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NONSTEADY-STATE MODEL FOR KINETICS OF RADICAL CHAIN POLYMERIZATION. 1. DIRECT PHOTOINITIATION AND THERMAL INITIATION WITH CONSTANT MONOMER CONCENTRATION

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ABSTRACT

Chain radical polymerization with direct photoinitiation or thermal initiation and constant monomer concentration has been theoretically studied by dealing precisely with the kinetic differential equations. The expressions for molecular size distribution, number- and weight-average degrees of polymerization, and their dependence on the reaction conditions are derived in analytical form. A computation program allowed easy calculation of these parameters concerned with the resultant polymer.

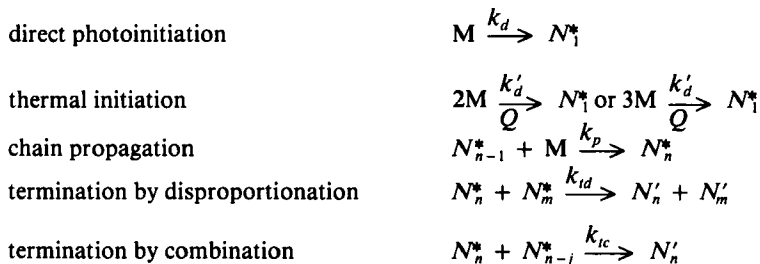
INTRODUCTION

The kinetic theory of radical chain polymerization, based on a steady-state assumption, has been widely accepted by polymer chemists for a long time [1, 2]. Although several authors [3, 4] have studied radical chain polymerization theoretically by means of a nonsteady-state method, there still appears to be a lack of satisfactory results on this topic. The lack is possibly due to the formidable nature of the kinetic differential equations. Recently, we explored the nonsteady-state kinetics

of free radical polymerization with instantaneous initiation and termination by disproportionation and combination [5, 6]. The outcome seems appropriate to a polymerization system initiated by plasma. As far as initiation is concerned, the problem is far more complicated. In order to solve this difficult problem in a step by step fashion, this work, as the first part of a series, deals with the kinetics of radical chain polymerization with direct photoinitiation or thermal initiation and constant monomer concentration. Expressions for the molecular size distribution function and other molecular parameters are given. The variation of monomer concentration with reaction time will be taken into account in the next part of this series.

MOLECULAR SIZE DISTRIBUTION OF RESULTANT POLYMER

From the point of view of mechanism, a radical chain polymerization consists of at least three elementary reactions, i.e., chain initiation, propagation, and termination by combination and disproportionation. The reaction scheme of free radical polymerization with direct photoinitiation or thermal initiation is as follows:



where k_d and k'_d are the rate constants for photo and thermal initiation, respectively; k_p represents the rate constant for propagation; k_{td} and k_{tc} are the rate constants for disproportionation and combination, respectively; N_n^* is a chain radical with n monomeric units and N'_n denotes a terminated polymer with n monomeric units; and M indicates the monomer. The corresponding kinetic differential equations are

$$R_i = k_d M \quad (\text{for photoinitiation}) \quad (1)$$

$$R_i = k'_d M^2 \text{ or } R_i = k'_d M^3 \quad (\text{for thermal initiation}) \quad (2)$$

$$\frac{dN_1^*}{dt} = R_i - k_p MN_1^* - (k_{tc} + k_{td})N_1^* \sum_{n=1}^{\infty} N_n^* \tag{3}$$

$$\frac{dN_n^*}{dt} = k_p MN_{n-1}^* - (k_{tc} + k_{td})N_n^* \sum_{n=1}^{\infty} N_n^* - k_p MN_n^* \tag{4}$$

$n = 2, 3, 4, \dots$

$$\frac{dN'_n}{dt} = k_{td}N_n^* \sum_{n=1}^{\infty} N_n^* + \frac{1}{2} k_{tc} \sum_{j=1}^{n-1} N_j^* N_{n-j}^* \tag{5}$$

$$\frac{d \sum_{n=1}^{\infty} N_n^*}{dt} = R_i - (k_{tc} + k_{td}) \left(\sum_{n=1}^{\infty} N_n^* \right)^2 \tag{6}$$

