

Emulsion Polymerization Kinetics and its Reactor Design. II. The MWD Behavior in Isothermal Batch Operation

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Synopsis

The emulsion polymerization of styrene in an isothermal batch operation can be divided into three stages, and the corresponding kinetic rate equations are obtained from the experimental conversion-reaction time curve. The course of polymerization between the beginning of the reaction and any subsequent time is successfully computed for the reaction rate, the MWD, and the average degree of polymerization using the integrals of these rate equations, which could readily explain the behavior of the emulsion polymerization. A comparison is made between the theoretical results and the experimental data. Both the theoretical treatment and the experimental data predict that the MWD for a typical emulsion polymerization is characterized by the rapid decrease in \bar{M}_w/\bar{M}_n ratio at the entrance of the zero-order stage and a gradual increase in the first-order stage regardless of an autoacceleration effect. An autoacceleration effect in the first-order stage is, however, evidence for a typical emulsion polymerization.

INTRODUCTION

Presently available literature contain many investigations on emulsion polymerization. Smith and Ewart¹ first proposed a quantitative theory for emulsion polymerization of a water-insoluble monomer on the basis of Harkin's qualitative theory.² The Smith-Ewart theory has been generally supported by most researchers, because the predictions are reasonably amenable to experimental verification. It is well known that a typical emulsion polymerization with styrene monomer proceeds in three stages: the induction, the zero-order, and the first-order reaction stages. This feature for an emulsion polymerization has also been reexamined by us in our previous paper.³ The equations for each reaction stage as well as for an autoacceleration effect on the rate were separately obtained from the kinetic analysis of the experimental monomer conversion vs reaction time curve by applying the method of Omi's treatment.⁴ In the paper by Omi et al., these equations were not utilized to calculate the average molecular weight and the molecular weight distribution (MWD) as a function of reaction time owing to the lack of suitable solutions of the integrals of these semiexperimental equations. Friis et al.^{5,6} confirmed the validity of Ugelstad's model⁷ for systems with high desorption rate by simulating conversion histories for both vinyl acetate and vinyl chloride emulsion polymerization.

Recently, Harada et al.⁸ have studied the rate of emulsion polymerization of styrene through the course of reaction on the basis of a reaction model with the generating process of polymer particles. Unfortunately, it was still not possible to calculate the MWD through the course of the polymerization from the above

literature. The MWD as a function of reaction time in an emulsion polymerization has been successfully calculated first in our previous paper³ using the integrals of the rate equations and by introducing the ν method, as proposed by Imoto and co-workers.⁹ The behavior of an emulsion polymerization can be now grasped more clearly through such an analysis. From the stand point of the reactor design, we are primarily interested in deriving the relations for the reaction rate, the average molecular weight, and/or the MWD over the whole course of polymerization. On the other hand, the invention of gel permeation chromatograph (GPC) provides a highly accurate method for the determination of the MWD of polymers. In this paper the MWD and the average molecular weight as a function of reaction time computed theoretically from the integrals of the rate equations are compared with the experimental data measured by GPC.

EXPERIMENTAL

Materials. Styrene monomer was distilled from extra pure grade reagent under a reduced pressure of 30 mmHg. The emulsifier used was sodium lauryl sulfate of extra pure grade. Potassium persulfate of reagent grade was used as the initiator.

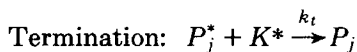
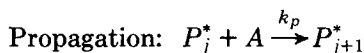
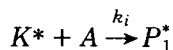
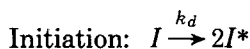
Emulsion Polymerization. Emulsion polymerization was carried out in a three-neck flask apparatus equipped with a stirrer, nitrogen inlet, and condenser by ordinary procedures under the reaction conditions presented in the caption of Figure 1.

Measurement of GPC. The MWD and the average degree of polymerization were determined by GPC using a Waters Associates machine (model ALC/GPC-20) with five 7 mm \times 30 cm columns packed with the Styragel of 500, 1×10^3 , 1×10^4 , 1×10^5 , and 1×10^6 Å, respectively.

Computation. The computer used for calculation of the reaction rate, the MWD, and the average degree of polymerization from the integrals of the kinetic equations was a CDC 3150, which has sufficient storage for our purposes. The integrals of the equations were solved by applying Simpson's rule.¹⁰

THEORETICAL CONSIDERATION

A kinetic model of emulsion polymerization on the basis of the Smith-Ewart theory can be expressed as follows:



Here I , K , A , and P represent the initiator in the reaction mixture, the initiator in the polymer particles, the monomer in the polymer particles, and the polymer

itself, respectively. The four equations can now be expressed for each stage of reaction by using the experimental monomer conversion versus reaction time curve of Figure 1. The mathematical solutions of these equations for obtaining the molecular weight distributions as well as the degrees of polymerization can be accomplished by integration with the help of a computer. The detailed mathematical treatment has already been reported in our previous paper,³ which essentially is also shown in the Appendix of this paper. The assumptions that the propagation proceeds in the polymer particles and the termination occurs only by the collision with the initiator radical are made in the above model. According to the above kinetic model, the third term in Eq. (2) of the Appendix should have been $k_t[K^*][A]$. However, in accordance with the assumption that each polymer particle contains no more than one radical, we have written the term as $k_t[K^*][\bar{N} - \bar{P}^*]$, which represents the radical entry rate into particles with zero radicals for our mathematical modeling.

