

Simulation and Optimal Design of Seeded Continuous Emulsion Polymerization Process

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Synopsis

Simulation and optimal design of the reactor for the seeded continuous emulsion polymerization process have been done in this work. An internal mixer (Toray Hi-Mixer) as seeder connected with a stirred tank is designed to correlate conversion, molecular weight, and MWD with the model simulation proposed. An optimal mean residence time of seeder $(\bar{\theta}_s)_c$ is found to lie between $(\bar{\theta}_1)_{\text{opt}}$ and t_{in} , where $(\bar{\theta}_1)_{\text{opt}} = (3aS_0/2r_i\eta N_a\alpha)^{3/5}$ and $t_{\text{in}} = 1.57(aS_0/r_i\eta N_A)^{3.5}$. The optimal design of the process is performed according to the above relations under several polymerization conditions. In general, the increase in number of stages inside the seeder can reduce the volume of CSTR for a required production. Molecular weight of products is increased by increasing the number of stages inside the seeder, by decreasing the concentration of the initiator, and by increasing the concentration of the emulsifier under the optimal conditions.

INTRODUCTION

Continuous emulsion polymerization is becoming more and more important for the mass production of polymers of consistent quality. The kinetics of continuous emulsion polymerization have received much attention in the literature since the appearance study of Wall and his co-workers.¹

The kinetics of the continuous emulsion polymerization of styrene have been studied theoretically and experimentally by Gershberg and Longfield,² applying the Smith-Ewart theory,³ and also by Sato and Taniyama⁴ and Omi et al.⁵ Nomura et al.⁶ have proposed a new reaction model based on generating polymer particles for continuous flow operation. Recently, Poehlein and co-workers⁷ have done both modeling and experimenting works with continuous emulsion polymerization reactors, especially that concerning the oscillatory nature of the reactors. Hamielec and co-workers⁹ have also done some useful work in this area.

A mathematical model based on generating polymer particles for continuous flow operation has been introduced by us in order to predict adequately the MWD as a function of the mean residence time and to provide a guide for the design of a suitable continuous type reactor.^{9,10} It is known, however, that it is difficult to obtain a high conversion of emulsion polymerization by a conventional CSTR. According to our theoretical investigation,¹¹ it is logically possible to increase ultimate conversion and molecular weight of polymers in the emulsion polymerization by using a seeder connected with the CSTR. In this paper, the effect of this seeded continuous emulsion polymerization reactor (SCEPR) on the conversion and molecular weight of polymer is discussed in order to enhance innovation for the continuous emulsion operation in industry.

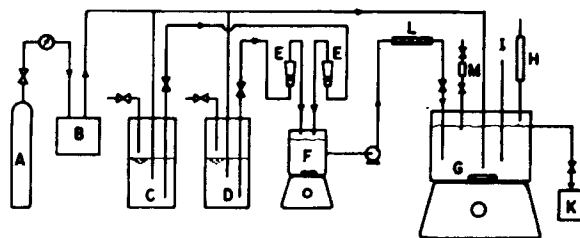


Fig. 1 Flow diagram of polymerization apparatus: (A) compressed nitrogen; (B) pyrogallol solution, concentrated sulphuric acid, and calcium chloride; (C) head tank of styrene; (D) head tank of initiator and emulsifier aqueous solution; (E) flow meter; (F) premixer; (G) reactor; (H) condenser; (I) thermometer; (K) product sample receiver; (L) Toray Hi-Mixer; (M) initiator solution.

EXPERIMENTAL

Materials: Styrene monomer was distilled from industrial grade under a reduced pressure of about 20 mm Hg. Sodium lauryl sulfate of extra pure grade was used as the emulsifier. Potassium persulfate of reagent grade was used as the initiator.

Apparatus: Emulsion polymerization was carried out in a four-neck flask reactor followed by a seeder, with thermometer, nitrogen inlet, feed inlet, and condenser. In addition, a premixer was equipped for mixing of all components before feeding to seeder. The apparatus used is illustrated in Figure 1.

Hi-Mixer: The Toray Hi-Mixer was used as a function of the seeder in this study. The Hi-Mixer used in this study consists of 20 elements in a cylindrical pipe with total length of 22.4 cm and nominal diameter of 1.0 cm. The Hi-Mixer elements are specially modified as shown in Figure 2. It enables fine dispersion merely by passing fluid through cylindrical passages within the unit. In these cylindrical passages the fluid is displaced by the vortex effect caused by the work of the spiral vanes, and is united again into the intermediate chamber for further dividing. It is, therefore, an exceptionally efficient internal mixer without any moving parts.

Molecular Weight: Determinations of average molecular weight and MWD of polymer produced were determined by GPC utilizing the Water Associate Instrument (Model ALC/GPC-200). The pore sizes of five columns were 500, 10^3 , 10^4 , 10^5 , and 10^6 Å. The flow rate of solvent of Toluene was 2.0 mL/min, at 23°C. The method proposed by Smith¹² was used to correct for the GPC instrument spreading. The weight average molecular weight of polymer product

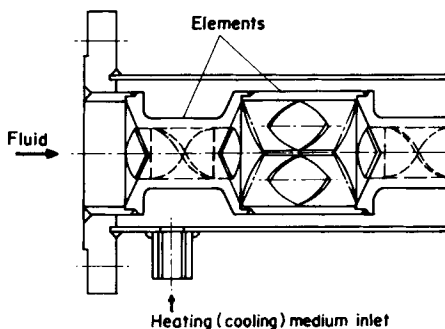
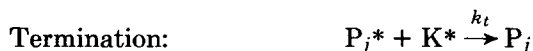
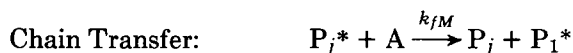
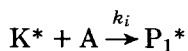


Fig. 2. Connection of Hi-Mixer elements.

was also determined by a light scattering photometer (Model 2000 D-M) for reference to extrapolate the GPC calibration curve.

THEORETICAL CONSIDERATION¹¹

A kinetic model of emulsion polymerization of styrene on the basis of Smith-Ewart theory is expressed as the following equations:



Here I, K*, A, and P represent the initiator in the reaction mixture, the initiator radical in the polymer particles, the monomer in the polymer particles, and polymer itself, respectively. Figure 3 illustrates the flow patterns in the model of SCER.

