

Suspension Polymerization of Methyl Methacrylate. I. Modeling of Reaction Kinetics

CHEN-CHONG LIN and YAO-FENG WANG, *Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China*

Synopsis

A semiempirical model, which can simulate the behavior of free-radical polymerization of MMA in the suspension process, is proposed. Correlation of apparent termination rate constant with conversion of such system is established as follows, $\log(k_t/k_D) = n \log x' + C$. It is found that the large values of n correspond to a large gel effect and vice versa. As conversion is increased, the chains become longer and the polydispersity of product becomes larger. As temperature is increased, the polydispersity also becomes larger.

INTRODUCTION

In the suspension polymerization, both monomer and initiator are contained in the dispersed phase of droplets, which can be considered as a microbatch reactor. The behavior inside the droplets is essentially like the bulk polymerizations. Thus this system does not seem to present completely novel problems in the area of reaction analysis. The phenomena of coalescence and rapture in the dispersed phase are, however, subjects to be discussed: steady-state conditions to avoid uncontrollable reactors due to the accumulation of heat in the dispersed droplets, the maximum temperature of the dispersed droplets, and the stability of temperature control in the polymerization reactor.¹ Bero and Rosner² pointed out that the surface area of the polymer particles produced and the concentration of monomer adsorbed on that surface control the overall reaction rate. Despite the many bulk polymerization modelings which have appeared, few have dealt with the suspension polymerization process to predict both conversion and molecular weight average during the course of polymerization.

Experimental Methods

A 2-L split reactor flask with a stirring device and baffle was used for polymerization. The reactor was heated by an electric mantle connected to the power supply through a variable transformer to maintain the reactor temperature within $\pm 0.5^\circ\text{C}$. The charge to the reactor consisted of a solution of distilled water (375 mL) containing 0.3% by weight of partially hydrolyzed PVA, methyl methacrylate (MMA) (40 g), and 0.5% by weight of benzoyl peroxide on the MMA monomer, 0.08 mL of 2-methyl-propanthiol as a chain transfer agent, and 10 mL of phosphoric acid as a buffer solution in order to maintain pH value at 6.86. The reaction was stopped at the desired interval by cooling down the total mixture and filtrating and washing quickly the solid product. The dried product was then

weighed to determine the conversion. Molecular weight distribution of products was determined by GPC.

MODEL DEVELOPMENT

Correlation of Apparent Termination Rate Constant with Conversion

It is assumed that the reaction mechanism in the suspension polymerization is essentially the same as that in bulk polymerization except the termination rate constant differs as a result of the viscosity increase in the reaction system.

For a free radical polymerization system, the conversion as a function of time can be generally expressed as follows:

$$\frac{dx}{dt} = k_p(1-x) \left[\frac{2fk_d[I]}{k_t} \exp(-k_d t) \right]^{1/2} \quad (1)$$

Under the integration of eq. (1) with the boundary condition of $t = 0, x = 0$, it gives

$$-[I]^{1/2} \ln(1-x) = 2k_p(2f/k_t k_d)^{1/2} [1 - \exp(-k_d t/2)] \quad (2)$$

This equation is applicable only when the termination rate constant is independent of the gel effect, so that with the two rate equations with and without autoacceleration one obtains the following relationship:

$$\frac{dx'}{dx} = \frac{(1-x')}{(1-x)} \cdot \left(\frac{k_t}{k_t'} \right)^{1/2} \quad (3)$$

where superscript prime always refers to the observed or apparent values with autoacceleration effect.

