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Influence of Termination and Transfer on Molecular Weight Distribution of Polymers. I. Disproportionation and Combination

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ABSTRACT

Expressions for the molecular size distribution, the average degree of polymerization, etc. are derived by means of the nonsteady-state method for addition polymerization with instantaneous initiation, termination by disproportionation, and combination. Furthermore, a theoretical method is established with which the curves of the differential molecular weight distribution and the values of other molecular parameters can be calculated from the initial conditions of polymerization and the monomer conversion or reaction time. This theory is suited to such types of polymerization as that of vinyl monomers radiated by ^{60}Co under deep-freezing conditions, the resultant not very reactive free radical accumulating, then stopping the radiation, and letting the polymerization begin at a higher temperature.

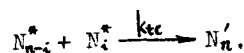
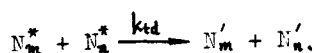
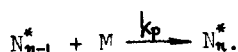
INTRODUCTION

It is well known that chain transfer and termination have an important effect upon the molecular size distribution and other molecular parameters of the polymer formed. So far, only monomer transfer and monomer termination have been rigorously studied by way of non-

steady-state analysis [1-9]. Tompa [10] has explored the kinetics of free-radical polymerization without the assumption of a stationary state. In order to simplify this complicated problem, Tang [11] focused his attention on the influence of chain termination and proposed a simplified scheme, i.e., polymerization with instantaneous initiation and termination by disproportionation and combination. He dealt with this scheme by a statistical method and gave a set of kinetic differential equations but without a solution. This work introduces a special technique by which this set of differential equations is transformed into a linear one with variable coefficients, which can be solved. On the basis of this, rigorous expressions for the molecular size distribution and other molecular parameters are obtained. The technique used in this paper can also be applied to ionic polymerization with spontaneous termination, spontaneous transfer, termination by impurity or transfer to impurity, etc. The results will be reported in further parts of this series.

1. KINETIC DIFFERENTIAL EQUATIONS AND MOLECULAR SIZE DISTRIBUTION FUNCTION

First, we adopt the following nomenclature. M , residual monomer concentration; N_n^* , growing n -mer concentration; N_n' , terminated n -mer concentration; k_p , the rate constant for chain propagation; k_{tc} , the rate constant for termination by combination; k_{td} , the rate constant for termination by disproportionation. For polymerization with instantaneous initiation and termination by disproportionation and combination, the chemical equations may be written as



The corresponding kinetic differential equations are

$$\frac{dN_i^*}{dt} = -k_p M N_i^* - (k_{td} + k_{tc}) N_i^* \sum_{n=1}^{\infty} N_n^* \quad (1)$$

$$\frac{dN_n^*}{dt} = k_p M N_{n-1}^* - k_p M N_n^* - (k_{td} + k_{tc}) N_n^* \sum_{n=1}^{\infty} N_n^* \quad , \quad n \geq 2. \quad (2)$$

$$\frac{dN_n^*}{dt} = k_{td} N_n^* \sum_{n=1}^{\infty} N_n^* + \frac{k_{tc}}{2} \sum_{i=1}^{n-1} N_{n-i}^* N_i^* \quad , \quad n \geq 1. \quad (3)$$

$$\frac{dM}{dt} = -k_p M \sum_{n=1}^{\infty} N_n^* \quad (4)$$

$$\frac{d \sum_{n=1}^{\infty} N_n^*}{dt} = -(k_{td} + k_{tc}) \left(\sum_{n=1}^{\infty} N_n^* \right)^2 \quad (5)$$

The initial conditions are

$$N_1^*|_{t=0} = I_0 ; \quad N_{n \geq 2}^*|_{t=0} = 0 ; \quad N_n'|_{t=0} = 0 ; \quad M|_{t=0} = M_0 - I_0 ,$$

where I_0 and M_0 are, respectively, the concentration of initiator and monomer added to the polymerization system. Let

$$x = k_p \int_0^t \sum_{n=1}^{\infty} N_n^* dt \quad (6)$$

or

$$\frac{dx}{dt} = k_p \sum_{n=1}^{\infty} N_n^* \quad (7)$$

and put $k_{td}/k_p = a$ and $k_{tc}/k_p = b$. Then Eqs. (4) and (5) can be transformed into the following forms:

$$\frac{dM}{dx} = -M. \quad (8)$$

$$\frac{d \sum_{n=1}^{\infty} N_n^*}{dx} = -(a+b) \sum_{n=1}^{\infty} N_n^* \quad (9)$$

Solving Eqs. (8) and (9) and utilizing the initial conditions: $\sum_{n=1}^{\infty} N_n^*|_{x=0} = I_0$ and $M|_{x=0} = M_0 - I_0$, we obtain

$$M = (M_0 - I_0) e^{-x} \quad (10)$$

$$\sum_{n=1}^{\infty} N_n^* = I_0 e^{-(a+b)x} \quad (11)$$

By virtue of Eqs. (7), (10), and (11), the set of differential Eqs. (1)-(3) is transformed into a linear one with variable coefficient:

$$\frac{dN_i^*}{dx} = -(a+b+Ke^{(a+b-1)x})N_i^* \quad (12)$$

$$\frac{dN_n^*}{dx} = Ke^{(a+b-1)x}N_{n-1}^* - (a+b+Ke^{(a+b-1)x})N_n^* \quad , n \geq 2. \quad (13)$$

$$\frac{dN_n'}{dx} = aN_n^* + \frac{be^{(a+b)x}}{2I_0} \sum_{i=1}^{n-1} N_{n-i}^* N_i^* \quad , n \geq 1. \quad (14)$$

where $K = (M_0 - I_0)/I_0$. The corresponding initial conditions become: $N_i^*|_{x=0} = I_0$; $N_{n \geq 2}^*|_{x=0} = 0$; $N_n'|_{x=0} = 0$. If $(a+b) \neq 1$, solution of Eqs. (12 and 13) gives the molecular size distribution function for the growing chains:

$$N_n^* = \frac{I_0}{(n-1)!} \left[\frac{K}{a+b-1} (e^{(a+b-1)x} - 1) \right]^{n-1} \exp \left[-(a+b)x + \frac{K}{a+b-1} (1 - e^{(a+b-1)x}) \right] \quad (15)$$