The initial condition of the differential equations

$$N_n^*|_{t=0} = N'_n|_{t=0} = 0, \quad n = 1, 2, 3, \dots \tag{7}$$

Assuming that the monomer is continuously supplied to compensate for its consumption during the polymerization, i.e., monomer concentration remains constant, then the rate of initiation, R_i , is constant. The expression of radical concentration is simply the solution of Eq. (6):

$$\sum_{n=1}^{\infty} N_n^* = \left(\frac{R_i}{k_{tc} + k_{td}} \right)^{\frac{1}{2}} th \left\{ [R_i(k_{tc} + k_{td})]^{\frac{1}{2}} t \right\} \tag{8}$$

By solving Eqs. (3) and (4), the molecular weight distribution function for the growing chains is found:

$$N_n^* = R_i \frac{(a + b)^{n-1}}{2^{n-1}} \frac{e^{-at}}{1 + e^{(b-a)t}} \left[\frac{1}{a^n} \sum_{i=n}^{\infty} \frac{(at)^i}{i!} + \frac{1}{b^n} \sum_{i=n}^{\infty} \frac{(bt)^i}{i!} \right] \tag{9}$$

where $a = k_p M + [R_i(k_{tc} + k_{td})]^{\frac{1}{2}}$ and $b = k_p M - [R_i(k_{tc} + k_{td})]^{\frac{1}{2}}$.
 From Eq. (5), we obtain the MWD function for terminated polymer:

$$N'_n = \int_0^t (k_{td}N_n^* \sum_{n=1}^{\infty} N_n^* + \frac{1}{2} k_{tc} \sum_{i=1}^{n-1} N_i^* N_{n-i}^*) dt \tag{10a}$$

According to Eqs. (8) and (9), Eq. (10a) can be written as

$$\begin{aligned}
N'_n &= \frac{k_{td}R_i^2(a+b)^{n-1}}{2^{n-2}(a-b)} \int_0^t \left\{ \frac{e^{-at}[1 - e^{(b-a)t}]}{[1 + e^{(b-a)t}]^2} \right. \\
&\quad \left. \left[\frac{1}{a^n} \sum_{i=n}^{\infty} \frac{(at)^i}{i!} + \frac{1}{b^n} \sum_{i=n}^{\infty} \frac{(bt)^i}{i!} \right] \right\} dt + \frac{k_{tc}R_i^2(a+b)^{n-2}}{2^{n-1}} \\
&\quad \int_0^t \left\{ (n-1) \left(\frac{e^{2at}}{a^n} + \frac{e^{2bt}}{b^n} \right) + \frac{2t^{n-1}}{(n-2)!} \right. \\
&\quad \left. \left[\frac{1}{a} (2^{n-2} - e^{at}) + \frac{1}{b} (2^{n-2} - e^{bt}) \right] + \frac{2e^{at}}{a^{n-1}} \right. \\
&\quad \left. \left[t - \frac{n-1}{a} + \frac{1 + e^{(b-a)t}}{a-b} \right] \sum_{i=0}^{n-2} \frac{(at)^i}{i!} + \frac{2e^{bt}}{b^{n-1}} \right. \\
&\quad \left. \left[t - \frac{n-1}{b} - \frac{1 + e^{(a-b)t}}{a-b} \right] \sum_{i=0}^{n-2} \frac{(bt)^i}{i!} + \frac{1}{b^{n-1}} \right. \\
&\quad \left. \left(\frac{2}{a-b} + \frac{n-1}{b} - 2t \right) \sum_{i=0}^{n-2} \frac{(2bt)^i}{i!} - \frac{1}{a^{n-1}} \right. \\
&\quad \left. \left(\frac{2}{a-b} - \frac{n-1}{b} + 2t \right) \sum_{i=0}^{n-2} \frac{(2at)^i}{i!} \right\} \frac{dt}{(e^{at} + e^{bt})^2} \quad (10b)
\end{aligned}$$

The MWD function for the total polymers is

$$N_n = N_n^* + N'_n \quad (11)$$

Even though Eq. (11) is rather complicated, it is easy for us to carry out numerical calculations by computer.