RESULTS AND DISCUSSION

Figure 1 is a typical experimental conversion versus reaction time relationship of styrene monomer emulsion polymerization, where sodium lauryl sulfate is used as an emulsifier in this experiment. As will be seen, it also proceeds in three stages as obtained by Omi's result, where sodium oleate or sodium stearate is used as emulsifier. The dotted line in Figure 1 indicates the hypothetical curve

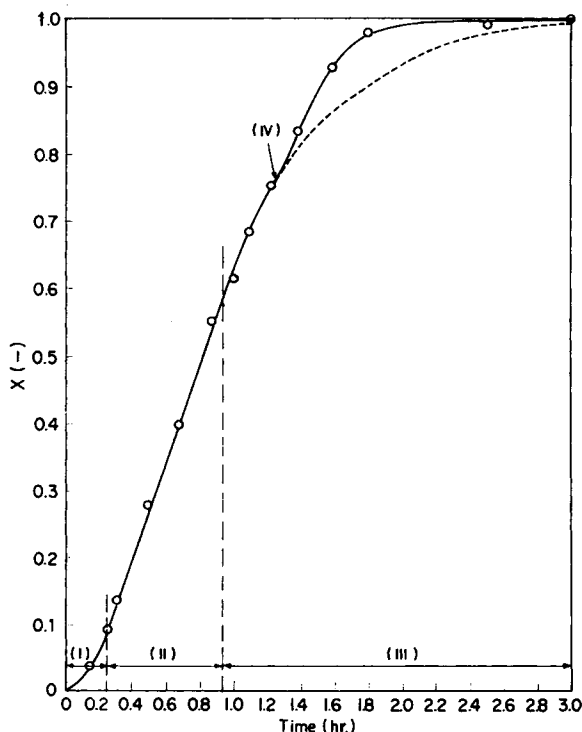


Fig. 1. Experimental monomer conversion vs reaction time curve. (I) Induction reaction stage, (II) zero-order reaction stage, (III) first-order reaction stage, (IV) starting point of autoacceleration. Experimental condition: distilled water, 640 ml; styrene, 160 ml; sodium lauryl sulfate, 1.50 g; potassium persulfate, 0.55 g; 60°C, 700 rpm.

of nonautoacceleration effect at the first-order stage, and the point (IV) indicates the starting point of acceleration. The entire course of this reaction can be followed readily by the mathematical expressions of eqs. (12), (13), (15), and (17) of the Appendix. Figure 2 shows the corresponding polymerization rate vs reaction time curve calculated from the above kinetic equations. The dotted line shows again the hypothetical case of nonautoacceleration effect at the first-order stage. Equations (26) and (27) in the Appendix were successfully integrated to obtain the overall molecular weight distributions as a function of reaction time between the beginning of the reaction and any subsequent time. The numerical values listed in Table I were experimentally obtained or evaluated and used as the basis of computation.

The rate constant at the zero-order stage, for instance, can be calculated from eq. (13) of the Appendix, once the value of \hat{N}^0 for this system is known. Namely,

$$k_p = R_p^0/[A^0]_p \hat{N}^0$$

Since it is found experimentally by Omi et al.⁴ that the relation $R_p^0/\hat{N}^0 = 5.4 \times 10^{-16}$ g/hr is independent of the concentrations of monomer, initiator, and emulsifier, and also keeps nearly constant for two kinds of anionic emulsifier,

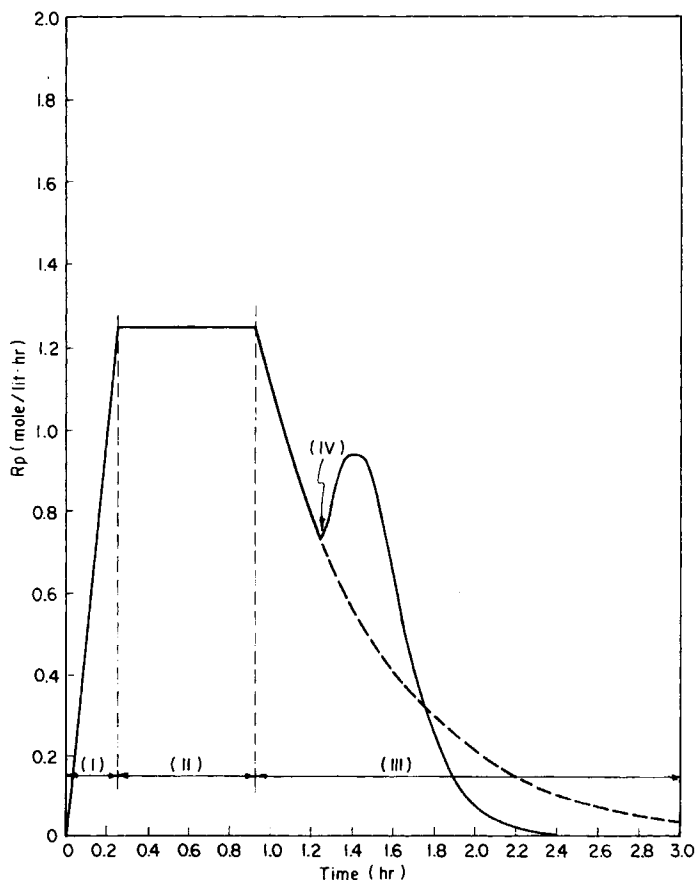


Fig. 2. Calculated rate of polymerization vs reaction time curve.

TABLE I
Numerical Values used for Calculation^a

ϵk_d	$= 5.3 \times 10^{-3} \text{ hr}^{-1}$
$[I_0]$	$= 2.55 \times 10^{-3} \text{ moles/liter}$
k_p	$= 1.654 \times 10^6 \text{ liter polymer particle/mole hr}$
ϵ	$= 0.8$
p	$= 1/2$
$[A^0]$	$= 3.93 \text{ moles/liter}$
ϕ	$= 5.33$
ρ	$= 1.54 \times 10^{-6} \text{ moles/liter hr}$
$[M_0]$	$= 1.736 \text{ moles/liter}$
\hat{N}^0	$= 3.85 \times 10^{-7} \text{ moles/liter}$
t_{in}	$= 0.25 \text{ hr}$
t_{en}	$= 0.924 \text{ hr}$
t_a	$= 1.25 \text{ hr}$
X_a	$= 0.756$
X_{en}	$= 0.575$
α	$= 11.9$

^a All data were obtained experimentally in this experiment.

the value of \hat{N}^0 is calculated from the above relation to be 3.85×10^{-7} moles/liter for this system.