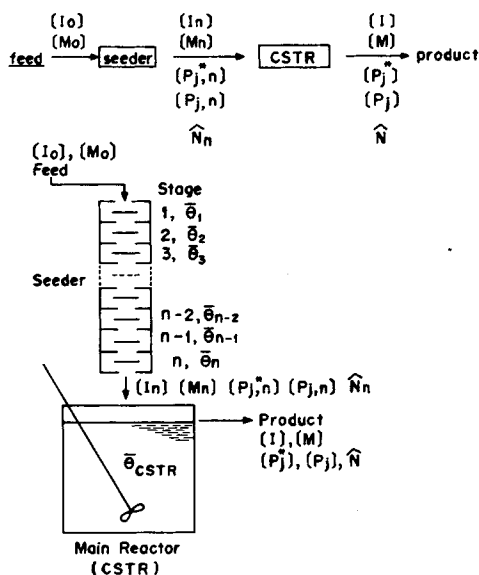


Fig. 3. Schematic representation of seeded continuous emulsion polymerization process indicating symbols used in simulation.

Seeder

It is assumed that the function of the seeder (Hi-Mixer) can be simulated approximately by multistage stirred tanks, if the residence time of each stage of the tank is sufficiently small, and $\bar{\theta}_1 = \bar{\theta}_2 = \dots = \bar{\theta}_i = \dots = \bar{\theta}_n$.

Under the assumption of steady state and complete mixing in each stage, the concentration of polymer particles in the n th stage of seeder, \hat{N}_n , is given by

$$\hat{N}_n = \begin{cases} \hat{N}_n = \sum_{i=1}^n N_i, & \text{if } \hat{N}_n \geq \hat{N}_{n-1} \\ \hat{N}_{n-1} = \sum_{i=1}^{n-1} N_i, & \text{if } \hat{N}_n < \hat{N}_{n-1} \end{cases} \quad (1)$$

where

$$N_n = \hat{N}_1 \left\{ 1 - N_A \alpha \bar{\theta}_1^{2/3} \left[\sum_{j=1}^{n-1} \frac{N_j}{(n-j)!} \frac{\Gamma(n-j+5/3)}{\Gamma(5/3)} \right] / aS_0 \right\} \quad (2)$$

$$N_1 = \hat{N}_1 = \frac{r_i \eta \bar{\theta}_1}{1 + r_i \eta N_a \alpha \bar{\theta}_1^{5/3} / aS_0} \quad (3)$$

The conversion in the n th stage of seeder is given by

$$x_n = \frac{[M_0] - [M_n]}{[M_0]} = \frac{k_p [A^0] \bar{\theta}_1}{[M_0]} (\hat{P}_1^* + \hat{P}_2^* + \dots + \hat{P}_n^*) \quad (4)$$

where

$$\hat{P}_1^* = \frac{1}{-1/r_i \bar{\theta}_1 + 2/\hat{N}_1} \quad (5)$$

$$\hat{P}_n^* \left(\frac{2r_i}{\hat{N}_n} - \frac{1}{\bar{\theta}_1} + \frac{2\hat{N}_{n-1}}{\bar{\theta}_1 \hat{N}_n} \right) = \frac{\hat{P}_{n-1}^*}{\bar{\theta}_1} + r_i \quad (6)$$

The number average degree of polymerization in the n th stage of seeder can be calculated by

$$\bar{P}_{n,n} = \frac{\sum_{j=1}^{\infty} j [P_{j,n}]}{\hat{P}_n} = \frac{[M_0] - [M_n]}{\hat{P}_n} = \frac{[M_0] x_n}{\hat{P}_n} \quad (7)$$

where

$$\frac{\hat{P}_n}{\bar{\theta}_1} = nk_d \epsilon [I_0] - \frac{\hat{P}_n^*}{2\bar{\theta}_1} + k_{fM} [A^0] (\hat{P}_1^* + \hat{P}_2^* + \dots + \hat{P}_n^*) \quad (8)$$

The weight average degree of polymerization for polymers in the n th stage of seeder is given by

$$\begin{aligned} \bar{P}_{w,n} &= \frac{\sum_{j=1}^{\infty} j^2 [P_{j,n}]}{\sum_{j=1}^{\infty} j [P_{j,n}]} \\ &= [2x_1 \nu_1 + 2(x_2 - x_1) \nu_2 + \dots + 2(x_n - x_{n-1}) \nu_n] / x_n \end{aligned} \quad (9)$$

where

$$\nu_n = \beta_n / (1 - \beta_n) \quad (10)$$

$$\beta_1 = k_p [A^0] / \{1/\bar{\theta}_1 + k_p [A^0] + k_t [K^*]_1 + k_{fM} [A^0]\} \quad (11)$$

$$\beta_n = k_p [A^0] / \{k_p [A^0] + k_t [K^*]_n + k_{fM} [A^0]\} \quad (n \neq 1) \quad (12)$$

A Seeder Followed by CSTR

As shown in Figure 3, a CSTR (main reactor) is connected with a seeder. Assuming the steady state and complete mixing, the concentration of polymer particles in the main reactor, \hat{N} , is given by

$$\hat{N} = \begin{cases} N + \hat{N}_n, & \text{if } N \geq 0 \\ \hat{N}_n, & \text{if } N < 0 \end{cases} \quad (13)$$

where

$$N = \frac{\eta r_i \bar{\theta}_{CSTR} - \frac{\eta r_i \bar{\theta}_{CSTR}}{aS_0} [A_{p,\bar{\theta}_{CSTR}}(N_1) + A_{p,\bar{\theta}_{CSTR}}(N_2) + \dots + A_{p,\bar{\theta}_{CSTR}}(N_n)]}{1 + \eta r_i \bar{\theta}_{CSTR}^{5/3} N_A \alpha / aS_0} \quad (14)$$

The conversion is represented by

$$x = \frac{[M_0] - [M]}{[M_0]} = x_n + \frac{0.5 k_p [A^0] \hat{N} \bar{\theta}_{CSTR}}{[M_0]} \quad (x < 0.43) \quad (15)$$

or

$$x = \frac{[M_0] - [M]}{[M_0]} = \frac{x_n + 0.5 k_p \phi \hat{N} \bar{\theta}_{CSTR}}{1 + 0.5 k_p \phi \hat{N} \bar{\theta}_{CSTR}} \quad (x \geq 0.43) \quad (16)$$

The number average degree of polymerization in the main reactor is given by

$$\bar{P}_n = \sum_{j=1}^{\infty} j[P_j] / \hat{P} = [M_0] x / \hat{P} \quad (17)$$

where

$$\hat{P} = \hat{P}_n + k_d \epsilon [I] \bar{\theta}_{CSTR} + [M_0] (x - x_n) k_{fM} / k_p \quad (18)$$

The weight average degree of polymerization for polymers in the main reactor is given by

$$\bar{P}_w = \sum_{j=1}^{\infty} j^2 [P_j] / \sum_{j=1}^{\infty} j [P_j] = [\bar{P}_{w,n} x_n + 2(x - x_n) \nu] / x \quad (19)$$

where

$$\nu = \frac{\beta}{1 - \beta} = \frac{[M_0] (x - x_n) \bar{\theta}_{CSTR}}{k_d \epsilon [I] + [M_0] (x - x_n) k_{fM} / \bar{\theta}_{CSTR} k_p} \quad (20)$$

RESULTS AND DISCUSSION

Experimental conditions and numerical values of emulsion polymerization of styrene as listed in Table I are used for calculation of our simulation model as illustrated in Figure 3 by using foregoing mathematical equations developed in the above considerations.