Substitution of Eq. (15) into Eq. (14) gives the molecular size distribution function for the terminated polymer:

$$\begin{aligned} N_n' &= \frac{aI_0}{(n-1)!} \left(\frac{K}{a+b-1} \right)^{n-1} \int_0^x (e^{(a+b-1)x} - 1)^{n-1} \exp \left[-(a+b)x + \frac{K}{a+b-1} (1 - e^{(a+b-1)x}) \right] dx \\ &\quad + \frac{bI_0}{2(n-2)!} \left(\frac{2K}{a+b-1} \right)^{n-2} \int_0^x (e^{(a+b-1)x} - 1)^{n-2} \exp \left[-(a+b)x + \frac{2K}{a+b-1} (1 - e^{(a+b-1)x}) \right] dx. \end{aligned} \quad (16)$$

Though Eq. (16) cannot be expressed as an elementary function, the value of the integral may be calculated numerically by computer. Evidently, the molecular size distribution function for the total polymers is

$$N_n = N_n^* + N_n' \quad (17)$$

The special case of $(a+b) = 1$ will be studied below.

2. AVERAGE DEGREE OF POLYMERIZATION AND OTHER MOLECULAR PARAMETERS

In order to obtain a series of molecular parameters, it is necessary to derive the statistical moments of N_n^* , N_n' , and N_n from the corresponding molecular size distribution functions. Equation (15) may be used to derive the following formulas:

$$\sum_{n=1}^{\infty} n N_n^* = I_0 e^{-(a+b)x} \left[1 + \frac{K}{a+b-1} (e^{(a+b-1)x} - 1) \right]. \quad (18)$$

$$\sum_{n=1}^{\infty} n^2 N_n^* = I_0 e^{-(a+b)x} \left\{ 1 + \frac{3K}{a+b-1} (e^{(a+b-1)x} - 1) + \left[\frac{K}{a+b-1} (e^{(a+b-1)x} - 1) \right]^2 \right\}. \quad (19)$$

Similarly, we may obtain from Eq. (16),

$$\sum_{n=1}^{\infty} N_n' = \frac{I_0 (2a+b)}{2(a+b)} (1 - e^{-(a+b)x}). \quad (20)$$

$$\sum_{n=1}^{\infty} n N_n' = I_0 \left[\left(1 - \frac{K}{a+b-1} \right) (1 - e^{-(a+b)x}) + \frac{(a+b)K}{a+b-1} (1 - e^{-x}) \right]. \quad (21)$$

$$\begin{aligned} \sum_{n=1}^{\infty} n^2 N_n' = I_0 & \left\{ \frac{a+2b}{a+b-2} \left(\frac{K}{a+b-1} \right)^2 (e^{(a+b-2)x} - 1) + \frac{K}{a+b-1} \left[3a+5b - \frac{2K(a+2b)}{a+b-1} \right] (1 - e^{-x}) \right. \\ & \left. + \frac{1}{a+b} \left[a+2b - \frac{K(3a+5b)}{a+b-1} + (a+2b) \left(\frac{K}{a+b-1} \right)^2 \right] (1 - e^{-(a+b)x}) \right\}. \quad (22) \end{aligned}$$

Thus, the statistical moments for the total polymers are

$$\sum_{n=1}^{\infty} N_n = \frac{I_0}{2(a+b)} (2a+b + b e^{-(a+b)x}). \quad (23)$$

$$\sum_{n=1}^{\infty} n N_n = I_0 [1 + K(1 - e^{-x})]. \quad (24)$$

$$\sum_{n=1}^{\infty} n^2 N_n = I_0 \left\{ 1 + K \left[3 + \frac{2(b-K)}{a+b-1} - \frac{2bK}{(a+b-1)^2} \right] (1-e^{-x}) + \frac{K^2}{(a+b-1)(a+b-2)} \left(2 + \frac{b}{a+b-1} \right) \right. \\ \left. \left(e^{(a+b-2)x} - 1 \right) + \frac{b}{a+b} \left(1 - \frac{K}{a+b-1} \right)^2 (1 - e^{-(a+b)x}) \right\}. \quad (25)$$

According to the definition, it is easy to obtain from Eqs. (23)-(25) the number- and weight-average degrees of polymerization for all the polymers generated in the polymerization system:

$$\bar{P}_n = \frac{2(a+b)[1+K(1-e^{-x})]}{2a+b(1+e^{-(a+b)x})}. \quad (26)$$

$$\bar{P}_w = \left\{ 1 + K \left[3 + \frac{2(b-K)}{a+b-1} - \frac{2bK}{(a+b-1)^2} \right] (1-e^{-x}) + \frac{K^2}{(a+b-1)(a+b-2)} \left(2 + \frac{b}{a+b-1} \right) \left(e^{(a+b-2)x} - 1 \right) \right. \\ \left. + \frac{b}{a+b} \left(1 - \frac{K}{a+b-1} \right)^2 (1 - e^{-(a+b)x}) \right\} / [1+K(1-e^{-x})]. \quad (27)$$