At the first-order stage, the value of ϕ was evaluated to be 5.33 by assuming the following relation:

$$\phi = \frac{[A]}{[M]} \simeq \frac{[A^0]}{[M]_{x=x_{en}}} = 5.33$$

where

$$[M]_{x=x_{en}} = [M_0] (1 - x_{en})$$

At $x = x_{en}$,

$$R_{pf}|_{x=x_{en}} = k_p [A^0] p \hat{N}^0 = k'_p [M]_{x=x_{en}} p \hat{N}^0$$

where k_p and k'_p represent the rate constants based on polymer particle and on the reaction mixture, respectively. Thus, $k'_p = \phi k_p$, and the reaction rate at the first-order stage R_{pf} can be expressed by the following equation:

$$R_{pf} = k'_p [M] p \hat{N}^0 = \phi k_p [M] p \hat{N}^0$$

The value of α can be also determined by applying the Omi's equation⁴:

$$R_{pa} = R_{pf} [1 + \alpha (x - x_a)]$$

or

$$R_{pa}/R_{pf} = 1 + \alpha (x - x_a)$$

Thus, a plot of R_{pa}/R_{pf} vs x should be linear, and its slope will give the value of α , which was calculated to be 11.9 in this experiment.

The value of η in Eq. (47) of the Appendix can be also obtained as follows. Let

$$\bar{P}_{na}(t) = \left(A + \int_{t_a}^t e^{-k_d t} v_a dt \right) / f(t)$$

where

$$A = \int_0^{t_{in}} e^{-k_d t} \nu_i dt + \int_{t_{in}}^{t_{en}} e^{-k_d t} \nu_z dt + \int_{t_{en}}^{t_a} e^{-k_d t} \nu_f dt$$

and

$$f(t) = \int_0^t e^{-k_d t} dt$$

Since

$$\frac{d[\bar{P}_{na}(t)f(t) - A]}{dt} = e^{-k_d t} \nu_a = \frac{Be^{ct} R_{pa}}{k_d \epsilon [I_0]}$$

and if we let

$$g(t) \equiv \frac{k_d \epsilon [I_0]}{R_{pa}} \frac{d[\bar{P}_{na}(t)f(t) - A]}{dt}$$

therefore

$$g(t) = Be^{ct} \quad \text{or} \quad \ln g(t) = \ln B + ct$$

A plot of $\ln g(t)$ vs t should be linear, which can be extrapolated without difficulty to obtain the values of B and c .

The corresponding value of η can be now calculated from the relation of $\eta = Be^{ct}$ to be

$$\begin{aligned} \eta &= 1.0 && \text{for } t < 1.6 \text{ hr} \\ \eta &= 4.05 \times 10^{-4} e^{5.0t} && \text{for } t \geq 1.6 \text{ hr} \end{aligned}$$

The results computed with $t = 0.1, 0.15, 0.2, 1.0, 1.5, 2.0, 2.5$, and 3.0 hr for $F(t, j)_w$ are shown in Figure 3. Experimental observations with samples for the five reaction times are now shown in Figure 4. It will be seen that the same feature in the MWD for the experimental result as for the calculated one is obtained. It is to be noted that the distribution is sharpened and that the peak moves to higher molecular weight with increasing reaction time until about 1 hr and moves back again to lower molecular weights after 1 hr of the reaction time. This behavior of an emulsion polymerization has never been found in any past literature. It is further pointed out that the general feature of the MWD is not altered in the case of nonautoacceleration effect as shown in Figure 5.

Once the MWD function is determined, the average molecular weight or the instantaneous average degrees of polymerization are derived theoretically by using eqs. (37) and (38) in Appendix. The overall number and weight average degrees of polymerization can now be expressed by eqs. (39) and (40) in the Appendix. The results computed by eq. (39) with $\epsilon k_d = 4.7 \times 10^{-3}, 5.3 \times 10^{-3}$, and $5.9 \times 10^{-3} \text{ hr}^{-1}$ are shown in Figure 6, where black circles represent the experimental measurements, and dotted lines show the case of nonautoacceleration effect. The experimental values best fit with the theoretical curve with autoacceleration effect by $\epsilon k_d = 5.3 \times 10^{-3} \text{ hr}^{-1}$. This value is in agreement with the value of the potassium persulfate decomposition rate constant ($\epsilon k_d = 10.0 \times 10^{-7} \text{ sec}^{-1}$) given in the literature.¹¹ By dividing eq. (40) by (39), we obtain the heterogeneity index, \bar{M}_w/\bar{M}_n , as

$$\frac{\bar{M}_w(t)}{\bar{M}_n(t)} = \frac{\bar{P}_w(t)}{\bar{P}_n(t)} = \frac{\int_0^t R_p \bar{p}_w(t) dt}{[M_0] - [M]} \frac{\int_0^t k_d \epsilon [I] dt}{\int_0^t k_d \epsilon [I] \bar{p}_n(t) dt}$$