AVERAGE DEGREE OF POLYMERIZATION

It is known that the number- and weight-average degrees of polymerization of polymers are determined by the statistical moments of the MWD function. Combination of Eqs. (3), (4), and (5) gives

$$\begin{aligned} \frac{d \sum_{n=1}^{\infty} n^s N_n}{dt} &= R_i + \frac{a+b}{2} \sum_{n=1}^{\infty} [(n+1)^s - n^s] N_n^* \\ &\quad - k_{td} \sum_{n=1}^{\infty} n^s N_n^* \sum_{n=1}^{\infty} N_n^* + \frac{1}{2} k_{tc} \sum_{n=1}^{\infty} n^s \sum_{i=1}^{n-1} \\ &\quad N_{n-i}^* N_i^*, \quad s = 0, 1, 2 \end{aligned} \tag{12}$$

The statistical moments of the total polymer derived from Eq. (12) are listed below:

$$\begin{aligned} \sum_{n=1}^{\infty} N_n &= \frac{2R_i}{(a-b)^2} \\ &\quad \left\{ \left[\frac{1}{2} (a-b)^2 - k_{tc} R_i \right] t + \frac{2k_{tc} R_i}{(a-b)} \frac{1 - e^{(b-a)t}}{1 + e^{(b-a)t}} \right\} \end{aligned} \tag{13}$$

$$\sum_{n=1}^{\infty} n N_n = \frac{2R_i}{(a-b)^2} \left\{ (a+b) \ln \left[\frac{1 + e^{(a-b)t}}{2} \right] - b(a-b)t \right\} \tag{14}$$

$$\begin{aligned} \sum_{n=1}^{\infty} n^2 N_n &= \frac{2R_i(a+b)}{(a-b)^2} \left\{ \left[3 + \frac{8k_{tc} R_i}{(a-b)^2} \right] \ln \left(\frac{e^{at} + e^{bt}}{2} \right) \right. \\ &\quad + \frac{16k_{tc} R_i}{(a-b)^2} \frac{e^{\frac{1}{2}(a+b)t}}{e^{at} + e^{bt}} + \frac{16k_{tc} ab R_i}{(a+b)(a-b)^3} \\ &\quad \left. \frac{1 - e^{(b-a)t}}{1 + e^{(b-a)t}} - \frac{2ab}{a+b} \left[1 + \frac{4k_{tc} R_i}{(a-b)^2} \right] t - \frac{a+b}{a-b} \right. \\ &\quad \left. \left[1 + \frac{4k_{tc} R_i}{(a-b)^2} \right] \left[4 \operatorname{arctg} \left(e^{\frac{a-b}{2}t} \right) - \Pi \right] - \frac{8k_{tc} R_i}{(a-b)^2} \right\} \end{aligned} \tag{15}$$

The definitions of the number- and weight-average degrees of polymerization are

$$\bar{P}_n = \sum_{n=1}^{\infty} nN_n / \sum_{n=1}^{\infty} N_n \quad (16)$$

$$\bar{P}_w = \sum_{n=1}^{\infty} n^2 N_n / \sum_{n=1}^{\infty} n N_n \quad (17)$$

Finally, the expressions for the number- and weight-average degrees of polymerization are obtained by substituting Eqs. (13), (14), and (15) into Eqs. (16) and (17).