TABLE I
 Polymerization Condition and Numerical Values in Emulsion Polymerization of Styrene^{6,8,9}

Emulsion polymerization condition	
Sodium lauryl sulfate	12.50 (g/L H ₂ O)
Potassium persulfate	1.25 (g/L H ₂ O)
Styrene	0.50 (g/L H ₂ O)
Temperature	50°C
Numerical values	
$[I_0] = 2.976 \times 10^{-3}$	(mol/L)
$k_d \epsilon = 2.394 \times 10^{-3}$	(h ⁻¹)
$[M_0] = 3.094$	(mol/L)
$k_p = 7.632 \times 10^5$	(L/mol·h)
$[A^0] = 5.48$	(mol/L)
$S_i = 2.79 \times 10^{-2}$	(mol/L)
$a = 2.11 \times 10^9$	(cm ² /mol)
$v_p = 1.0$	(cm ³ /g)
$v_m = 1.107$	(cm ³ /g)
$S_{CMC} = 1.116 \times 10^{-3}$	(mol/L)
$k_{fM} = 3.8$	(L/mol·h)
$\eta = 0.4$	

Seeder

The growing chain in micelles will be generated in this stage. The experimental determination of the residence time distribution (RTD) was accomplished for a Hi-Mixer by a stimulus response technique, using NaCl as tracer material in the inlet fluid stream. The tracer concentration was determined by conductivity measurements. Danckwerts¹³ introduced the notation that the dimensionless response to an up-step injection of tracer be called the F curve. The F curve (with the tracer concentration referred to that of entering the stream C_0) and the dimensionless time (t) given by $t = \bar{\theta}/\bar{\theta}_s$ ($\bar{\theta}_s = \sum_{i=1}^n \bar{\theta}_i$) is shown in Figure 4, where the solid lines describe the theoretical response curves for a series of stirred tanks calculated from the following equation¹⁴:

$$\frac{C}{C_0} = 1 - e^{-n\theta/\bar{\theta}_s} \left[1 + \frac{n\theta}{\bar{\theta}_s} + \frac{1}{2!} \left(\frac{n\theta}{\bar{\theta}_s} \right)^2 + \dots + \frac{1}{(n-1)!} \left(\frac{n\theta}{\bar{\theta}_s} \right)^{n-1} \right] \quad (21)$$

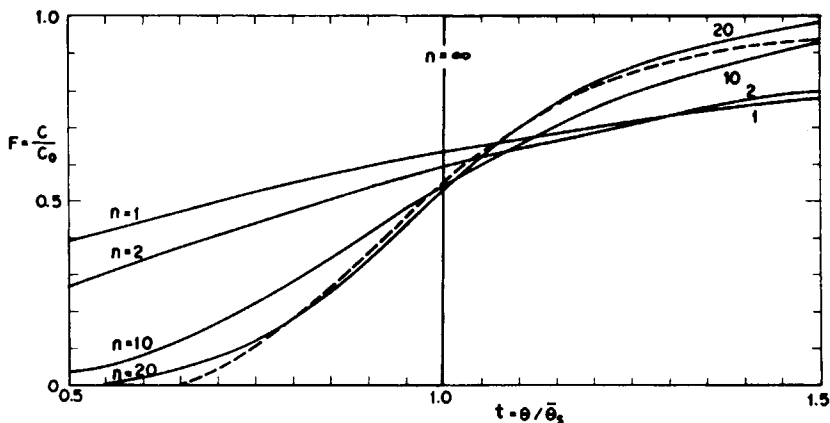


Fig. 4. RTD of multistage stirred tanks. Dotted line represents the experimental data for Hi-Mixer used.

where C and C_0 represent the tracer concentrations of outlet and inlet streams, respectively.

It is obvious that the experimental response of Hi-Mixer used in this study can be fitted approximately to the RTD for 20-stage stirred tanks ($n = 20, \bar{\theta}_s = 20 \times \bar{\theta}_i$). Hence, a prediction is adopted by assuming that Hi-Mixer be simulated by a series of 20-stage stirred tanks.

According to eqs. (1), (2), and (3), the influence of mean residence time in each stage of seeder ($\bar{\theta}_i$) on the concentration of polymer particles can be predicted as reported in our previous paper.¹¹ It has been already shown that when $\bar{\theta}_i = 0.01$ – 0.05 h, the concentration of polymer particles in the 20th stage decreases with increasing the mean residence time ($\bar{\theta}_i$). On the other hand, if the mean residence time of each stage is very short, such as $\bar{\theta}_i = 0.001$ – 0.01 h, the concentration of polymer particles in the 20th stage increases with increasing the mean residence time ($\bar{\theta}_i$). Therefore, the flow rate, namely, the size of the seeder, is an important factor to be considered for the emulsion polymerization process. In this study the mean residence time of each stage has been kept at values below 0.01 h. The relationship between conversion and mean residence time of reaction mixture in the seeder ($\bar{\theta}_s = 20 \times \bar{\theta}_i$) can be estimated by eq. (4). The effect of mean residence time on average degree of polymerization in the seeder can be also predicted from eqs. (7) and (9), as described in our previous paper.¹¹

A Seeder Followed by CSTR

The theoretical prediction for the concentration of polymer particles in the CSTR following the seeder of $n = 20$ can be made from eqs. (13) and (14). We call such a process seeded continuous emulsion polymerization (SCEP). It has been demonstrated also that the concentration of polymer particles reaches the