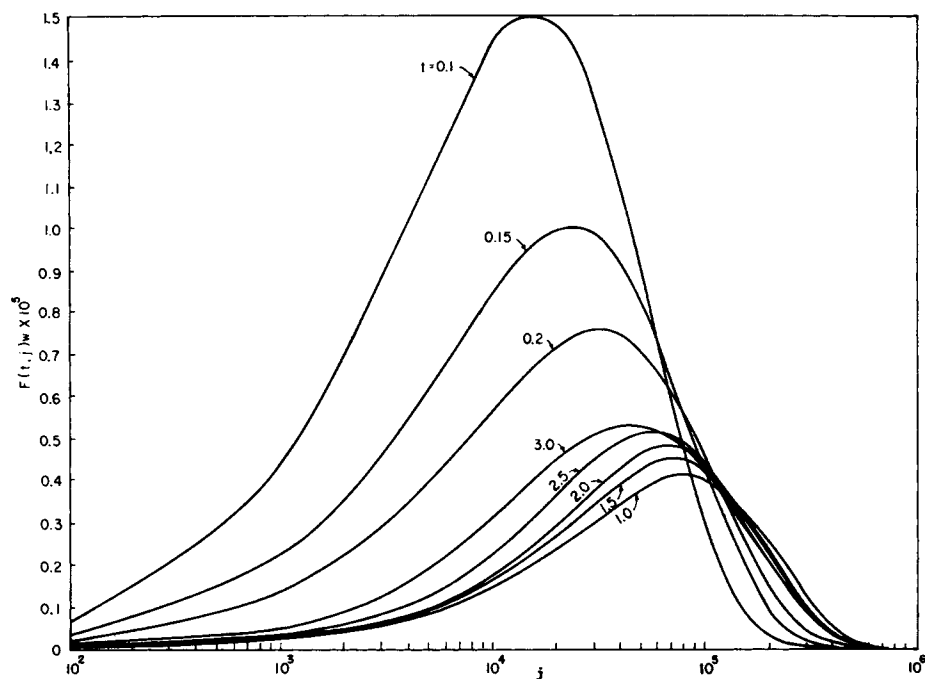


Fig. 3. Calculated MWD for an emulsion polymerization of styrene as a function of reaction time.

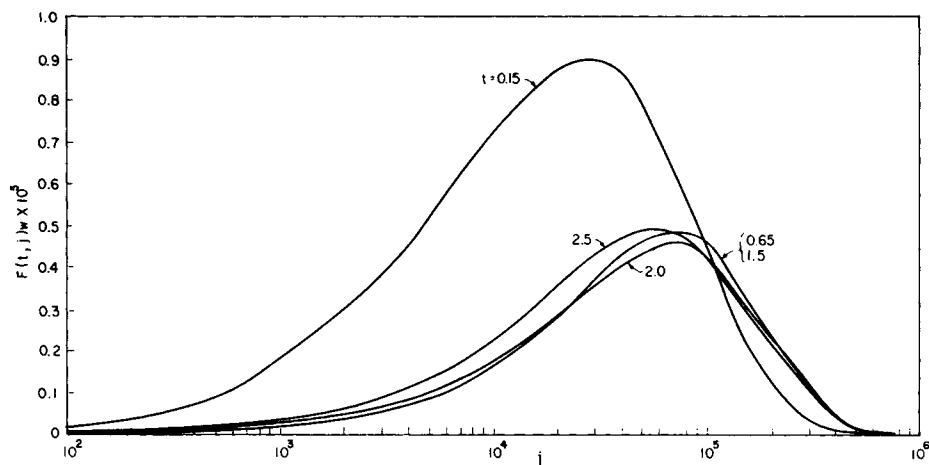


Fig. 4. Experimental MWD for an emulsion polymerization of styrene as a function of reaction time.

The ratio (\bar{M}_w/\bar{M}_n) calculated as a function of time is shown in Figure 7, where some experimental results, represented by black circles, are also shown for comparison. It is seen that the experimental data fit well with the theoretical curve of an autoacceleration effect. The ratio decreases rapidly as the reaction enters the first-order stage and increases gradually through the latter stage of reaction. Consider the fact that the radical concentration within the particle increases and $[A]$ decreases within the particle at this stage. For this reason,

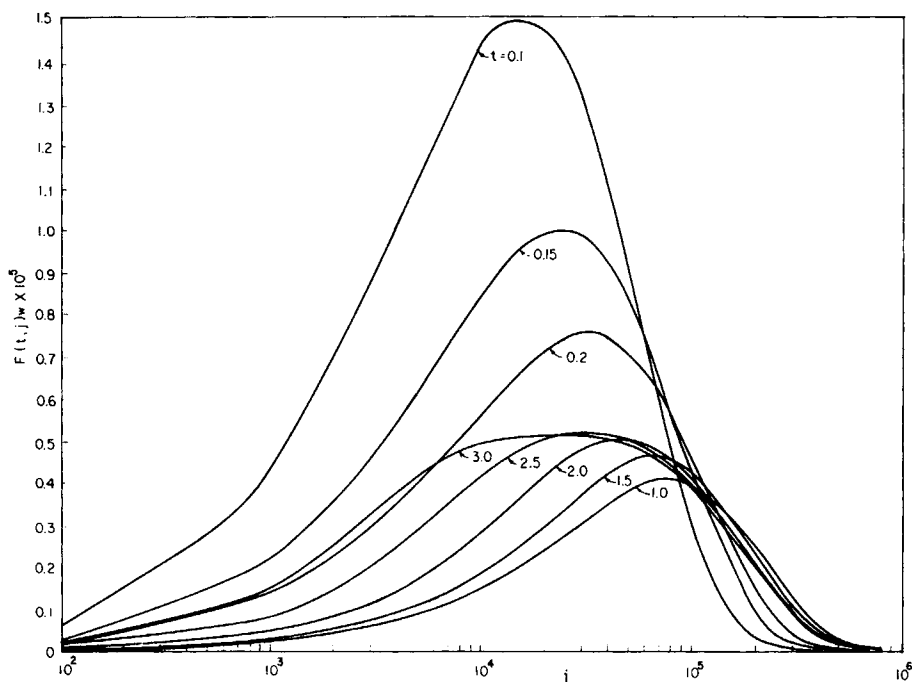


Fig. 5. Calculated MWD for an emulsion polymerization of styrene as a function of time in the case of nonautoacceleration effect.

the polymer chain produced at this stage will be shorter than that produced at the zero-order stage, where the Smith-Ewart theory is thought to be valid and $[A]$ remains approximately constant.