NUMERICAL RESULTS AND DISCUSSION

As early as in the 1930s, Schulz [7] and Flory [8] derived the “most probable” distribution, the MWD of a polymer from random polymerization, and described its application to polymers. This distribution is so important in polymer science that for nearly six decades it has been employed by polymer scientists. When used in the case of radical polymerization, however, the Schulz–Flory distribution is restricted to the situation where initiation rate and monomer concentration are maintained constant and the propagating chains are stopped by a first-order process which may be either a chain transfer step or, in the case of a radical center, disproportionation. Thus, the Schulz–Flory distribution represents instantaneous distribution under the steady-state condition of the reaction. By considering monomer consumption, Bamford et al. [9] found that the effect of a change of monomer concentration on the MWD of polymers is not very significant below 25% conversion, but above this the shift toward lower molecular weight is very noticeable. The ratio \bar{P}_w/\bar{P}_n is 2.0 at the beginning of the reaction, and it changes little over the first 25% conversion. Although complex cases concerning the mode of termination were dealt with by several authors [10–13] later on, the outcomes still seem restrained to depict the MWD of polymers in the steady-state stage of polymerization.

Mathematically, the distribution functions for the cases which cover both steady- and nonsteady-state stages of the reaction will often be very complicated, like the equations given in the previous section. However, with the aid of a computer we are able to calculate easily the MWD and other molecular parameters of the resultant polymer based on a certain reaction time and the pertinent reaction conditions. Figures 1 and 2 present the MWD curves of the polymer produced by photoinitiation

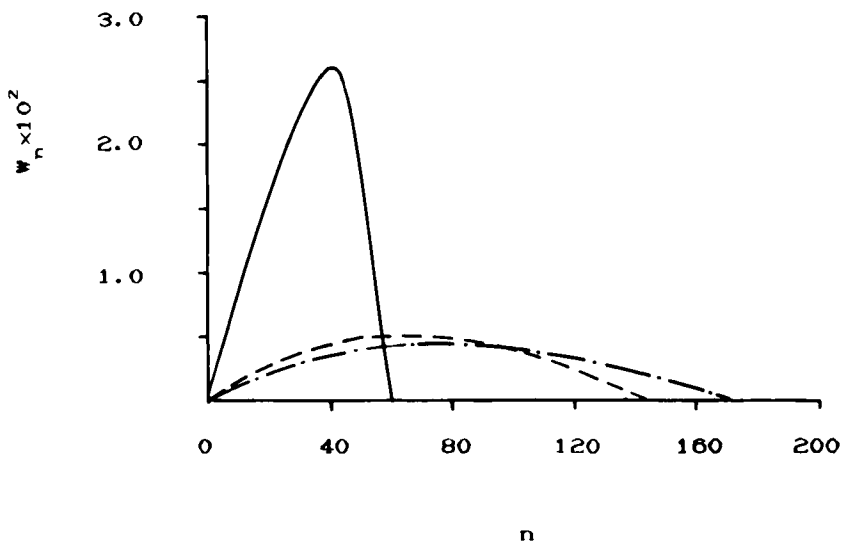


FIG. 1. MWD curves of polymer in photoinitiation. $W_n = nN_n / \sum_{n=1}^{\infty} nN_n$, $k_d = 10^{-5} \text{ s}^{-1}$; $k_p = 10^3 \text{ L}/(\text{mol}\cdot\text{s})$; $M_0 = 0.5 \text{ mol/L}$; $k_{tc} = k_{td} = 10^7 \text{ L}/(\text{mol}\cdot\text{s})$; (—) $t = 0.2 \text{ s}$; (---) $t = 0.5 \text{ s}$; (- · -) $t = 1.0 \text{ s}$.