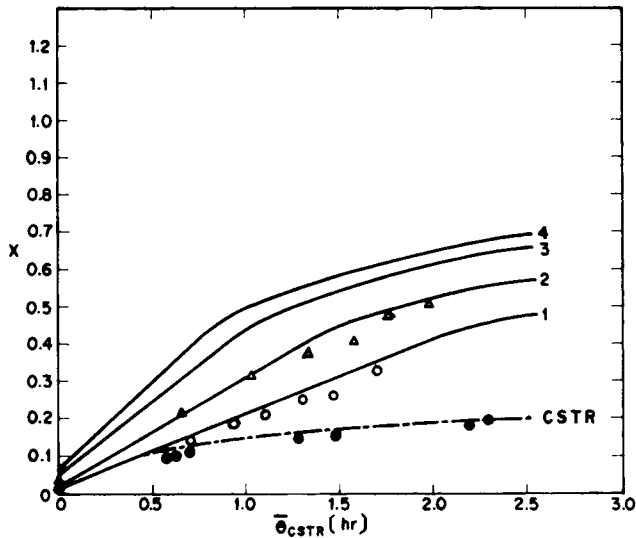


Fig. 5. Theoretical plot of conversion vs. $\bar{\theta}_{CSTR}$ in various flow rates. Length of seeder = 22.4 cm ($n = 20$); nominal diam of seeder = 1.00 cm. (— —) normal CSTR ($n = 0$); (O, Δ , \bullet) Experimental data: Flow rate (cc/min) [$\bar{\theta}_s$ (h)]: (O, 1) 2.40 [0.056]; (Δ , 2) 1.60 [0.084]; (3) 0.96 [0.14]; (4) 0.67 [0.2]. (\bullet) CSTR ($n = 0$).

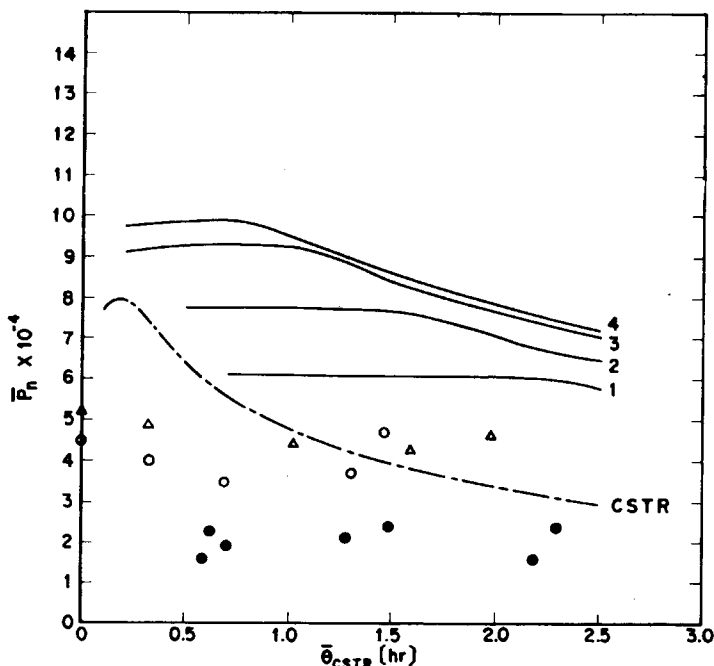


Fig. 6. Theoretical plot of \bar{P}_n vs $\bar{\theta}_{\text{CSTR}}$ in various flow rates. Length of seeder = 22.4 cm ($n = 20$); nominal diam of seeder = 1.00 cm. (— —) normal CSTR ($n = 0$); (O, Δ , \bullet) Experimental data: Flow rate (cc/min) [$\bar{\theta}_s$ (h)]: (O, 1) 2.40 [0.056]; (Δ , 2) 1.60 [0.084]; (3) 0.96 [0.14]; (4) 0.67 [0.2]. (\bullet) CSTR ($n = 0$).

higher values by increasing the mean residence time of seeder ($\bar{\theta}_s$), but keeps a constant value throughout the mean residence time of the CSTR ($\bar{\theta}_{\text{CSTR}}$).¹¹ However, when no seeder is used (i.e., $n = 0$), the concentration of polymer particles will decrease monotonously with increasing $\bar{\theta}_{\text{CSTR}}$. The relationship between conversion out of the CSTR and size of the seeder or flow rate of the reaction mixture can be estimated from eqs. (15) or (16). Both theoretical and experimental data are shown in Figure 5. As seen in Figure 5, the conversion will increase with decreasing the flow rate of mixture, namely with increasing the mean residence time ($\bar{\theta}_s$ or $\bar{\theta}_{\text{CSTR}}$). Two sets of experimental data with the flow rate of 2.40 (curve 1) and 1.60 (curve 2) (cc/min) are in good agreement with theoretical prediction. The dashed curve in the figure shows the case of without seeder ($n = 0$), namely of a normal CSTR, where the conversion cannot reach a higher value even in a large residence time. Under our experimental conditions, no significant oscillations in the "steady" operation of such reactors have been observed.

Figures 6 and 7 are the plots of eqs. (17) and (19), respectively, for various values of $\bar{\theta}_{\text{CSTR}}$ and $\bar{\theta}_s$ as well. The dashed line again represents a CSTR. The calculated chain length is progressively displaced toward a smaller one with a greater mean residence time for CSTR. But this trend will be mitigated for SCEP. A large discrepancy between the theoretical and experimental molecular weights is exhibited in both \bar{P}_n and \bar{P}_w . At least two factors may be pointed as responsible for the discrepancy between the model predictions and the experimental results. First, the model for particle formation inside the seeder used

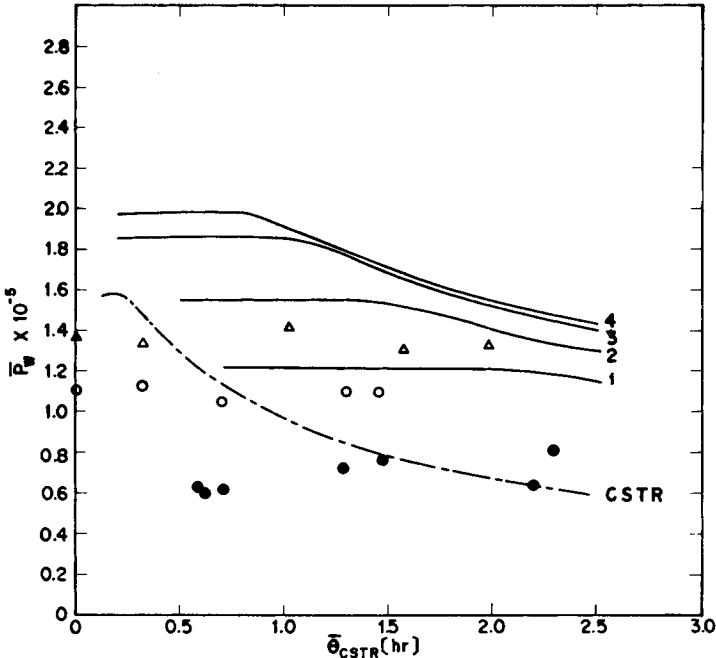


Fig. 7. Theoretical plot of \bar{P}_w vs. $\bar{\theta}_{CSTR}$ in various flow rates. Length of seeder = 22.4 cm ($n = 20$); nominal diam of seeder = 1.00 cm. (---) normal CSTR ($n = 0$); (O, Δ , \bullet) Experimental data: Flow rate (cc/min) [$\bar{\theta}_s$ (h)]: (O,1) 2.40 [0.056]; (Δ ,2) 1.60 [0.084]; (3) 0.96 [0.14]; (4) 0.67 [0.2]. (\bullet) CSTR ($n = 0$).