The mole fractions of the growing polymer and the terminated one are, respectively:

$$f_n^* = \frac{2(a+b)}{b + (2a+b)e^{(a+b)x}}. \quad (28)$$

$$f_n' = \frac{(2a+b)(1 - e^{-(a+b)x})}{2a+b(1+e^{-(a+b)x})}. \quad (29)$$

From Eqs. (18), (21), and (24), the weight fractions of the growing polymer and the terminated one, respectively, are obtained:

$$f_w^* = \frac{1 + \frac{K}{a+b-1} (e^{(a+b-1)x} - 1)}{[1+K(1-e^{-x})] e^{(a+b)x}}. \quad (30)$$

$$\bar{f}'_w = \frac{K(a+b)(1-e^{-x}) + (a+b-1-K)(1-e^{-(a+b)x})}{(a+b-1)[1+K(1-e^{-x})]} \quad (31)$$

From Eq. (37) below we know that if the polymerization time is long enough, the value of x will approach infinity. Then Eq. (26) gives

$$\lim_{x \rightarrow \infty} \bar{P}_n = \frac{2(a+b)(1+K)}{2a+b} \quad (32)$$

that is,

$$\bar{P}_n(\max) = \frac{2(a+b)}{2a+b} \cdot \frac{M_0}{I_0} \quad (33)$$

which is the maximum number-average degree of polymerization. Evidently,

$$M_0/I_0 \leq \bar{P}_n(\max) \leq 2M_0/I_0 \quad (34)$$

If $a < 2$, there is also a maximum weight-average degree of polymerization (omitted here).

3. DETERMINATION OF THE VARIABLE x

All of the formulas given above have the same variable x , Eq. (6). Obviously, it is important to determine the value of x from polymerization conditions. From Eq. (10) we have

$$x = \ln \frac{1-\alpha}{1-y} \quad (35)$$

where $\alpha = I_0/M_0$ and y is the monomer conversion (or $y = (M_0 - M)/M_0$). Alternatively, x can be calculated from polymerization time t . Equation (5) gives

$$\sum_{n=1}^{\infty} N_n^* = \frac{I_0}{1 + I_0(k_{td} + k_{tc})t} \quad (36)$$

Combining Eq. (11) with Eq. (36), the relationship between x and t is obtained:

$$x = \frac{1}{a+b} \ln [1 + I_0 (k_{td} + k_{tc}) t]. \quad (37)$$

Undoubtedly, it is more convenient to calculate the value of x from the reaction time t . The monomer conversion is also a function of polymerization time:

$$y = 1 - \frac{M_0 - I_0}{M_0} \left[1 + I_0 (k_{td} + k_{tc}) t \right]^{-\frac{1}{a+b}}. \quad (38)$$

Consequently, the molecular parameters at any moment can be calculated if K_p , k_{tc} , k_{td} , I_0 , and M_0 are known.

4. TERMINATION BY DISPROPORTIONATION OR COMBINATION

In the polymerization system with termination only by disproportionation, that is, $b = 0$, the molecular size distribution functions for the growing and terminated chains are simplified into the following forms:

$$N_n^* = \frac{I_0}{(n-1)!} \left[\frac{K}{a-1} (e^{(a-1)x} - 1) \right]^{n-1} \exp \left[-ax + \frac{K}{a-1} (1 - e^{(a-1)x}) \right]. \quad (39)$$

$$N_n' = \frac{aI_0}{(n-1)!} \left(\frac{K}{a-1} \right)^{n-1} \int_0^x (e^{(a-1)x} - 1)^{n-1} \exp \left[-ax + \frac{K}{a-1} (1 - e^{(a-1)x}) \right] dx. \quad (40)$$

Similarly, for termination only by combination, the corresponding molecular size distribution functions are simplified as well:

$$N_n^* = \frac{I_0}{(n-1)!} \left[\frac{K}{b-1} (e^{(b-1)x} - 1) \right]^{n-1} \exp \left[-bx + \frac{K}{b-1} (1 - e^{(b-1)x}) \right]. \quad (41)$$

$$N_n' = \frac{bI_0}{2(n-2)!} \left(\frac{2K}{b-1} \right)^{n-2} \int_0^x [e^{(b-1)x} - 1]^{n-2} \exp \left[-bx + \frac{2K}{b-1} (1 - e^{(b-1)x}) \right] dx. \quad (42)$$