It follows that the degree of polymerization decreases and the ratio \bar{M}_w/\bar{M}_n increases in the first-order stage (see Figs. 6 and 7). It is also observed that the rise in \bar{M}_w/\bar{M}_n through the latter stage is more rapid in the case of nonautoacceleration effect, in which the unbalance between increasing radical concentration and decreasing $[A]$ is more evident. The observed tendency of the ratio \bar{M}_w/\bar{M}_n as seen in Figure 7 seems to coincide with this speculation. This feature may be characteristic of a typical emulsion polymerization. Therefore, it should be possible to obtain the feature in the MWD and use such information to choose an optimum condition for batch or continuous emulsion polymerization by integration of the rate equations which are experimentally obtained.

Appendix

Mechanism

According to this model, the following equations are obtained for the respective materials:

$$\frac{d[I]}{dt} = -k_d[I] \quad (1)$$

$$\frac{d[I^*]}{dt} = 2k_d[I] - k_t[K^*]\bar{P} - k_i[K^*](\bar{N} - \bar{P}^*) \quad (2)$$

$$\frac{d[M]}{dt} = -k_p[A]\bar{P}^* \quad (3)$$

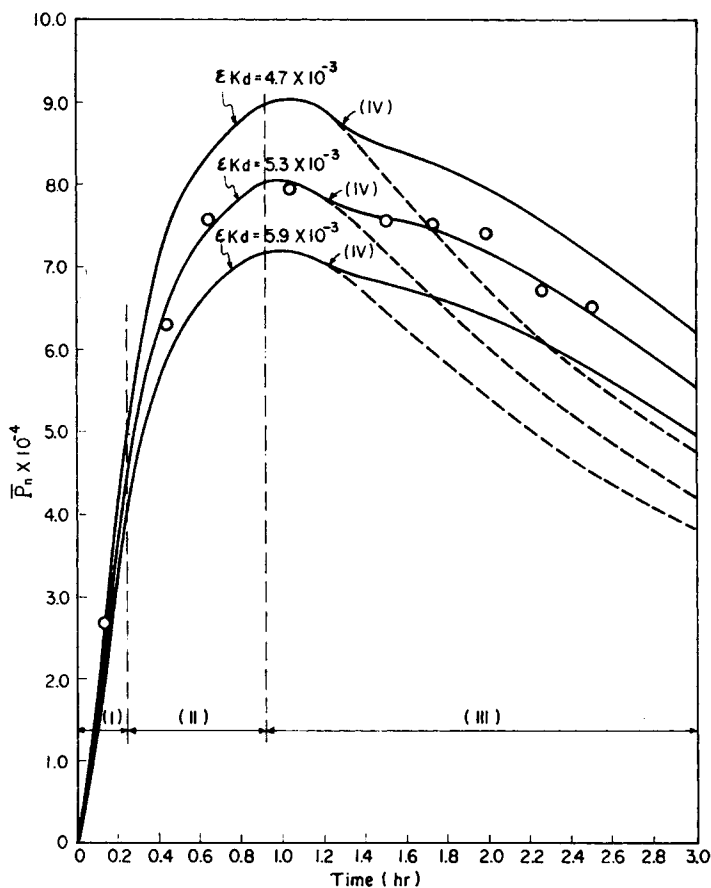


Fig. 6. Calculated number average molecular weight vs. reaction time curve for an emulsion polymerization of styrene (circles represent the experimental measurements and the dotted curves show the case of nonautoacceleration effect).

$$\frac{d[P_1^*]}{dt} = k_i[K^*](\hat{N} - \hat{P}^*) - k_p[A][P_1^*] - k_t[K^*][P_1^*] \quad (4)$$

$$\frac{d[P_j^*]}{dt} = k_p[A][P_{j-1}^*] - k_p[A][P_j^*] - k_t[K^*][P_j^*] \quad (5)$$

$$\frac{d[P_j]}{dt} = k_t[P_j^*][K^*] \quad (6)$$

where

ϵ = efficiency of initiator, $P_1^*, P_2^*, \dots, P_j^*$ = 1-mer, 2-mer, \dots , j -mer polymer radicals, $\hat{P}^* = \sum [P_j^*]$, total concentration of polymer radicals, \hat{N} = number of polymer particles per liter of system volume.

An assumption that each micelle polymer particle contains no more than one polymerizing radical is made in the above equations.

Applying the stationary-state method to evaluate the concentration of the radical materials, the following equations may be derived:

$$\begin{aligned} 2k_d\epsilon[I] &= k_t[K^*]\hat{P}^* + k_i[K^*](\hat{N} - \hat{P}) \\ k_i[K^*](\hat{N} - \hat{P}^*) &= k_t[K^*]\hat{P}^* \end{aligned} \quad (7)$$