in this work may be inaccurate, since it was assumed that the function of seeder (Hi-Mixer) can be simulated by multistage stirred tanks. Secondly, the theoretical model assumes a complete mixing. However, this condition may not be fulfilled experimentally, which will be more significant for small values of the mean residence time. Based on the theoretical simulation, the degree of polymerization in the SCEPR will reach the higher values by increasing the mean residence time of the seeder ($\bar{\theta}_s$), but will decrease with increasing the mean residence time of CSTR ($\bar{\theta}_{CSTR}$). Moreover, the degree of polymerization experimentally obtained in the SCEPR is about two times higher than that obtained in the conventional CSTR.

According to calculations, the ratio $\bar{M}_w/\bar{M}_n (= \bar{P}_w/\bar{P}_n)$ in the SCEPR remains constant at 2. Figure 8 shows the experimental values higher than the theoretical

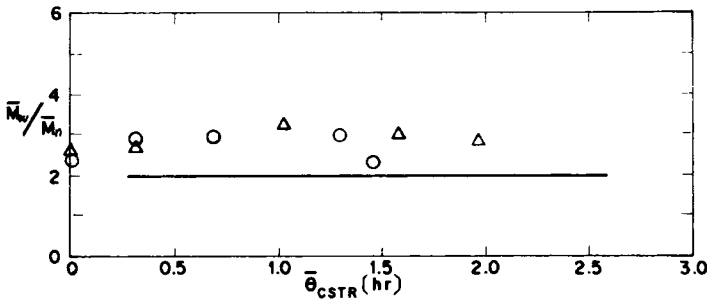


Fig. 8. Plots of \bar{M}_w/\bar{M}_n vs. $\bar{\theta}_{CSTR}$. (O, Δ) Experimental data for flow rate 2.4 and 1.6 cc/min, respectively. $n = 20$.

ones. It results from the nonideal values of \bar{M}_n and \bar{M}_w , which are obtained experimentally.

Optimal Design of SCEPR

It is seen from theoretical and experimental results that an SCEPR can increase both conversion and molecular weight of polymers. The calculation of eqs. (1), (2), and (3) gives the concentration of polymer particles of a seeder having n stages as a function of mean residence time of the seeder at the i th stage ($\bar{\theta}_i$) within the seeder. The mean residence time of seeder ($\bar{\theta}_s$) having n stages equals $n \times \bar{\theta}_i$. The computed results are shown in Figures 9–13. for several polymerization conditions. It is found that a maximum concentration takes place at the points where the value of $n \times \bar{\theta}_i$ takes a specified value [denoted as $(\bar{\theta}_s)_c$] for each seeder. For example, $(\bar{\theta}_s)_c \cong 0.2$ h in Figure 9, $(\bar{\theta}_s)_c \cong 0.13$ h in Figure 10, $(\bar{\theta}_s)_c \cong 0.3$ h in Figure 11, $(\bar{\theta}_s)_c \cong 0.3$ h in Figure 12, and $(\bar{\theta}_s)_c \cong 0.13$ h in Figure 13. Theoretically, the optimal $\bar{\theta}_s$ [i.e., $(\bar{\theta}_s)_c$] should lie between $(\bar{\theta}_1)_{\text{opt}}$ (i.e., $n = 1$) and t_{in} (i.e., $n = \infty$). Therefore, the value of $(\bar{\theta}_1)_{\text{opt}}$ can be obtained by solving the following equation:

$$\left. \frac{d\hat{N}_1}{d\bar{\theta}_1} \right|_{(\bar{\theta}_1)_{\text{opt}}} = 0 \quad (22)$$

where the value of \hat{N}_1 is obtainable from eq. (3). The solution is

$$(\bar{\theta}_1)_{\text{opt}} = (3aS_0/2r_i\eta N_A \alpha)^{3/5} \quad (23)$$

while t_{in} , the time when reaction shifts from induction stage to the zero order stage in batch operation, can be expressed from the following equation¹⁵:

$$t_{\text{in}} = 1.57(aS_0/r_i\eta N_A \alpha)^{3/5} \quad (24)$$

Figure 14 and Table II show the values of $(\bar{\theta}_1)_{\text{opt}}$ and t_{in} for several reaction conditions. It is found that the calculated values coincide well with those found in Figures 9–13. Moreover, the maximum value is increased as the value of n

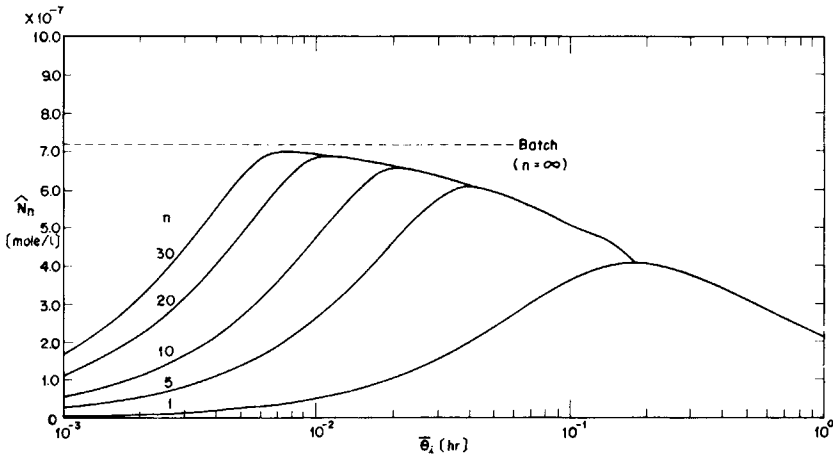


Fig. 9. Plot of concentration of polymer particles (\hat{N}_n) vs. mean residence time of seeder at i th stage ($\bar{\theta}_i$): $S_i = 12.5$ g/L H_2O ; $I_0 = 1.25$ g/L H_2O .