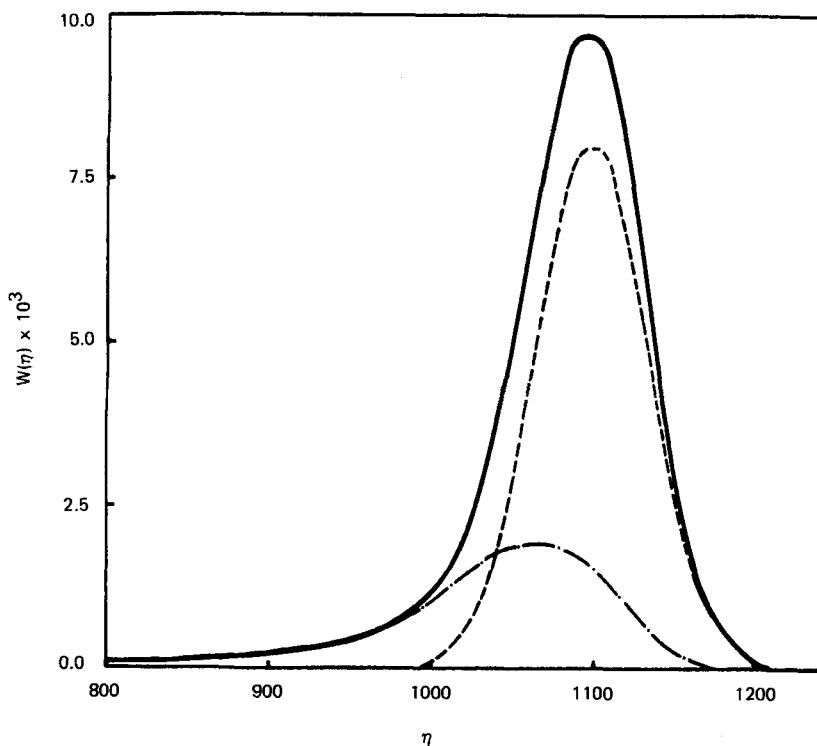


FIG. 1. Curves of the differential molecular weight distribution. $k_p = 10 \text{ L}/(\text{mol}\cdot\text{s})$; $k_{td} = 1 \text{ L}/(\text{mol}\cdot\text{s})$; $I_0 = 10^{-3} \text{ mol/L}$; $M_0 = 1 \text{ mol/L}$; $t = 650 \text{ s}$; (---) growing polymer; (-·-) terminated polymer; (—) total polymers.

Apparently, Eqs. (39) and (41) are almost identical with Eq. (15), which means that the molecular size distribution of a growing polymer is independent of the type of termination. Figures 1 and 2 are the curves of the differential molecular weight distribution of the polymer formed in polymerization with termination by disproportionation. From the distribution functions given above, other parameters can be obtained. The results are listed in Table 1. When the rate constants of termination are different, the relation between the polydispersity and the polymerization time are as shown in Figs. 3 and 4.

TABLE 1. The Molecular Parameters for Polymerization with Termination by Disproportionation or Combination

Parameters	Disproportionation	Combination
$\sum_{n=1}^{\infty} N_n$	I_0	$\frac{I_0}{2} (1 + e^{-bx})$
$\sum_{n=1}^{\infty} n N_n$	$I_0 [1 + K(1 - e^{-x})]$	$I_0 [1 + K(1 - e^{-x})]$
$\sum_{n=1}^{\infty} n^2 N_n$	$I_0 \left\{ 1 + K \left(3 - \frac{2K}{a-1} \right) (1 - e^{-x}) + \frac{2K^2}{(a-1)(a-2)} (e^{(a-2)x} - 1) \right\}$	$I_0 \left\{ 2 + 5K - \frac{4K^2}{b-2} + \frac{K}{b-1} \left[3 - 5b + \frac{3K(2b-1)}{b-1} \right] e^{-x} - \left(1 - \frac{K^2}{b-1} \right) e^{-bx} + \left(\frac{3b-2}{b-2} \right) \left(\frac{K}{b-1} \right)^2 e^{(b-2)x} \right\}$
\bar{P}_n	$1 + K(1 - e^{-x})$	$\frac{2 [1 + K(1 - e^{-x})]}{1 + e^{-bx}}$
\bar{P}_w	$\frac{1 + K \left(3 - \frac{2K}{a-1} \right) (1 - e^{-x}) + \frac{2K^2}{(a-1)(a-2)} (e^{(a-2)x} - 1)}{1 + K(1 - e^{-x})}$	$\left\{ 2 + 5K - \frac{4K^2}{b-2} + \frac{K}{b-1} \left[3 - 5b + \frac{3K(2b-1)}{b-1} \right] e^{-x} - \left(1 - \frac{K^2}{b-1} \right) e^{-bx} + \left(\frac{3b-2}{b-2} \right) \left(\frac{K}{b-1} \right)^2 e^{(b-2)x} \right\} / [1 + K(1 - e^{-x})]$
$\frac{\bar{P}_w}{\bar{P}_n}$	$\frac{1 + K \left(3 - \frac{2K}{a-1} \right) (1 - e^{-x}) + \frac{2K^2}{(a-1)(a-2)} (e^{(a-2)x} - 1)}{[1 + K(1 - e^{-x})]^2}$	$(1 + e^{-bx}) \left\{ 2 + 5K - \frac{4K^2}{b-2} + \frac{K}{b-1} \left[3 - 5b + \frac{3K(2b-1)}{b-1} \right] e^{-x} - \left(1 - \frac{K^2}{b-1} \right) e^{-bx} + \left(\frac{3b-2}{b-2} \right) \left(\frac{K}{b-1} \right)^2 e^{(b-2)x} \right\} / \left\{ 2 [1 + K(1 - e^{-x})]^2 \right\}$

$\bar{P}_r(\max)$	M_0/I_0	$2M_0/I_0$
$\bar{P}_w(\max)$ ($a, b < z$)	$\frac{(a-2)(1+3K) - 2K^2}{(a-2)(1+K)}$	$\frac{(b-2)(2+5K) - 4K^2}{(b-2)(1+K)}$
$\lim_{z \rightarrow \infty} \frac{\bar{P}_w}{\bar{P}_r}$ ($a, b < z$)	$\frac{(a-2)(1+3K) - 2K^2}{(a-2)(1+K)^2}$	$\frac{(b-2)(2+5K) - 4K^2}{(b-2)(1+K)^2}$
f_n^*	e^{-ax}	$1 - th\left(\frac{b}{2}x\right)$
f_n'	$1 - e^{-ax}$	$th\left(\frac{b}{2}x\right)$
f_w^*	$\frac{(a-1) + K(e^{(a-1)x} - 1)}{(a-1)[1+K(1-e^{-x})]} e^{ax}$	$\frac{(b-1) + K(e^{(b-1)x} - 1)}{(b-1)[1+K(1-e^{-x})]} e^{bx}$
f_w'	$\frac{aK(1-e^{-x}) + (a-1-K)(1-e^{-ax})}{(a-1)[1+K(1-e^{-x})]}$	$\frac{bK(1-e^{-x}) + (b-1-K)(1-e^{-bx})}{(b-1)[1+K(1-e^{-x})]}$
x	$\frac{1}{a} \ln(1+I_0 k e^{at})$ or $\ln \frac{1-\alpha}{1-y}$	$\frac{1}{b} \ln(1+I_0 k e^{bt})$ or $\ln \frac{1-\alpha}{1-y}$