therefore,

$$k_d\epsilon[I] = k_t[K^*]\hat{P}^* \quad (8)$$

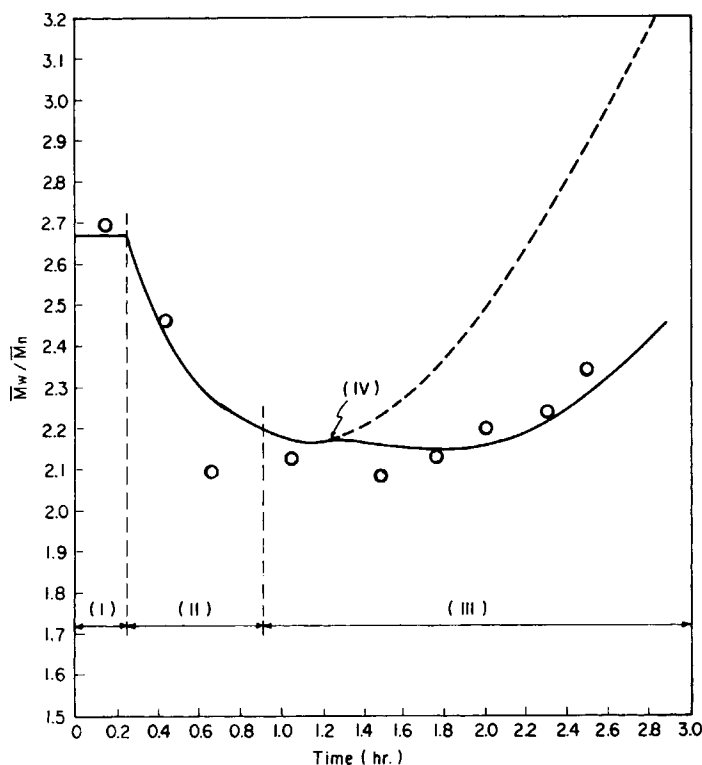


Fig. 7. Calculated \bar{M}_w/\bar{M}_n ratio vs reaction time relationship (circles represent the experimental measurements and the dotted curve shows the case of nonautoacceleration effect).

From eq. (7)

$$\hat{P}^* = p\hat{N} \quad (9)$$

where

$$p = k_i/(k_i + k_t)$$

Equation (9) means that the total concentration of polymer radicals in the polymer particles is directly proportional to number of polymer particles. According to the analysis in this paper, excellent quantitative agreement can be obtained between theoretical and experimental values of the reaction rate over entire range of reaction if the value of p is set to $1/2$ according to Smith-Ewart theory.

Reaction Rate Equations

As shown in Figure 1, the path of polymerization in batch operation can be divided into three reaction stages. The kinetic analysis of the experimental data obtained will be accomplished for each reaction stage below.

1. Induction stage ($0 \leq t \leq t_{in}$): The rate of polymerization in the induction stage (R_{pi}) is given by

$$R_{pi} = \frac{-d[M]}{dt} = k_p[A]\hat{P}^* = k_p[A^0]p\hat{N} \quad (10)$$

where $[A]$ remains constant, denoted by $[A^0]$, as long as the number of monomer droplets is large enough to diffuse the monomer into the micelle polymer particles.

Assuming that the rate of particle formation (ρ) keeps constant, thus it gives

$$\frac{d\hat{N}}{dt} = \rho, \quad \hat{N} = \rho t \quad (11)$$

and then

$$R_{pi} = k_p[A^0]p\rho t \quad (12)$$

This means that the reaction rate in the induction stage is proportional to reaction time.

2. Zero-order stage ($t_{in} \leq t \leq t_{en}$): The number of polymer particles remains constant, denoted by \hat{N}^0 , in this stage as postulated by Smith and Ewart.¹ Therefore, the rate of polymerization in zero-order stage (R_{pz}) keeps a constant value denoted by R_p^0 .

$$R_{pz} = \frac{-d[M]}{dt} = k_p[A^0]p\hat{N}^0 \equiv R_p^0 \quad (13)$$

In calculating R_{pz} , p was set equal to $1/2$. It is well known that the growing monomer-polymer particles contain a free radical only half of the time or that the particles grow in alternating periods of activity and inactivity.

3. First-order state ($t_{en} \leq t \leq t_a$): All of the monomer droplets disappear in this stage and the concentration of monomer dissolved in particles is no longer constant. Thus, the rate of polymerization (R_{pf}) is now proportional to the monomer concentration:

$$R_{pf} = \frac{-d[M]}{dt} = k_p[A]p\hat{N}^0 \equiv \phi k_p[M]p\hat{N}^0 \quad (14)$$

where $\phi = [A]/[M]$ and $[M]$ the concentration of monomer in the system. Or

$$R_{pf} = p\hat{N}^0 k_p [A^0] e^{-\phi k_p p \hat{N}^0 (t - t_{en})} \quad (15)$$

4. Autoacceleration region: If the autoacceleration effect at the first-order stage is taken into account ($t_a \leq t$), the rate of reaction should be corrected by multiplying a factor γ , where $\gamma = 1 + \alpha(x - x_a)$, α is a constant, which is experimentally determinable, and $x = ([M_0] - [M])/[M_0]$ is defined as the conversion at an arbitrary reaction time. So

$$R_{pa} = R_{pf}\gamma = R_{pf}[1 + \alpha(x - x_a)] \quad (16)$$

or

$$R_{pa} = [M_0](w + s)ue^{ut}/(1 - se^{ut})^2 \quad (17)$$

where

$$\begin{aligned} u &= -\phi k_p p \hat{N}^0 (\alpha + 1 - \alpha x_a), \\ w &= e^{-u t_a} (x_a - 1)(1 - \alpha x_a), \\ s &= \alpha (x_a - 1) e^{-u t_a}. \end{aligned}$$

Molecular Weight Distribution

Although the instantaneous degree of polymerization can be calculated from eqs. (4) and (5), the solution is not obtainable unless the instantaneous concentration is available.