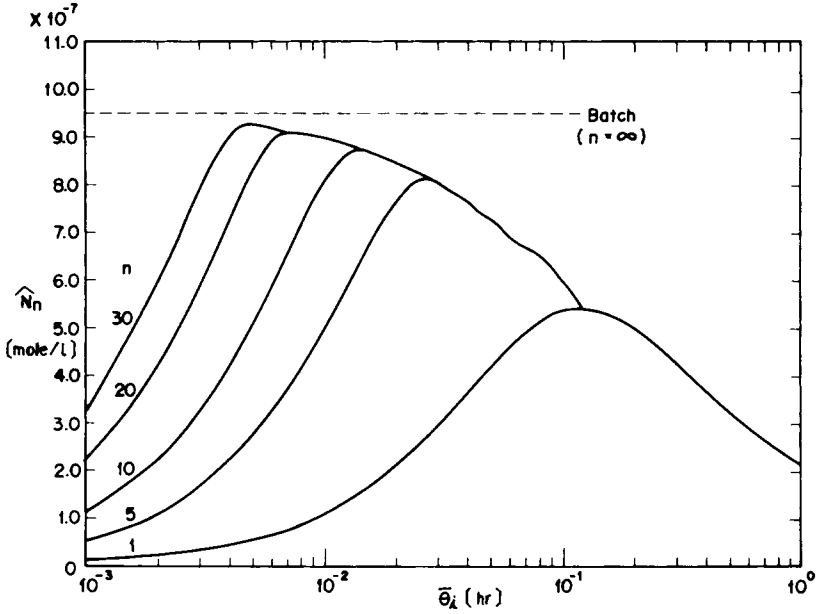


Fig. 10. Plot of concentration of polymer particles (\hat{N}_n) vs. mean residence time of seeder at i th stage ($\bar{\theta}_i$): $S_i = 12.5$ g/L H_2O ; $I_0 = 2.5$ g/L H_2O .

increase. The concentration of polymer particles (\hat{N}_n) approaches the value of a batch reactor if the number of stage of seeder increases. The dotted lines in Figures 9–13 represents the limited concentration of polymer particles in a batch operation in which $n = \infty$. As shown in Figure 14, the t_{in} and $(\bar{\theta}_1)_{opt}$ increase as the emulsifier concentration (S_i) increases, but decrease as the initiator concentration (I_0) increases. The same results can also be found in eqs. (23) and

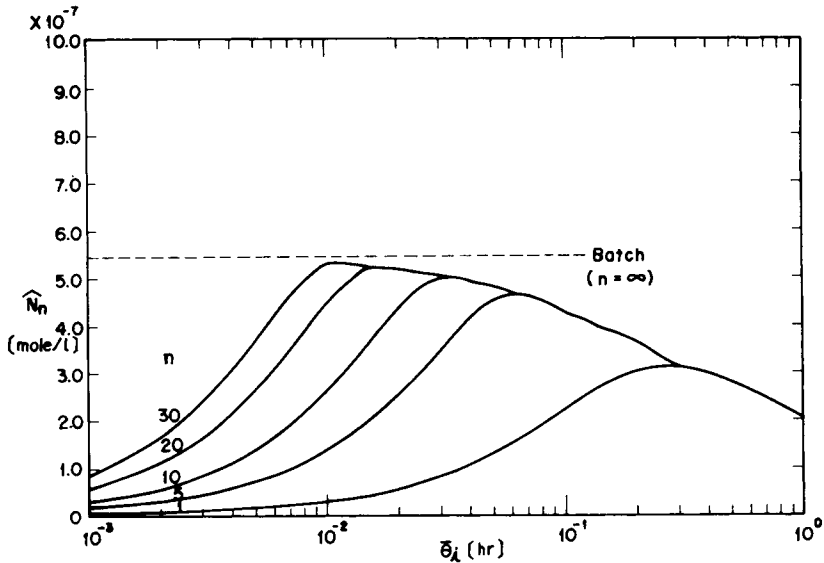


Fig. 11. Plot of concentration of polymer particles (\hat{N}_n) vs. mean residence time of seeder at i th stage ($\bar{\theta}_i$): $S_i = 12.5$ g/L H_2O ; $I_0 = 0.625$ g/L H_2O .

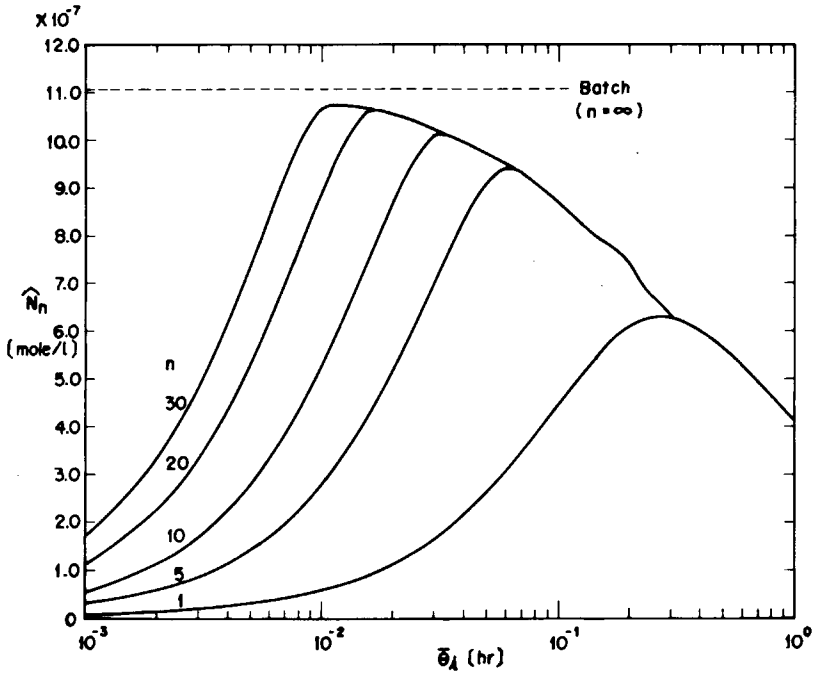


Fig. 12. Plot of concentration of polymer particles (\hat{N}_n) vs. mean residence time of seeder at i th stage ($\bar{\theta}_i$): $S_i = 25.0$ g/L H_2O ; $I_0 = 1.25$ g/L H_2O .

(24), where t_{in} and $(\bar{\theta}_i)_{opt}$ are dependent upon emulsifier concentration and initiator concentration, but independent of monomer concentration. If the volume of the seeder and the flow rate of reaction mixture are properly designed to satisfy these optimal conditions, the maximum effect of the seeder on yield will be obtained.

