I	initiator concentration, $\text{g}/\text{cc-water}$ or $\text{molecule}/\text{cc water}$
k_1	rate constant defined by eq. (B) in Table I, $\text{cc water}/\text{molecule sec}$
k_2	rate constant defined by eq. (C) or (D) in Table I, $\text{cc water}/\text{molecule sec}$
k_d	decomposition rate constant of initiator, $1/\text{sec}$
k_o	$\{36\pi/[(1 - \varphi_o)^2 a_s^3 \rho^2]\}^{1/3}$
k_p	propagation rate constant, $1/\text{g-mole sec}$
k_{fm}	transfer rate constant to monomer, $1/\text{g-mole sec}$
k_{ft}	transfer rate constant to transfer agent, $1/\text{g-mole sec}$
M	monomer concentration in aqueous phase, $\text{g}/\text{cc water}$
M_p	monomer concentration in polymer particle, $\text{g-mole}/\text{l.}$
M_m	aggregation number of micelle
M_{pc}	saturation concentration of monomer in polymer particles, $\text{g-mole}/\text{l.}$
M_w	molecular weight of monomer, $\text{g}/\text{g-mole}$
m_s	concentration of micelle emulsifier, $\text{molecule}/\text{cc water}$
N	number of dead polymer particles, $\text{particles}/\text{cc water}$
N^*	number of active polymer particles, $\text{particles}/\text{cc water}$
N^*_j	number of active particles containing a radical of j monomer units, $\text{particles}/\text{cc water}$
N_T	total number of polymer particles, $\text{particles}/\text{cc water}$
N_A	Avogadro's number, $\text{molecule}/\text{g-mole}$
$N_{T1 \text{ max}}$	maximum number of polymer particles formed at the first reactor stage, $\text{particles}/\text{cc water}$
$N_{T \text{ batch}}$	number of polymer particles formed in batch operation, $\text{particles}/\text{cc water}$
\bar{P}_μ	viscosity average degree of polymerization
P_j	dead polymer containing j monomer units, $\text{molecule}/\text{cc water}$
R^*	concentration of initiator radicals in the aqueous phase, $\text{molecule}/\text{cc water}$
r_i	generation rate of initiator radical, $\text{molecule}/\text{cc water sec}$
S	concentration of total emulsifier, $\text{molecule}/\text{cc water}$ or $\text{g}/\text{l. water}$
S_m	concentration of micelle emulsifier, $\text{g}/\text{l. water}$ or $\text{molecule}/\text{cc water}$
t_{cl}	disappearance time of micelle, sec or min
T	concentration of transfer agent, $\text{g}/\text{cc water}$
T_p	concentration of transfer agent in polymer particle, $\text{g-mole}/\text{l.}$
\bar{v}	average volume of polymer particle, $\text{cc}/\text{particle}$
X_M	monomer conversion
X_{MC2}	monomer conversion when monomer droplets just disappear,
θ	mean residence time, sec or min
φ	monomer weight fraction in the polymer particles

ρ density of polymer particles, g/cc
 ϵ $k_2 M_m / k_1$

Subscripts

F feed stream
 h, i, k h -, i -, k th reactor stage
 n number of the reactor stage
 0 initial condition

The authors wish to express their thanks to Prof. Magari for allowing them to use the electron microscope in his laboratory and to Mr. Nakagawara for carrying out the experimental work.

References

1. F. T. Wall, C. J. Delbecq, and R. E. Florin, *J. Polym. Sci.*, **9**, 177 (1952).
2. D. B. Gershberg and E. Longfield, A. I. Ch. E. Symposium on Polymerization Kinetics and Catalyst Systems, Part I, 1961.
3. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
4. T. Sato and I. Taniyama, *Kogyo Kagaku Zasshi*, **68**, 106 (1965).
5. W. Eguchi and M. Harada, *Advance in Chemical Engineering*, Vol. 1, Nikkan Kogyo Shinbun, Tokyo, 1967, p. 199.
6. S. Omi, T. Ueda, and H. Kubota: *J. Chem. Eng. Japan*, **2**, 193 (1969).
7. M. Harada, M. Nomura, H. Kojima, W. Eguchi, and S. Nagata, *J. Appl. Polymer Sci.*, to be published.
8. M. Nomura, M. Harada, W. Eguchi, and S. Nagata, *J. Appl. Polymer Sci.*, to be published.

Received September 1, 1970

Revised November 6, 1970