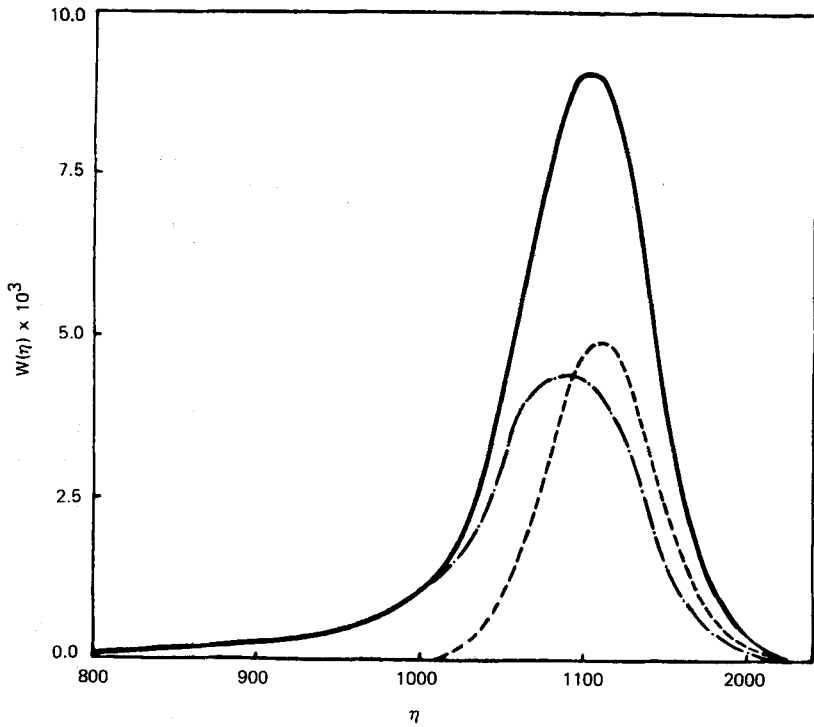


FIG. 2. Curves of the differential molecular weight distribution. $t = 1700$ s; the other values and symbols are identical with those in Fig. 1.

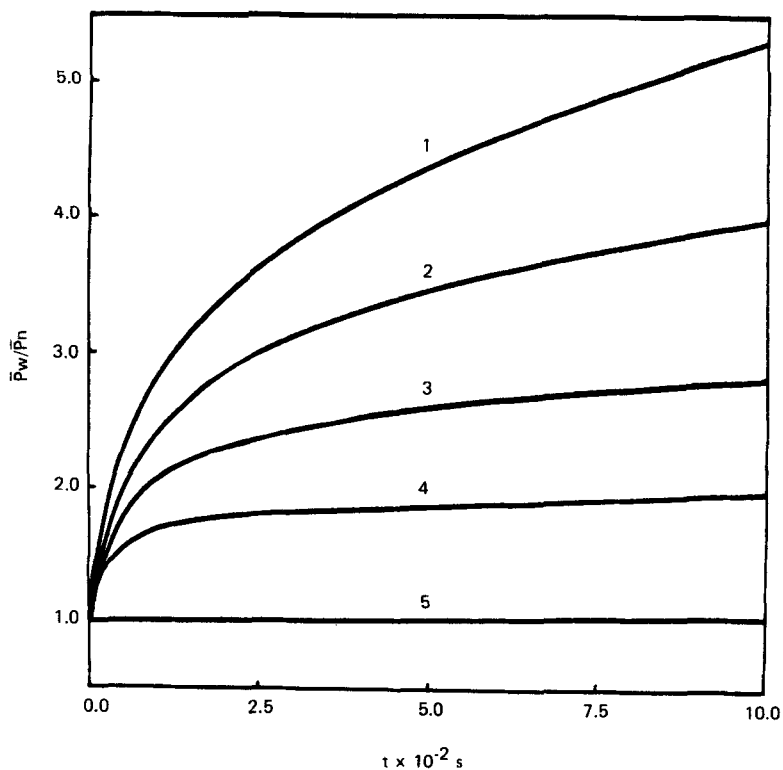


FIG. 3. \bar{P}_w/\bar{P}_n vs t for termination by disproportionation. $k_p = 10^3$ L/(mol·s); $I_0 = 10^{-3}$ mol/L; $M_0 = 1$ mol/L; (1) $a = 2.5$; (2) $a = 2$; (3) $a = 1.5$; (4) $a = 1$; (5) $a = 0.1$.