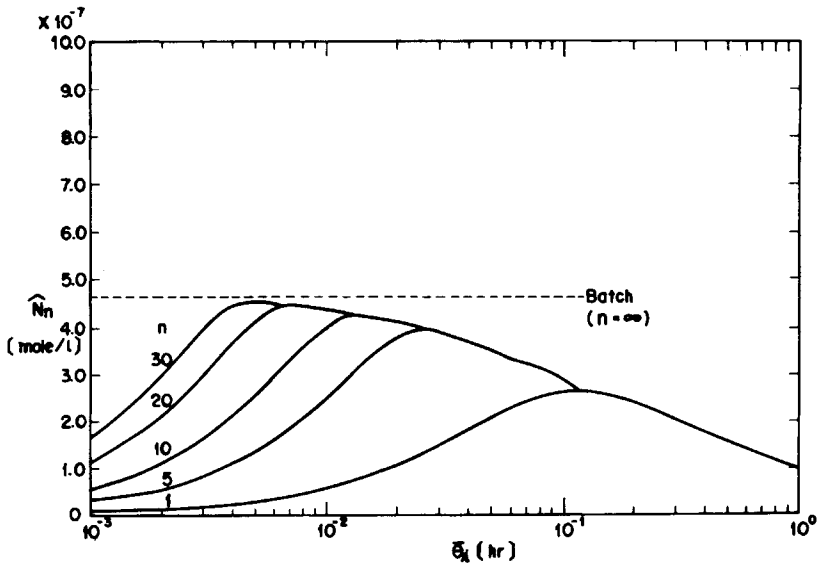


Fig. 13. Plot of concentration of polymer particles (\hat{N}_n) vs. mean residence time of seeder at i th stage ($\bar{\theta}_i$): $S_i = 6.25$ g/L H_2O ; $I_0 = 1.25$ g/L H_2O .

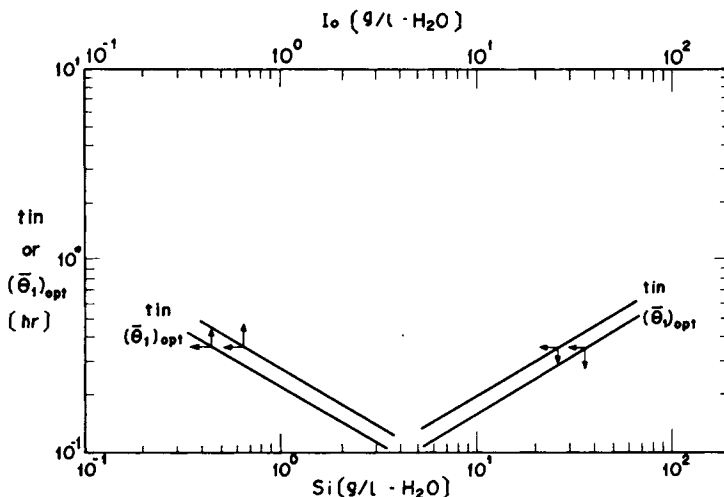


Fig. 14. Plots of $(\bar{\theta}_1)_{\text{opt}}$ or t_{in} vs. concentration of initiator (I_0) at $S_i = 12.5$ g/L H_2O and concentration of emulsifier (S_i) at $I_0 = 1.25$ g/L H_2O .

Three cases were run based on our simulation model to show the effect of the number of stages of the seeder and the volume of CSTR on the conversion, production, and molecular weight of product as well.

Case I: Influence of Number of Stages inside the Seeder

The product of this case is chosen as the conversion at 90% under the reaction condition of Table I. It is set to be $\theta_s = 0.2$ h, because this is the optimal design according to the simulation model as discussed above. Table III shows the simulated results of relationships among the number of stages of the seeder, volume of CSTR, conversion, production, and molecular weight of the product. It is seen that the increase in the number of stages inside the seeder can reduce the volume of CSTR for a required production. Molecular weight of products is also increased as the number of stages of the seeder is increased.

Case II: Influence of Concentration of Emulsifier

This case is chosen as $x = 90\%$ and $S_i = 6.25$ g/L H_2O , while the other conditions are the same as those of Table I. It is set to be $\theta_s = 0.12$ h. Table IV illustrates the calculated results. In this case the molecular weight of product is small in comparison with case I. This means that the molecular weight of the

TABLE II
 $(\bar{\theta}_1)_{\text{opt}}$ and t_{in} for Several Reaction Conditions

S_i (g/L H_2O)	I_0 (g/L H_2O)	$(\bar{\theta}_1)_{\text{opt}}$ (h)	t_{in} (h)
12.5	1.25	0.18	0.22
25.0	1.25	0.28	0.34
6.25	1.25	0.12	0.15
12.5	2.50	0.12	0.15
12.5	0.625	0.27	0.33

TABLE III
Design for Seeded Continuous System ($\bar{\theta}_s = 0.2$ h, $x = 0.9$, $S_i = 12.5$ g/L H₂O, $I_0 = 1.25$ g/L H₂O)

n	V_s (L)	V_{CSTR} (L)	F_{mix} (L/h)	$\bar{\theta}_{\text{CSTR}}$ (h)	Production (metric tons/day)	\bar{P}_n
1	26.9	2323.4	134.3	17.3	1.0	2.01×10^4
1	80.7	6970.2	402.9	17.3	3.0	2.01×10^4
5	26.9	1535.0	134.3	11.43	1.0	2.88×10^4
5	80.7	4605.0	402.9	11.43	3.0	2.88×10^4
10	26.9	1424.9	134.3	10.61	1.0	3.07×10^4
10	80.7	4274.7	402.9	10.61	3.0	3.07×10^4
20	26.9	1343.0	134.3	10.0	1.0	3.22×10^4
20	80.7	4029.0	402.9	10.0	3.0	3.22×10^4
30	26.9	1336.3	134.3	9.95	1.0	3.23×10^4
30	80.7	4008.9	402.9	9.95	3.0	3.23×10^4

product will decrease with decreasing the concentration of emulsifier under the optimal condition. The volume of seeder required is decreased, but the volume of CSTR required is increased in comparison with case I.

Case III: Influence of Concentration of Initiator

This case is chosen as $x = 90\%$ and $I_0 = 0.625$ g/L H₂O, while the other conditions are the same as those of Table I. It is set to be $\bar{\theta}_s = 0.27$ h. Table V illustrates the calculated results. In this case the molecular weight of the product is increased in comparison with case I. This means that the molecular weight of the product will increase with decreasing the concentration of initiator under the optimal condition. The volume of the seeder required is increased and the volume of CSTR required is also increased in comparison with case I.