The conversion without autoacceleration, x , can be calculated from eq. (2) by using known values of established rate constant such as those in bulk polymerization of MMA.^{3,4}

$$\begin{aligned} k_p &= 6.6 \times 10^5 \exp(-4.7 \times 10^3/RT) \\ k_d &= 1.18 \times 10^{14} \exp(-3.0 \times 10^3/RT) \\ k_t &= 2.7674 \times 10^8 \exp(-1.5612 \times 10^3/RT) \\ k_f &= 1.62 \times 10^{-2} \exp(-4.478 \times 10^3/RT) \end{aligned} \quad (4)$$

Further assuming that the apparent termination consists of chemical and diffusional parts, the following relation can be provided:

$$\frac{1}{k_t'} = \frac{1}{k_t} + \frac{1}{k_D} \quad (5)$$

$$\left(\frac{k_t}{k_D} \right) = \frac{k_t}{k_t'} - 1 \quad (6)$$

The value of k_t/k_D is expected to be the function of conversion, initiator concentration, and reaction temperature as well. In the case of the constant temperature and initiator concentration, the value becomes a function of conversion only; hence

$$\frac{k_t}{k_D} = F(x'^n) \quad (7)$$

$$\log \frac{k_t}{k_D} = n \log x' + C \quad (8)$$

A plot of $\log (k_t/k_D)$ vs. $\log x'$ would give a straight line with a slope of n .

In the other hand, the total free radical concentration can be expressed as

$$\bar{P}^* = \left[\frac{2fk_d I \exp(-k_d t)}{k_t'} \right]^{1/2} = \left[\frac{R_i}{k_t'} \right]^{1/2} \quad (9)$$

where $R_i = 2fk_d[I]$ and $[I] = [I]_0 \exp(-k_d t)$ under the isothermal operation.

Upon the choice of a dimensionless parameter, we get

$$P_1^* = \left[\frac{R_i}{k_t'} \right]^{1/2} (1 - \alpha) \quad (10)$$

⋮ ⋮ ⋮

$$P_r^* = \left[\frac{R_i}{k_t'} \right]^{1/2} (1 - \alpha) \alpha^{r-1} \quad (11)$$

where α (the probability of propagation) is given by

$$\alpha = \frac{k_p[M]}{k_p[M] + k_f[M] + (R_i \cdot k_t')^{1/2}} \quad (12)$$

Finally, the rate of polymer formation is expressed as

$$\begin{aligned} \frac{dp_r}{dt} &= \frac{1}{2} k_t' \sum p_x^* p_{r-x} + k_f M p_r^* \\ &= \frac{(1 - \alpha)^2}{2} R_i (r - 1) \alpha^{r-2} + (1 - \alpha) \alpha^{(r-1)} k_f M (1 - \alpha) \left(\frac{R_i}{k_t'} \right)^{1/2} \end{aligned} \quad (13)$$

The weight fraction of polymers having molecular weight p_r is given by

$$w_r = \frac{r \cdot p_r}{M_0 x'} \quad (14)$$

and

$$\bar{X}_n = \frac{\sum_{r=1}^{\infty} r \cdot p_r}{\sum_{r=1}^{\infty} p_r} = \frac{M_0 x'}{\int_0^t \sum_{r=1}^{\infty} (dp_r/dt) dt} \quad (15)$$

$$\bar{X}_w = \frac{\sum_{r=1}^{\infty} r^2 p_r}{\sum_{r=1}^{\infty} r p_r} = \frac{\int_0^t \sum_{r=1}^{\infty} r^2 (dp_r/dt) dt}{M_0 x'} \quad (16)$$

By solving numerically the differential equations (15) and (16), together with correlation (8), it is possible to simulate the suspension polymerization process.

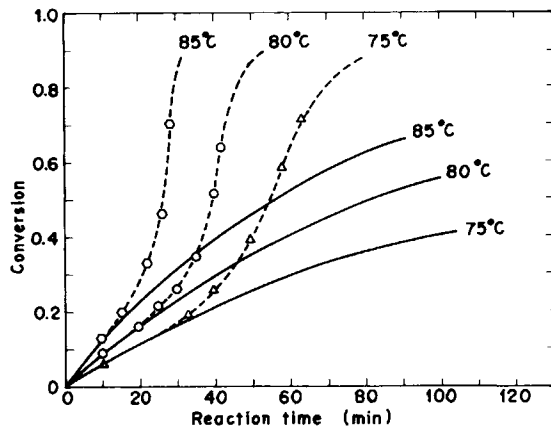


Fig. 1. Comparison between observed and calculated conversions in suspension polymerization of MMA. (—) Curves calculated by eq. (2); (---) experimental.