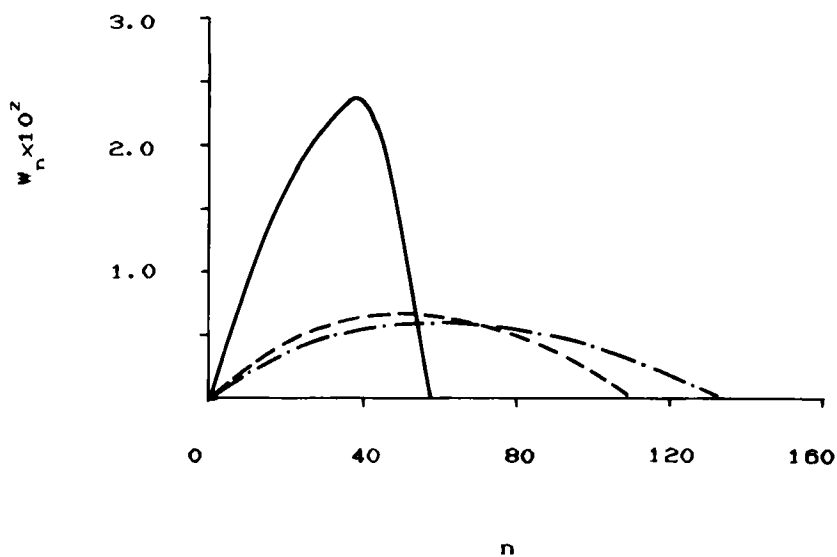


FIG. 2. MWD curves of polymer in thermal initiation ($R_i = k_d' M^2$). $k_d' = 10^{-5} \text{ s}^{-1}$; others are identical with those in Fig 1.

and thermal initiation, respectively. The rapid decrease of short chains is obvious and expected in the nonsteady-state stage of the reaction, as shown in both cases. Figure 3 shows the influence of termination on the MWD of polymers generated by photoinitiation. The MWD of polymers is evidently dependent on the type of termination of growing chains. In polymerization which undergoes termination only by combination, the MWD obtained is narrower than that obtained from termination predominantly by disproportionation. The dispersity of the polymer increases if termination occurs by both combination and disproportionation. A similar conclusion is also reached for the thermally initiated case, as shown in Fig. 4.

Figure 5 gives the MWD curves at various initial monomer concentrations. Obviously, the more monomer at the beginning of the reaction, the wider the MWD of the resultant polymer.

Figure 6 presents the dependence of the number-average degree of polymerization (\bar{P}_n) of polymers on the reaction time in polymerization with photoinitiation. At first, \bar{P}_n increases dramatically, and then it is maintained invariant at a given monomer concentration. The \bar{P}_n maximum depends only on the initial concentration of monomer, regardless of the reaction time. There is also a similar trend for thermally initiated polymerization, as shown in Fig. 7. The limitation of \bar{P}_n is as follows:

$$\lim_{t \rightarrow \infty} \bar{P}_n = \frac{2[k_{tc} + k_{td} + k_p MR_i^{-1/2}(k_{tc} + k_{td})^2]}{k_{tc} + 2k_{td}}$$

$$= \begin{cases} \frac{2\{k_{tc} + k_{td} + k_p[(k_{tc} + k_{td})M/k_d]^2\}}{k_{tc} + 2k_{td}}, & \text{photoinitiation} \\ \frac{2\{k_{tc} + k_{td} + k_p[(k_{tc} + k_{td})/k_d']^2\}}{k_{tc} + 2k_{td}}, & \text{thermal initiation:} \\ & R_i = k_d' M^2 \\ \frac{2\{k_{tc} + k_{td} + k_p[(k_{tc} + k_{td})/k_d' M]^2\}}{k_{tc} + 2k_{td}}, & R_i = k_d' M_3 \end{cases}$$

As we know, the breadth of the size distribution \bar{P}_w/\bar{P}_n in the most probable distribution where termination is by disproportionation has a limiting value of 2.0, and for polymerization where termination is by