According to the stationary state approximation, eq. (4) is expressed as

$$[P_1^*] = \frac{k_i[K^*](\hat{N} - \hat{P}^*)}{k_p[A] + k_t[K^*]} \equiv h\beta \quad (18)$$

where

$$h = \frac{k_i[K^*](1 - p)N}{k_p[A]} \quad \text{and} \quad \beta = \frac{k_p[A]}{k_p[A] + k_t[K^*]} \quad (19)$$

In the same way eq. (5) yields

$$[P_2^*] = \frac{k_p[A]}{k_p[A] + k_t[K^*]} [P_1^*]' \equiv h\beta^2 \quad (20)$$

Continuing in the same way, we get

$$[P_3^*] = h\beta^3 \quad \text{and} \quad [P_j^*] = h\beta^j \quad (21)$$

For the total polymer radicals we then get

$$\hat{P}^* = \sum_{j=1}^{\infty} [P_j^*] = h \left(\frac{\beta}{1 - \beta} \right) \quad (22)$$

The instantaneous number distribution function can be expressed by using the ν -method proposed by Imoto and co-workers⁹ as follows. If $\nu \gg 1$, we see at once that

$$f(t, j)_n = \frac{[P_j^*]}{\bar{P}^*} = \frac{d[P_j]}{d\bar{P}} \doteq \frac{1}{\nu} \exp\left(-\frac{j}{\nu}\right) \quad (23)$$

where

$$\nu = \frac{\beta}{1 - \beta} = \frac{k_p[A]\bar{P}^*}{k_t[K^*]\bar{P}^*} = \frac{R_p}{k_d\epsilon[I]} \quad (24)$$

In the same way, the corresponding weight distribution function is

$$f(t, j)_w = \frac{j[P_j^*]}{\sum j[P_j^*]} = \frac{j d[P_j]}{\sum j d[P_j]} \doteq \frac{j}{\nu^2} \exp\left(-\frac{j}{\nu}\right) \quad (25)$$

As defined the overall distribution functions are

$$F(t, j)_n = [P_j]/\bar{P} = \int_0^t k_d\epsilon[I]f(t, j)_n dt / \int_0^t k_d\epsilon[I] dt \quad (26)$$

$$F(t, j)_w = j[P_j]/\sum j[P_j] = \int_0^t R_p f(t, j)_w dt / ([M_0] - [M]) \quad (27)$$

1. Induction stage: Combining eqs. (12) and (24) gives

$$\nu_i = \frac{R_{pi}}{k_d\epsilon[I]} = \frac{R_{pi}}{k_d\epsilon[I_0]e^{-k_d t}} \quad (28)$$

From eqs. (25) and (27)

$$f_i(t, j)_w = \frac{j}{\nu_i^2} \exp\left(-\frac{j}{\nu_i}\right) \quad (29)$$

and

$$F_i(t, j)_w = \int_0^t k_p[A^0]p_{\rho} f_i(t, j)_w dt / ([M_0] - [M]) \quad (30)$$

In the application of eqs. (25) and (27), one should keep in mind that the equations were derived by the assumption of a steady-state condition. Since the concentration of polymer radicals \bar{P}^* is still very small in this stage, a stationary state method will produce only small error when eqs. (25) and (27) are used. Furthermore, the empirical R_{pi} is substituted in the calculation and eqs. (28)–(30) may be applicable with reasonable accuracy for this stage.

2. Zero-order stage: For this stage

$$\nu_z = \frac{R_p^0}{k_d\epsilon[I_0]e^{-k_d t}}, \quad f_z(t, j)_w = \frac{j}{\nu_z^2} \exp\left(-\frac{j}{\nu_z}\right) \quad (31)$$

and

$$F_z(t, j)_w = \left(\int_0^{t_{in}} R_{pi} f_i(t, j)_w dt + \int_{t_{in}}^t R_{pz}^0 f_z(t, j)_w dt \right) / ([M_0] - [M]) \quad (32)$$

3. First-order stage: For this stage

$$\nu_f = \frac{R_{pf}}{k_d\epsilon[I_0]e^{-k_d t}}, \quad f_f(t, j)_w = \frac{j}{\nu_f^2} \exp\left(-\frac{j}{\nu_f}\right) \quad (33)$$

and

$$F_f(t, j)_w = \left(\int_0^{t_{in}} R_{pi} f_i(t, j)_w dt + \int_{t_{in}}^{t_{en}} R_{pz}^0 f_z(t, j)_w dt + \int_{t_{en}}^t R_{pf} f_f(t, j)_w dt \right) / ([M_0] - [M]) \quad (34)$$

4. Autoacceleration: If the autoacceleration occurs at $x = x_a > x_{en}$, the rate of termination in this region is smaller than that of the other three regions due to the effect of viscosity. So ν_a should be corrected by multiplying a factor η . Let $\eta = Be^{ct}$, where B and c are constants, which are experimentally determinable. Then,

$$\nu_a = \frac{\eta R_{pa}}{k_d\epsilon[I_0]e^{-k_d t}}, \quad f_a(t, j)_w = \frac{j}{\nu_a^2} \exp\left(-\frac{j}{\nu_a}\right) \quad (35)$$

and

$$F_a(t, j)_w = \left(\int_0^{t_{in}} R_{pifi}(t, j)_w dt + \int_{t_{in}}^{t_{en}} R_{pfz}^0(t, j)_w dt + \int_{t_{en}}^{t_a} R_{pff}(t, j)_w dt + \int_{t_a}^t R_{pafa}(t, j)_w dt \right) / ([M_0] - [M]) \quad (36)$$

Degree of Polymerization

Once the molecular weight distribution function was determined, the average molecular weight or the average degree of polymerization is determinable theoretically:

$$\bar{P}_n(t) = \sum_{j=1}^{\infty} j f(t, j)_n = \sum_{j=1}^{\infty} \frac{j}{\nu} \exp\left(-\frac{j}{\nu}\right) \doteq \nu \quad (37)$$

$$\bar{P}_w(t) = \sum_{j=1}^{\infty} j f(t, j)_w = \sum_{j=1}^{\infty} \frac{j^2}{\nu^2} \exp\left(-\frac{j}{\nu}\right) \doteq 2\nu \quad (38)$$

where $\bar{P}_n(t)$ and $\bar{P}_w(t)$ represent the instantaneous number and weight average degrees of polymerization, respectively.