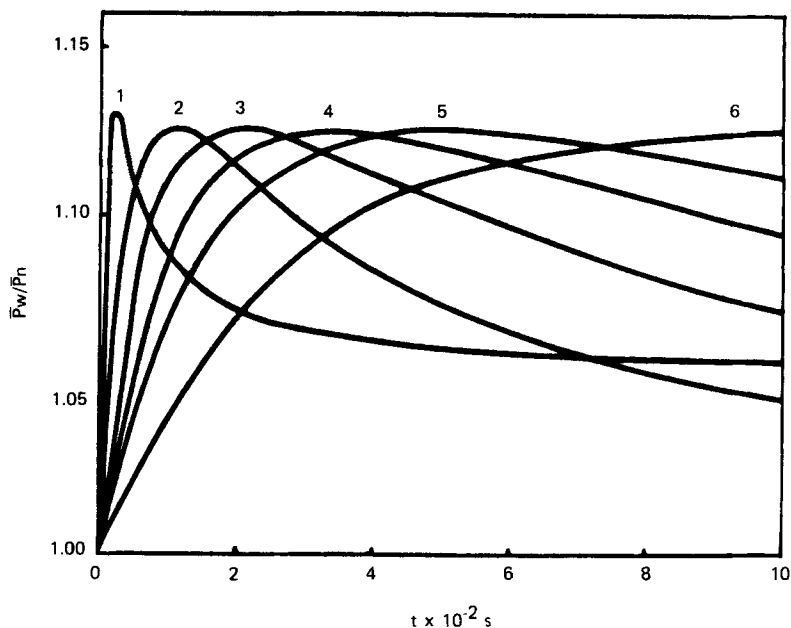


FIG. 4. \bar{P}_w/\bar{P}_n vs t for termination by combination. $k_p = 10^3$ L/(mol·s); $I_0 = 10^{-3}$ mol/L; $M_0 = 1$ mol/L; (1) $b = 0.1$; (2) $b = 0.01$; (3) $b = 0.005$; (4) $b = 0.003$; (5) $b = 0.002$; (6) $b = 0.001$.

5. THE CASE OF $(a + b) = 1$

Most of the formulas given above cannot be used for the case of $(a + b) = 1$, because $(a + b) = 1$ represents a singular point. According to L'Hospital's rule, we obtain

$$\lim_{(a+b) \rightarrow 1} \frac{e^{(a+b-1)x} - 1}{a+b-1} = x. \quad (43)$$

Then, Eqs. (15) and (16) simplify to:

$$N_n^* = \frac{L}{(n-1)!} (Kx)^{n-1} e^{-(1+K)x}, \quad (44)$$

$$N_n' = \frac{aI_0 K^{n-1}}{(1+K)^n} \Gamma_{(1+K)x}^{(n)} + \frac{bI_0 (2K)^{n-2}}{2(1+2K)^{n-1}} \Gamma_{(1+2K)x}^{(n-1)}, \quad (45)$$

where

$$\Gamma_{(1+K)x}(n) = \frac{1}{(n-1)!} \int_0^x [(1+K)x]^{n-1} e^{-(1+K)x} d[(1+K)x],$$

$$\Gamma_{(1+2K)x}(n-1) = \frac{1}{(n-2)!} \int_0^x [(1+2K)x]^{n-2} e^{-(1+2K)x} d[(1+2K)x]$$

are the incomplete gamma functions. If the gamma functions are expanded into the corresponding series, Eq. (45) becomes

$$N'_n = \frac{a I_0 K^{n-1} e^{-(1+K)x}}{(1+K)^n} \sum_{i=n}^{\infty} \frac{[(1+K)x]^i}{i!} + \frac{b I_0 (2K)^{n-2} e^{-(1+2K)x}}{2(1+2K)^{n-1}} \sum_{i=n-1}^{\infty} \frac{[(1+2K)x]^i}{i!} \quad (46)$$

In the limit of infinity, the expression for N'_n becomes

$$\lim_{x \rightarrow \infty} N'_n = \frac{a I_0 K^{n-1}}{(1+K)^n} + \frac{b I_0 (2K)^{n-2}}{2(1+2K)^{n-1}} \quad (47)$$

Equation (47) is the molecular size distribution function for $t \rightarrow \infty$ and $(a + b) = 1$. For the polymerization with disproportionation ($a = 1, b = 0$) or combination ($a = 0, b = 1$), the molecular size distribution functions of the growing chains are identical with Eq. (44). N'_n for termination by disproportionation is

$$N'_n = \frac{I_0 K^{n-1}}{(1+K)^n} \Gamma_{(1+K)x}(n) \quad (48)$$

Similarly, N'_n for termination by combination is

$$N'_n = \frac{I_0 (2K)^{n-2}}{2(1+2K)^{n-1}} \Gamma_{(1+2K)x}(n-1) \quad (49)$$

From the molecular size distribution on function, we can get other molecular parameters, which are listed in Table 2. Figures 5-7 indicate the differential molecular weight distribution for three cases treated above: $a = 1, b = 0$; $a = 0.5, b = 0.5$; and $a = 0, b = 1$.