RESULTS AND DISCUSSION

The observed conversions of MMA suspension polymerization in sets of different temperatures are presented in Figure 1, in which the curves calculated by eq. (2) are shown for comparison. It is obvious that the apparent reactions show the autoacceleration effects even in very early reaction periods, say at about 15% conversion.

Consistent with the generally accepted belief that high viscosities of polymerizing media, caused by high-molecular-weight polymer products, are responsible for diffusion-controlled termination, one might expect that the value of k_t/k_D increases as the reaction proceeds.

Plotting k_t/k_D so calculated through eq. (6) from Figure 1 vs. x' , a straight line is observed, as shown in Figure 2, from which the following empirical equations were found to be appropriate:

$$k_t' = k_t/[1 + 2345(x')^{4.9}] \quad \text{at } 75^\circ\text{C}$$

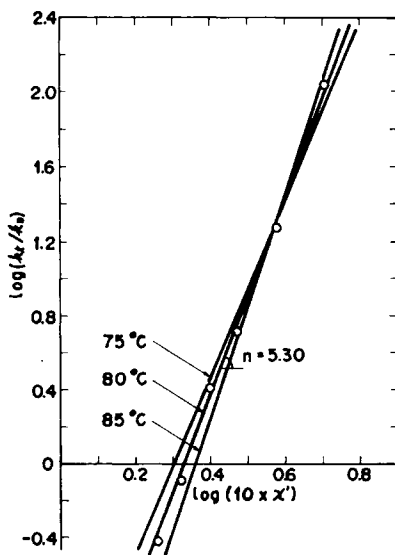


Fig. 2. Correlation of k_t/k_D with the observed conversion.

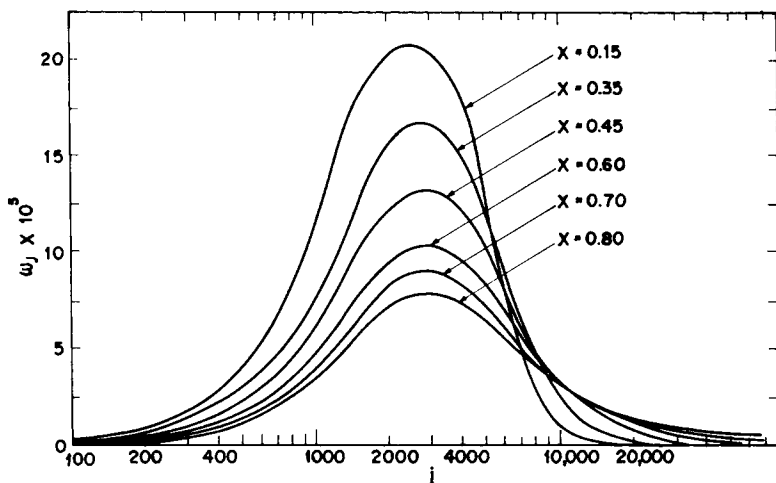


Fig. 3. Calculated MWD in different conversions at 80°C.

$$k_t = k_t / [1 + 3225(x')^{5.3}] \quad \text{at } 80^\circ\text{C} \quad (17)$$

$$k_t' = k_t / [1 + 8325(x')^{6.2}] \quad \text{at } 85^\circ\text{C}$$

It is found that the slope of n in eq. (8) is always smaller in the suspension process than that in the bulk polymerization of MMA as reported by the other authors.^{3,5} The large values of n correspond to a large gel effect and vice versa.

The combination of eqs. (17), (2), and (3), one obtains the apparent conversion by simulation, and, therefore, the molecular weight averages as a function of conversion are predictable from eqs. (5) and (16). Typical calculated curves through model are shown in Figure 3. One can see that, as conversion is increased, the chains become longer because the conversion effects the viscosity of polymerized media and, in turn, the diffusion-controlled termination. A comparison of calculated and observed MWD is shown in Figure 4.