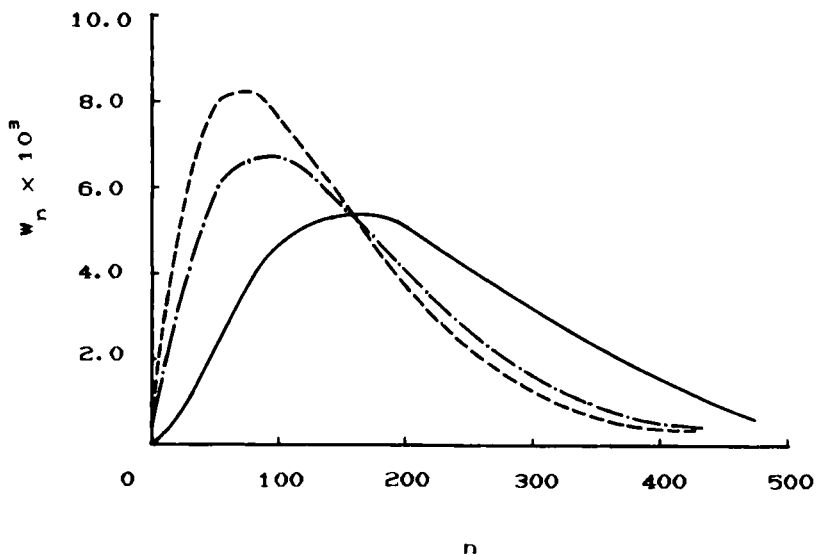


FIG. 3. MWD curves of polymer at different modes of termination in photo-initiation. (—) $k_{tc} = 0$, $k_{td} = 10^7$ L/(mol·s); (- - -) $k_{td} = 0$, $k_{tc} = 10^7$ L/(mol·s); (- · -) $k_{tc} = k_{td} = 10^7$ L/(mol·s); $t = 10$ s; others are identical with those in Fig. 1.

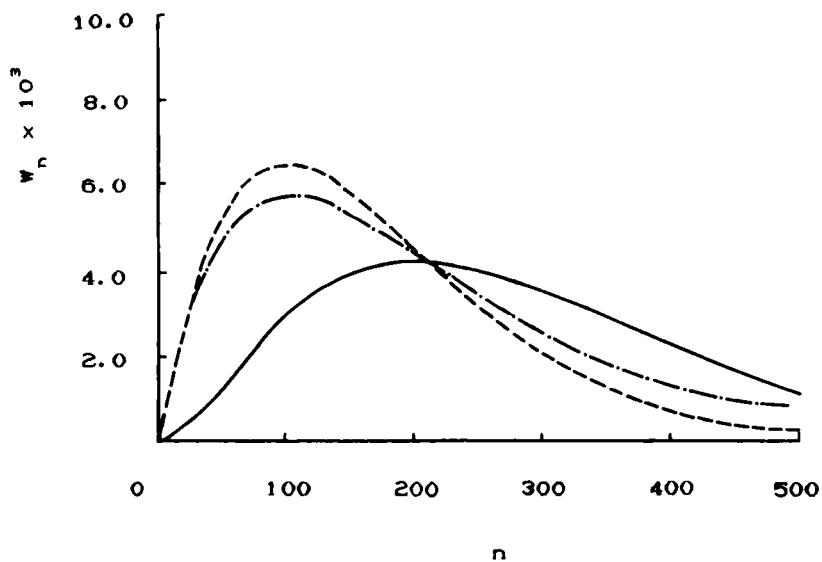


FIG. 4. MWD curves of polymer at different modes of termination in thermal initiation ($R_i = k_d' M^2$). $k_d' = 10^{-5}$ s $^{-1}$; others are identical with those in Fig. 3.