It is apparent from the theoretical calculations thus far that the volumes of seeder and CSTR become larger as production increased. A completely satisfactory design for an SCEPR can be performed by our simulation model which provides the guide for a continuous emulsion polymerization process in industrial production.

TABLE IV
Design for Seeded Continuous System ($\bar{\theta}_s = 0.12$ h, $x = 0.9$, $S_i = 6.25$ g/L H₂O, $I_0 = 1.25$ g/L H₂O)

n	V_s (L)	V_{CSTR} (L)	F_{mix} (L/h)	$\bar{\theta}_{\text{CSTR}}$ (h)	Production (metric tons/day)	\bar{P}_n
1	16.1	3757.7	134.3	27.98	1.0	1.30×10^4
1	48.3	11273.1	402.9	27.98	3.0	1.30×10^4
5	16.1	2522.2	134.3	18.78	1.0	1.88×10^4
5	48.3	7566.6	402.9	18.78	3.0	1.88×10^4
10	16.1	2354.3	134.3	17.53	1.0	1.99×10^4
10	48.3	7062.9	402.9	17.53	3.0	1.99×10^4
20	16.1	2271.0	134.3	16.91	1.0	2.06×10^4
20	48.3	6813.0	402.9	16.91	3.0	2.06×10^4
30	16.1	2242.8	134.3	16.70	1.0	2.08×10^4
30	48.3	6728.4	402.9	16.70	3.0	2.08×10^4

TABLE V
Design for Seeded Continuous System ($\bar{\theta}_s = 0.27$ h, $x = 0.9$, $S_i = 12.5$ g/L H₂O, $I_0 = 0.625$ g/L H₂O)

n	V_s (L)	V_{CSTR} (L)	F_{mix} (L/h)	$\bar{\theta}_{CSTR}$ (h)	Production (metric tons/day)	\bar{P}_n
1	36.26	3047.3	134.3	22.69	1.0	2.91×10^4
1	108.78	9141.9	402.9	22.69	3.0	2.91×10^4
5	36.26	2052.1	134.3	15.28	1.0	4.02×10^4
5	108.78	6156.3	402.9	15.28	3.0	4.02×10^4
10	36.26	1923.2	134.3	14.32	1.0	4.23×10^4
10	108.78	5769.6	402.9	14.32	3.0	4.23×10^4
20	36.26	1858.7	134.3	13.84	1.0	4.35×10^4
20	108.78	5576.1	402.9	13.84	3.0	4.35×10^4
30	36.26	1837.2	134.3	13.68	1.0	4.39×10^4
30	108.78	5511.6	402.9	13.68	3.0	4.39×10^4

CONCLUSION

Based on the comparison between experiment with Hi-Mixer as the seeder and the model proposed, it is apparent that an efficient internal mixer without any moving parts can be used for a new SCEP process. It is concluded that the SCEP can increase both conversion and molecular weight of products in comparison with the conventional continuous emulsion polymerization process. The increase in number of stages inside the seeder can reduce the volume of CSTR for a required production. Molecular weight of products is increased by increasing the number of stages inside the seeder, by decreasing the concentration of the initiator, and by increasing the concentration of the emulsifier under the optimal conditions. These attractive facts may be improving the use of SCEPR in place of the conventional CSTR for a practical emulsion polymerization in near future.

NOMENCLATURE

a	area occupied by a soap molecule (cm ² /mol)
$[A]$	concentration of monomer dissolved in polymer particles (mol/L polymer particle)
$[A^0]$	concentration of monomer above at zero-order stage, a constant (mol/L polymer particle)
F	F curve ($= C/C_0$)
$F_{mixture}$	flow rate of reaction mixture (L/h)
$[I]$	initiator concentration (mol/L)
$[I_0]$	initiator concentration in feed (mol/L)
j	number of mers in the polymer chain
k_i	rate constant for initiation (L/mol·h)
k_d	rate constant for initiator decomposition (h ⁻¹)
k_{fM}	rate constant for transfer to monomer (L/mol·h)
k_p	rate constant for propagation (L/mol·h)
k_t	rate constant of termination (L/mol·h)
$[K^*]$	concentration of initiator radicals dissolved in polymer particles in main reactor (mol/L)
$[K^*]_n$	concentration of initiator radicals dissolved in polymer particles in n th stage of seeder (mol/L)
$[M]$	monomer concentration in main reactor (mol/L)
$[M]_n$	monomer concentration in n th stage of seeder (mol/L)

$[M_0]$	monomer concentration in feed (mol/L)
\bar{M}_n	number average of molecular weight of polymer in main reactor (g/mol)
\bar{M}_w	weight average molecular weight of polymer in main reactor (g/mol)
\hat{N}	concentration of polymer particles in main reactor (mol/L)
\hat{N}_n	concentration of polymer particles in n th stage of seeder (mol/L)
N_n	$= \hat{N}_n - \hat{N}_{n-1}$
N_A	Avogadro's number
\hat{P}_n^*	total concentration of polymer radicals in n th stage of seeder
\hat{P}_n	total concentration of dead polymer in n th stage of seeder (mol/L)
\hat{P}	total concentration of dead polymer in main reactor (mol/L)
$[P_{j,n}]$	concentration of j -mer in n th stage of seeder (mol/L)
$[P_j]$	concentration of j -mer in main reactor (mol/L)
$\bar{P}_{n,n}$	number average degree of polymerization in n th stage of seeder
\bar{P}_n	number average degree of polymerization in main reactor
$\bar{P}_{w,n}$	weight average degree of polymerization in n th stage of seeder
\bar{P}_w	weight average degree of polymerization in main reactor
r_i	effective formation rate of radicals from initiator (mol/L-h)
S_i	emulsifier concentration in feed (mol/L)
S_{CMC}	critical micelle concentration (mol/L)
S_0	$= S_i - S_{CMC}$ (mol/L)
t	$= \theta/\bar{\theta}_s$, dimensionless time
x_n	monomer conversion in n th stage of seeder
x	monomer conversion in main reactor
V_s	volume of seeder (L)
V_{CSTR}	volume of CSTR (L)
Greek	
ϵ	efficiency of initiator
η	a correction factor attributed to the efficiency of capturing radicals as defined in Ref. 9
$\bar{\theta}_i$	mean residence time in i th stage of seeder (h)
$\bar{\theta}_s$	mean residence time of seeder (h)
$\bar{\theta}_{CSTR}$	mean residence time of CSTR (h)
θ	time (h)

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