TABLE 2. The Molecular Parameters for Several Special Cases

Parameters	$a+b=1$; $a, b \neq 0$	$a=1$; $b=0$	$a=0$; $b=1$
$\sum_{n=1}^{\infty} N_n$	$\frac{I_0}{2} [1+a+(1-a)e^{-x}]$	I_0	$\frac{I_0}{2} (1+e^{-x})$
$\sum_{n=1}^{\infty} nN_n$	$I_0 [1+K(1-e^{-x})]$	$I_0 [1+K(1-e^{-x})]$	$I_0 [1+K(1-e^{-x})]$
$\sum_{n=1}^{\infty} n^2 N_n$	$I_0 \{ [b+K+2K(1+b)(1+K)](1-e^{-x}) - 2K(b+K+bK)xe^{-x} - bK^2e^{-2x} \}$	$I_0 [1+3K(1-e^{-x}) + 2K^2(1-e^{-x} - xe^{-x})]$	$I_0 [1+(1+5K+4K^2)(1-e^{-x}) - 2K(1+2K)xe^{-x} - (Kx)^2e^{-2x}]$
\overline{P}_n	$\frac{2[1+K(1-e^{-x})]}{1+a+(1-a)e^{-x}}$	$1+K(1-e^{-x})$	$\frac{2[1+K(1-e^{-x})]}{1+e^{-x}}$
\overline{P}_w	$\frac{\{1+[b+K+2K(1+b)(1+K)](1-e^{-x}) - bK^2e^{-2x} - 2K(b+K+bK)xe^{-x}\}}{[1+K(1-e^{-x})]}$	$\frac{1+3K(1-e^{-x}) + 2K^2(1-e^{-x} - xe^{-x})}{1+K(1-e^{-x})}$	$\frac{1+(1+5K+4K^2)(1-e^{-x}) + 2K(1+2K)xe^{-x} - (Kx)^2e^{-2x}}{1+K(1-e^{-x})}$
$\frac{\overline{P}_w}{\overline{P}_n}$	$\frac{\{1+a+(1-a)e^{-x}\} \{1+[b+K+2K(1+b)(1+K)](1-e^{-x}) - 2K(b+K+bK)xe^{-x} - bK^2e^{-2x}\}}{\{2[1+K(1-e^{-x})]\}}$	$\frac{1+3K(1-e^{-x}) + 2K^2(1-e^{-x} - xe^{-x})}{[1+K(1-e^{-x})]^2}$	$\frac{(1+e^{-x}) \{1+(1+5K+4K^2)(1-e^{-x}) - (Kx)^2e^{-2x} + 2K(1+2K)xe^{-x}\}}{\{2[1+K(1-e^{-x})]^2\}}$

$\bar{P}_n(\max)$	$\frac{2}{1+a} \cdot \frac{M_0}{I_0}$	$\frac{M_0}{I_0}$	$\frac{2M_0}{I_0}$
$\bar{P}_w(\max)$	$\frac{1+b+K+2K(1+b)(1+K)}{1+K}$	$\frac{2M_0 - I_0}{I_0}$	$\frac{1+(1+K)(1+4K)}{1+K}$
$\lim_{x \rightarrow \infty} \frac{\bar{P}_w}{\bar{P}_n}$	$\frac{(1+a)[1+b+K+2K(1+b)(1+K)]}{2(1+K)^2}$	$\frac{2M_0 - I_0}{M_0}$	$\frac{1+(1+K)(1+4K)}{2(1+K)^2}$
f_n^*	$\frac{2e^{-x}}{1+a+(1-a)e^{-x}}$	e^{-x}	$1 - th\left(\frac{x}{2}\right)$
f_n'	$\frac{(1+a)(1-e^{-x})}{1+a+(1-a)e^{-x}}$	$1 - e^{-x}$	$th\left(\frac{x}{2}\right)$
f_w^*	$\frac{(1+K(x))e^{-x}}{1+K(1-e^{-x})}$	$\frac{(1+K(x))e^{-x}}{1+K(1-e^{-x})}$	$\frac{(1+K(x))e^{-x}}{1+K(1-e^{-x})}$
f_w'	$\frac{1+K - [1+K(1+x)]e^{-x}}{1+K(1-e^{-x})}$	$\frac{1+K - [1+K(1+x)]e^{-x}}{1+K(1-e^{-x})}$	$\frac{1+K - [1+K(1+x)]e^{-x}}{1+K(1-e^{-x})}$

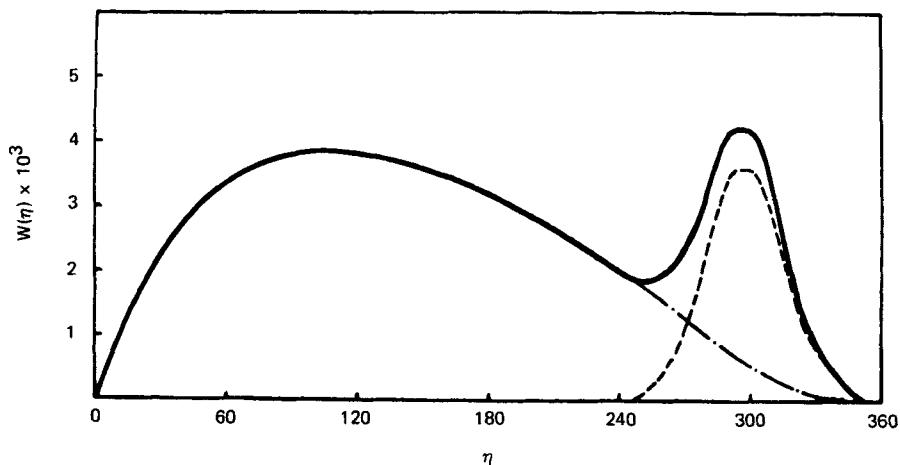


FIG. 5. Curves of the differential molecular weight distribution. $k_p = k_{td} = 10 \text{ L}/(\text{mol}\cdot\text{s})$; $k_{tc} = 0$; $I_0 = 10^{-2} \text{ mol/L}$; $M_0 = 1 \text{ mol/L}$; $t = 190 \text{ s}$; the plotting symbols used for the curves are identical with those in Fig. 1.