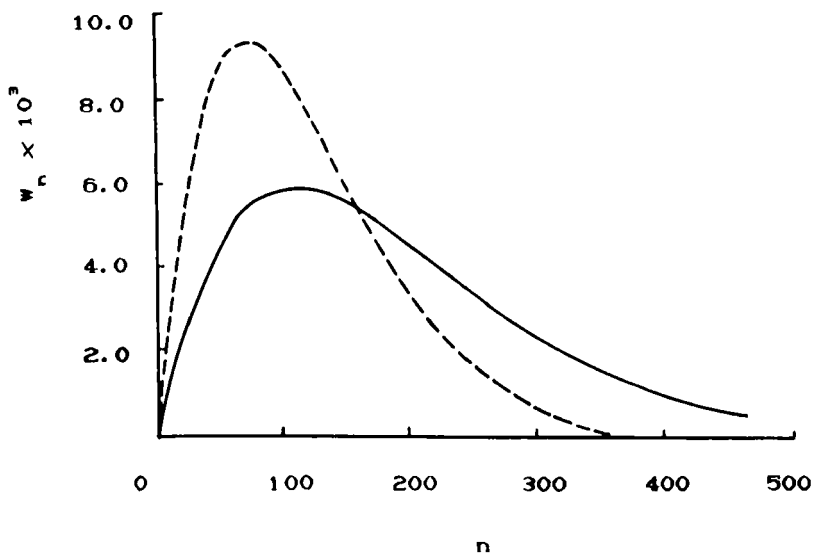


FIG. 5. MWD curves of polymer at various initial monomer concentrations in photoinitiation. (---) $M_0 = 0.5$ mol/L; (—) $M_0 = 1.2$ mol/L; others are identical with those in Fig. 1.

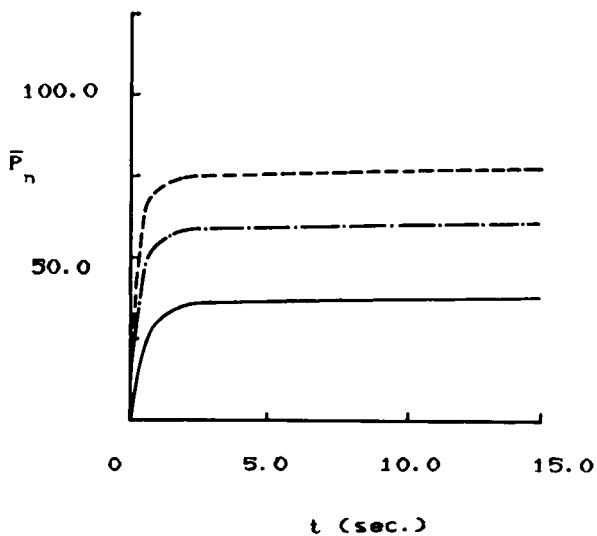


FIG. 6. Dependence of \bar{P}_n on reaction time at various initial concentrations of monomer in photoinitiation. (—) $M_0 = 0.2$ mol/L; (- · -) $M_0 = 0.5$ mol/L; (---) $M_0 = 0.8$ mol/L; others are identical with those in Fig. 1.

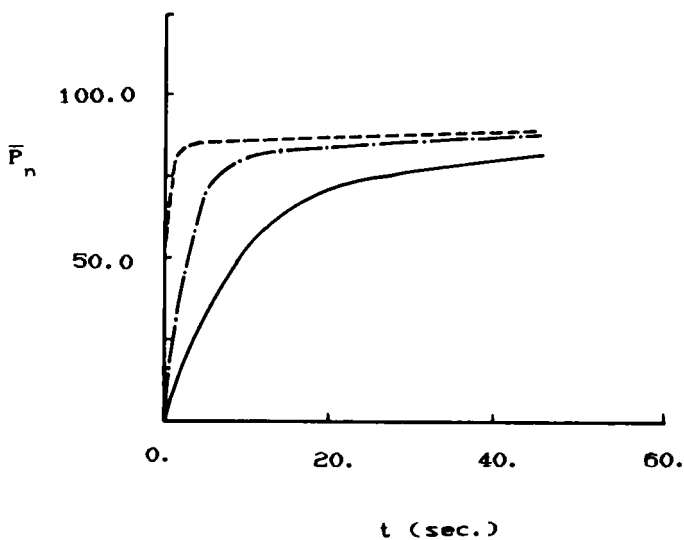


FIG. 7. Dependence of \bar{P}_n on reaction time at various initial concentrations of monomer in thermal initiation ($R_i = k_d' M^2$). $k_d' = 10^{-5} \text{ s}^{-1}$; others are identical with those in Fig. 6.