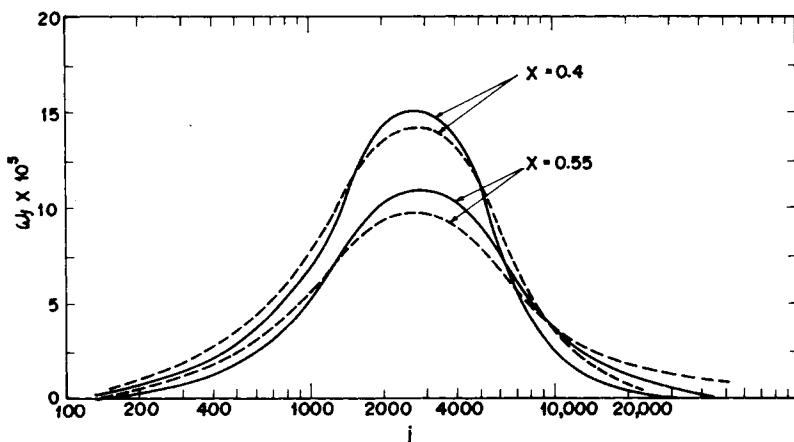


Fig. 4. Comparison between theoretical and experimental MWDs. (—) Calculated from model; (---) experimental.

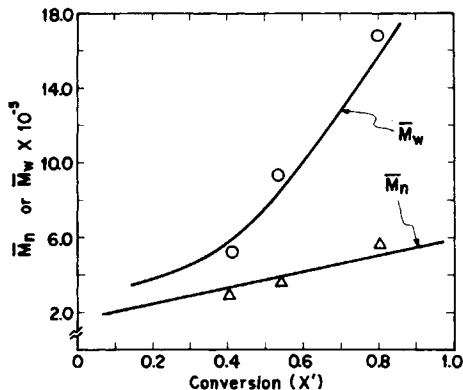


Fig. 5. Calculated \bar{M}_w and \bar{M}_n and three experimental values as function of conversion at 80°C. (—) Theoretical; (O), (Δ) experimental.

Little difference in the dependence of conversion on the MWD feature is resulted. Figure 5 shows a typical result on \bar{M}_n and \bar{M}_w as a function of conversion for 80°C. Three experimental data by GPC are also shown in the figure which are in good agreement with the theoretical predictions. Figure 6 shows the result on polydispersity, \bar{M}_w/\bar{M}_n , as a function of conversion for three reaction temperatures. It is clear that the polydispersity increases as the temperature increases at high conversion range.

CONCLUSION

This investigation has demonstrated that it is possible to simulate the behavior of free-radical polymerization in the suspension process through a semiempirical model developed above. The gel effect in the suspension process is caused by the diffusion-controlled termination. As conversion is increased, the chains become longer and the polydispersity becomes larger. Moreover, as temperature is increased, the polydispersity also becomes larger at high conversion range.

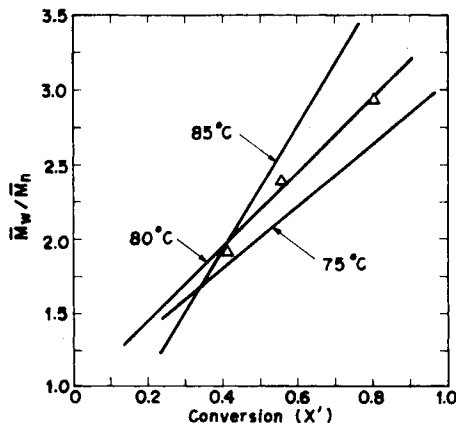


Fig. 6. Calculated polydispersity, \bar{M}_w/\bar{M}_n , and three experimental values (at 80°C) as a function of conversion. (—) Theoretical; (Δ) experimental.

References

1. S. B. Collins and J. G. Kundsén, *AIChE J.*, **16**, 1072 (1970).
2. M. Bero and T. Rosner, *Makromol. Chem.*, **136**, 1 (1970).
3. N. Ototake, F. Ueno, H. Terada and Y. Uraguchi, *J. Chem. Eng. Jpn.*, **1**, 67 (1968).
4. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 3rd ed. Wiley, New York, 1967.
5. G. Schultz and G. Harborth, *Makromol. Chem.*, **1**, 106 (1947).

Received April 2, 1981

Accepted June 2, 1981