The overall number and weight average degrees of polymerization are expressed as follows:

$$\begin{aligned} \bar{P}_n(t) &= \int_0^t k_d \epsilon [I] \bar{P}_n(t) dt / \int_0^t k_d \epsilon [I] dt \\ &= \int_0^t e^{-k_d t} \bar{P}_n(t) dt / \int_0^t e^{-k_d t} dt \end{aligned} \quad (39)$$

$$\bar{P}_w(t) = \int_0^t R_p \bar{P}_w(t) dt / ([M_0] - [M]) \quad (40)$$

1. Induction stage: For this stage

$$\bar{P}_{ni}(t) = \int_0^t e^{-k_d t} \nu_i dt / \int_0^t e^{-k_d t} dt \quad (41)$$

$$\bar{P}_{wi}(t) = \int_0^t R_{pi}(2\nu_i) dt / ([M_0] - [M]) \quad (42)$$

2. Zero-order stage: For this stage

$$\bar{P}_{nz}(t) = \left(\int_0^{t_{in}} e^{-k_d t} \nu_i dt + \int_{t_{in}}^t e^{-k_d t} \nu_z dt \right) / \int_0^t e^{-k_d t} dt \quad (43)$$

$$\bar{P}_{wz}(t) = \left(\int_0^{t_{in}} R_{pi}(2\nu_i) dt + \int_{t_{in}}^t R_p^0(2\nu_z) dt \right) / ([M_0] - [M]) \quad (44)$$

3. First-order stage: For this stage

$$\bar{P}_{nf}(t) = \left(\int_0^{t_{in}} e^{-k_d t} \nu_i dt + \int_{t_{in}}^{t_{en}} e^{-k_d t} \nu_z dt + \int_{t_{en}}^t e^{-k_d t} \nu_f dt \right) / \int_0^t e^{-k_d t} dt \quad (45)$$

$$\bar{P}_{wf}(t) = \left(\int_0^{t_{in}} R_{pi}(2\nu_i) dt + \int_{t_{in}}^{t_{en}} R_p^0(2\nu_z) dt + \int_{t_{en}}^t R_{pff}(2\nu_f) dt \right) / ([M_0] - [M]) \quad (46)$$

4. Autoacceleration: If autoacceleration takes place at $t = t_a > t_{en}$, then we get

$$\begin{aligned} \bar{P}_{na}(t) &= \left(\int_0^{t_{in}} e^{-k_d t} \nu_i dt + \int_{t_{in}}^{t_{en}} e^{-k_d t} \nu_z dt \right. \\ &\quad \left. + \int_{t_{en}}^{t_a} e^{-k_d t} \nu_f dt + \int_{t_a}^t e^{-k_d t} \nu_a dt \right) / \int_0^t e^{-k_d t} dt \end{aligned} \quad (47)$$

$$\begin{aligned} \bar{P}_{wa}(t) &= \left(\int_0^{t_{in}} R_{pi}(2\nu_i) dt + \int_{t_{in}}^{t_{en}} R_p^0(2\nu_z) dt \right. \\ &\quad \left. + \int_{t_{en}}^{t_a} R_{pff}(2\nu_f) dt + \int_{t_a}^t R_{pa}(2\nu_a) dt \right) / ([M_0] - [M]) \end{aligned} \quad (48)$$

Nomenclature

$[A]$	concentration of monomer dissolved in the polymer particles, based on polymer particle (moles/liter)
$[A^0]$	concentration of monomer above at zero order stage, a constant, based on polymer particle (moles/liter)
$f(t,j)_n$	instantaneous number distribution function
$f(t,j)_w$	instantaneous weight distribution function
$F(t,j)_n$	overall number distribution function
$F(t,j)_w$	overall weight distribution function
$[I]$	concentration of initiator at an arbitrary time (moles/liter)
$[I_0]$	initial concentration of initiator presented in the system, a constant (moles/liter)
j	number of mers in the polymer chain
k	} reaction rate constants for
k_d	
k_i	initiation based on polymer particle (liter/mole hr)
k_p	propagation based on polymer particle (liter/mole hr)
k_t	termination based on polymer particle (liter/mole hr)
$[K^*]$	concentration of active initiator dissolved in polymer particles based on polymer particle (moles/liter)
$[M]$	concentration of monomer presented in the system at an arbitrary time (moles/liter)
$[M_0]$	initial concentration of monomer presented in the system, a constant (moles/liter)
\tilde{N}	total number of polymer particles (moles/liter)
\tilde{N}^0	total number of polymer particles at the zero-order stage, a constant (moles/liter)
$[P_j^*]$	concentration of polymer radicals (moles/liter)
$[P_j]$	concentration of dead polymer (moles/liter)
$\bar{P}_n(t)$	overall number average degree of polymerization
$\bar{P}_w(t)$	overall weight average degree of polymerization
$\bar{p}_n(t)$	instantaneous number average degree of polymerization
$\bar{p}_w(t)$	instantaneous weight average degree of polymerization
\hat{P}^*	total concentration of polymer radicals (moles/liter)
\hat{P}	total concentration of dead polymer (moles/liter)
p	a ratio of rate constants as defined in Eq. (9)
R_p	rate of propagation (moles/liter hr)
R_p^0	rate of propagation at the zero-order stage, a constant (moles/liter hr)
t	time of reaction (hr)
t_{in}	time at $x = x_{in}$ (hr)
t_{en}	time at $x = x_{en}$ (hr)
t_a	time at x_a (hr)
x	monomer conversion
x_{en}	x at the time when the reaction shifts from the zero-order stage to the first-order stage
x_a	x at the time when the autoacceleration occurs
α	contribution term required on polymerization as defined in eq. (16)
β	a ratio of reaction rates as defined in eq. (19)
γ	correction factor required to calculate the reaction rate at autoacceleration region
ν	ratio between rate of propagation and termination as defined in eq. (24)
ρ	the rate of particle formation (moles/liter hr)
ϕ	ratio between monomer concentrations in the polymer particles and system as defined in eq. (14)
ϵ	initiator efficiency

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