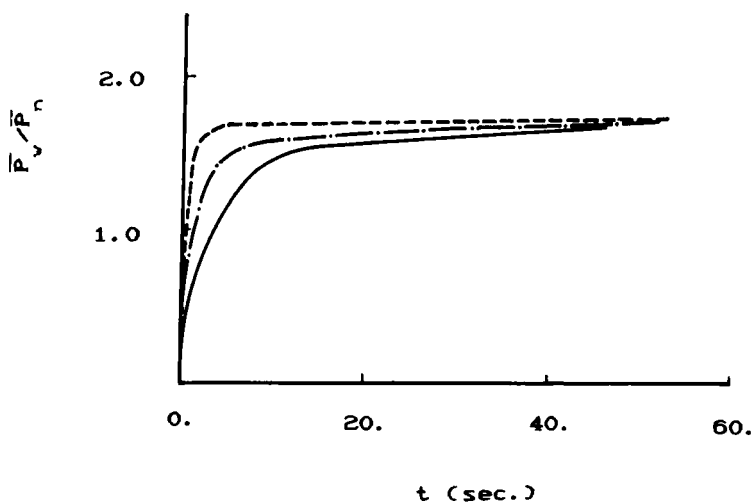


FIG. 8. Dependence of \bar{P}_w/\bar{P}_n on reaction time at various initial concentrations of monomer in photoinitiation. The reaction conditions are identical with those in Fig. 6.

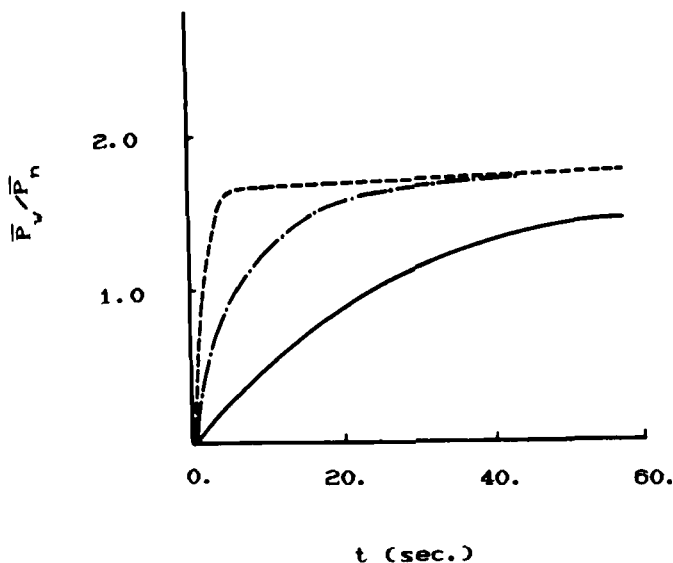


FIG. 9. Dependence of \bar{P}_w/\bar{P}_n on reaction time at various initial concentrations of monomer in thermal initiation ($R_i = k'_d M^2$). $k'_d = 10^{-5} \text{ s}^{-1}$; the reaction conditions are identical with those in Fig. 6.

combination, $\bar{P}_w/\bar{P}_n = 1.5$ [9]. It is explicitly reasonable that if termination occurs by both combination and disproportionation, then values of \bar{P}_w/\bar{P}_n inevitably fall between 1.5 and 2.0, as shown in Figs. 8 and 9.

Although the theoretical model suggested in this work assumes constant monomer concentration during the entire polymerization process, the results obtained by the nonsteady-state kinetic technique are appropriate for the lower monomer conversion region in polymerization with photoinitiation or thermal initiation, during which the monomer concentration changes only slightly.

CONCLUSION

According to the results of kinetic analysis, we conclude that the nonsteady-state stage of radical polymerization only proceeds for a short period, a minute or less. During this period the MWD curves and the breadth of size distribution of polymers change dramatically. Once the

reaction reaches the steady-state stage, the MWD curves depend mainly on the mode of the termination of growing chains and the initial monomer concentration. The values of $\overline{P}_w/\overline{P}_n$, the polydispersity index, fall between 1.5 and 2.0 in the case of terminations by both combination and disproportionation.

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