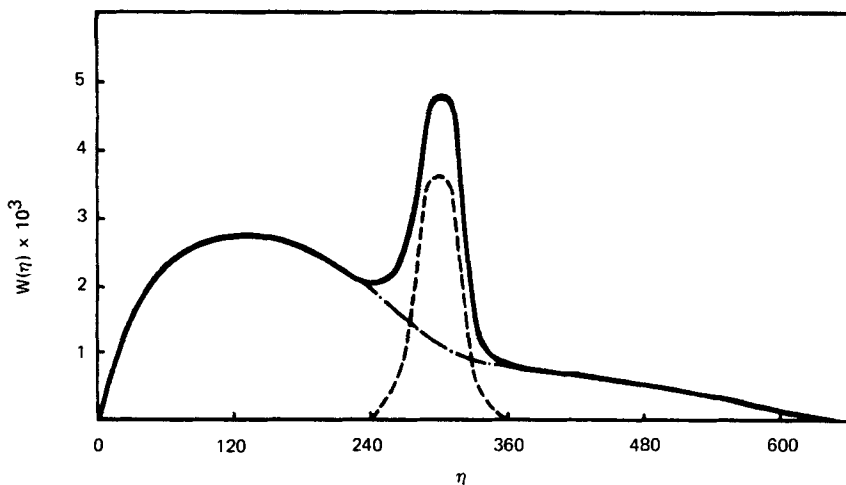


FIG. 6. Curves of the differential molecular weight distribution. $k_{tc} = k_{td} = 5 \text{ L}/(\text{mol}\cdot\text{s})$; the other values and symbols are identical with those in Fig. 5.

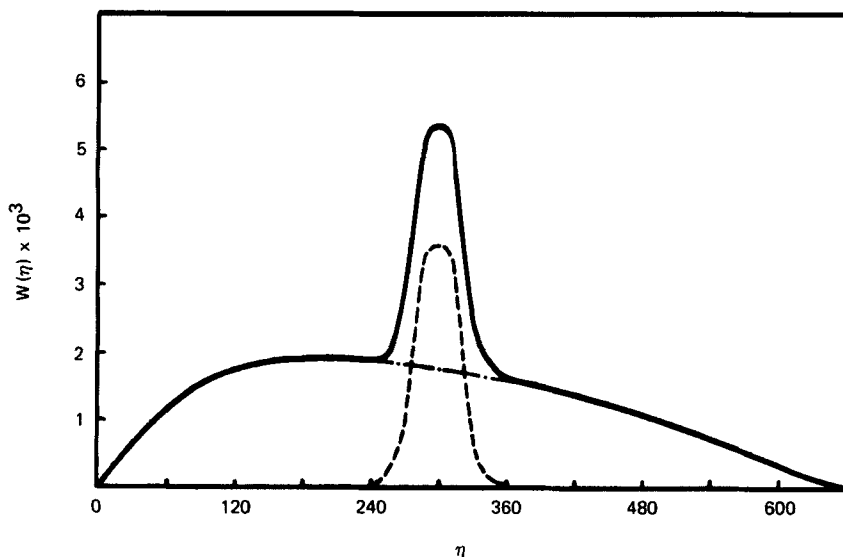


FIG. 7. Curves of the differential molecular weight distribution. $k_{td} = 0$; $k_{tc} = 1 \text{ L}/(\text{mol}\cdot\text{s})$; the other values and symbols are identical with those in Fig. 5.

There is another singular point at $(a + b) = 2$ for the second-order statistical moments, the weight-average degree of polymerization, and the polydispersity. In analogy to the case of $(a + b) = 1$, these molecular parameters can be derived from the corresponding formulas by taking the limit $(a + b) \rightarrow 2$, and the results are given in Table 3.

In summary, the nonsteady-state kinetics of free-radical polymerization is a complicated and difficult problem, and no satisfactory results have been obtained up to now. The polymerization scheme adopted in this paper, though simple, is meaningful to understand the influence of termination by disproportionation and combination on the molecular size distribution and other molecular parameters. The study on the influence of both monomer transfer and termination by disproportionation and combination on the molecular size distribution of polymer will soon be reported in the next part of this series. The nonsteady-state kinetic theory of free-radical polymerization will be published elsewhere.

TABLE 3. Several Molecular Parameters for $a + b = 2$

Type	Parameters	Expressions
$a+b=2$ $a, b \neq 0$	$\sum_{n=1}^{\infty} n^2 N_n$	$L_0 \left\{ 1 + K[3-2K+2b(1-K)](1-e^{-x}) + (2+b)K^2x + \frac{b}{2}(1-K)^2(1-e^{-2x}) \right\}$
	$\overline{P_w}$	$\frac{1 + K[3-2K+2b(1-K)](1-e^{-x}) + (2+b)K^2x + b(1-K)^2(1-e^{-2x})/2}{1 + K(1-e^{-x})}$
	$\frac{\overline{P_w}}{\overline{P_n}}$	$\frac{1 + K[3-2K+2b(1-K)](1-e^{-x}) + (2+b)K^2x + b(1-K)^2(1-e^{-2x})/2}{[1 + K(1-e^{-x})]^2}$
$a=2$ $b=0$	$\sum_{n=1}^{\infty} n^2 N_n$	$L_0 [1 + K(3-2K)(1-e^{-x}) + 2K^2x]$
	$\overline{P_w}$	$\frac{1 + K(3-2K)(1-e^{-x}) + 2K^2x}{1 + K(1-e^{-x})}$
	$\frac{\overline{P_w}}{\overline{P_n}}$	$\frac{1 + K(3-2K)(1-e^{-x}) + 2K^2x}{[1 + K(1-e^{-x})]^2}$
$a=0$ $b=2$	$\sum_{n=1}^{\infty} n^2 N_n$	$L_0 [1 + K(7-6K)(1-e^{-x}) + 4K^2x + (1-K)^2(1-e^{-2x})]$
	$\overline{P_w}$	$\frac{1 + K(7-6K)(1-e^{-x}) + 4K^2x + (1-K)^2(1-e^{-2x})}{1 + K(1-e^{-x})}$
	$\frac{\overline{P_w}}{\overline{P_n}}$	$\frac{1 + K(7-6K)(1-e^{-x}) + 4K^2x + (1-K)^2(1-e^{-2x})}{[1 + K(1-e^{-x})]^2}$

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