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Influence of Termination and Transfer on Molecular Weight Distribution of Polymers. III. Spontaneous Termination

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ABSTRACT

This article deals with the kinetics of ionic polymerization with instantaneous initiation and spontaneous termination. The set of kinetic differential equations was solved rigorously by means of nonsteady-state analysis. Even though the expressions of the molecular size distribution function and other molecular parameters include an exponential integral function, all the molecular parameters can easily be computed numerically. Thus, this work is significant for controlling and regulating the relevant polymerizations.

It has been reported [1-3] that spontaneous termination has an important effect on the molecular size distribution and other molecular parameters of the polymer formed in numerous cationic polymerizations. Because of the mathematical difficulty, the theoretical aspect of the problem has not been studied comprehensively. Fortunately, the kinetic treatment can be performed exactly by means of the variable transformation technique given in the first part of this series [4].

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1. MOLECULAR SIZE DISTRIBUTION

For a lot of cationic polymerization systems, initiation is very fast and can be assumed to be instantaneous. According to the mechanism proposed by Kennedy [2], the reaction scheme is

$$I + M \xrightarrow{\text{fast}} N_1^*$$

$$N_n^* + M \xrightarrow{k_p} N_{n+1}^* \quad , \; n=1,\ 2,\ \ldots$$

$$N_n^* \xrightarrow{k_t} N_n' \quad , \; n=1,\ 2,\ \ldots$$

where M, N_n*, and N_n' denote, respectively, the residue concentrations of the monomer, the active n-mer, and inactive n-mer; I is the concentration of the initiator; and k_p and k_t represent the rate constants for propagation and spontaneous termination, respectively.

The set of kinetic differential equations appropriate to the reaction scheme listed is

$$dN_1^*/dt = -(k_p M + k_t)\, N_1^* \tag{1}$$

$$dN_n^*/dt = k_p M N_{n-1}^* - (k_p M + k_t) N_n^* \quad , \; n \geq 2 \tag{2}$$

$$dN_n'/dt = k_t N_n^* \quad , \; n \geq 1 \tag{3}$$

$$d\sum_n N_n^*/dt = -k_t \sum_n N_n^* \tag{4}$$

$$dM/dt = -k_p M \sum_n N_n^* \tag{5}$$

The initial conditions of these differential equations are

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

where I_0 and M_0 are the respective concentrations of initiator and monomer at the start of polymerization.

The concentration of deactivated polymer, x, is given by

$$x = k_t \int_0^t \sum_n N_n^*\, dt \tag{6}$$

or

$$\frac{dx}{dt} = k_t \sum N_n^* \tag{7}$$

With $k_p/k_t = a$, Eqs. (4) and (5) can be transformed into the following forms:

$$\frac{d \sum_n N_n^*}{dx} = -1 \tag{8}$$

$$\frac{dM}{dx} = -aM \tag{9}$$

Solving Eqs. (8) and (9), we obtain

$$\sum_n N_n^* = I_0 - x \tag{10}$$

$$M = (M_0 - I_0) e^{-ax} \tag{11}$$

By the aid of Eqs. (7), (10), and (11), the set of differential equations (1)-(3) is transformed into a linear set with variable coefficients,

$$\frac{dN_1^*}{dx} = -[a(M_0 - I_0)\, e^{-ax} + 1] \frac{N_1^*}{I_0 - x} \tag{12}$$

$$\frac{dN_n^*}{dx} = \frac{a(M_0 - I_0) e^{-ax}}{I_0 - x} N_{n-1}^* - \frac{a(M_0 - I_0) e^{-ax} + 1}{I_0 - x} N_n^*, \quad n \geqslant 2 \tag{13}$$

$$\frac{dN_n'}{dx} = \frac{N_n^*}{I_0 - x} \quad , \quad n \geqslant 1 \tag{14}$$

The corresponding initial conditions become

$$N_1^* \Big|_{x=0} = I_0 \; ; \quad N_{n\geqslant 2}^* \Big|_{x=0} = N_n' \Big|_{x=0} = 0$$

From Eqs. (12)-(14) we can easily obtain the molecular size distribution functions of active and inactive chains:

$$N_n^* = \frac{I_0 - x}{(n-1)!} \left\{ A\left[Ei(aI_0) - Ei(aI_0 - ax)\right] \right\}^{n-1} \exp\left\{ -A\left[Ei(aI_0) - Ei(aI_0 - ax)\right] \right\} \tag{15}$$

$$N_n' = \frac{A^{n-1}}{(n-1)!}\int_0^x \left[Ei(aI_0) - Ei(aI_0 - ax)\right]^{n-1} \exp\left\{-A\left[Ei(aI_0) - Ei(aI_0 - ax)\right]\right\} dx \tag{16}$$

where

$$A = a(M_0 - I_0)\, e^{-aI_0},$$

Ei(x) is the exponential integral function [5] and is defined as

$$Ei(x) = \int \frac{e^x}{x}\, dx$$

or

$$Ei(x) = -\lim_{\varepsilon \to +0}\left[\int_{-x}^{-\varepsilon} \frac{e^{-t}}{t}\, dt + \int_{\varepsilon}^{\infty} \frac{e^{-t}}{t}\, dt\right], \quad (x > 0)$$

The molecular size distribution function for the total polymers is

$$N_n = N_n^* + N_n' \tag{17}$$

Although Eqs. (16) and (17) include the exponential integral function and the definite integration, the curves of molecular size distribution of the active chain, inactive chain, and total polymer can be calculated numerically.

2. DETERMINATION OF THE VARIABLE x

All of the formulas given above are functions of x. In order to estimate the values of x from polymerization conditions, y is defined as the monomer conversion, namely,

$$y = (M_0 - M)/M_0$$

From Eq. (11), we have

$$x = \frac{1}{a}\ln\frac{M_0 - I_0}{M_0(1 - y)} \tag{18}$$

Combining Eq. (7) with Eq. (10) yields

$$x = I_0(1 - e^{-k_t t}) \tag{19}$$

From Eqs. (18) and (19), the relation between y and t is obtained:

$$y = 1 - \frac{M_0 - I_0}{M_0} \exp\left\{-aI_0(1 - e^{-k_t t})\right\} \tag{20}$$

As t→∞, the limit of monomer conversion is

$$y(\infty) = 1 - \frac{M_0 - I_0}{I_0} e^{-aI_0} \tag{21}$$

Figure 1 shows that when a is less than 3 000 L/mol, the limit of monomer conversion cannot approach 100%. This conclusion is reasonable because all of the living chains have lost activity before the monomer is exhausted.

3. AVERAGE DEGREE OF POLYMERIZATION AND OTHER MOLECULAR PARAMETERS

The statistical moments of relevant polymers can be derived from differential Eqs. (12)-(14) or molecular size distribution functions (15) and (16). We obtain the same result from both methods:

$$\sum_n nN_n^* = (I_0 - x)\left\{A\left[Ei(aI_0) - Ei(aI_0 - ax)\right] + 1\right\} \tag{22}$$

$$\sum_n n^2 N_n^* = (I_0 - x)\left\{A\left[Ei(aI_0) - Ei(aI_0 - ax)\right] + \left[A\,Ei(aI_0) - A\,Ei(aI_0 - ax) + 1\right]^2\right\} \tag{23}$$

The zeroth-order statistical moment of living chains is given by Eq. (10), and the moments of deactivated chains are given by

$$\sum_n N_n' = x \tag{24}$$

$$\sum_n nN_n' = \frac{A}{a}(1 - e^{-ax})e^{aI_0} - \left\{A\left[Ei(aI_0) - Ei(aI_0 - ax)\right] + 1\right\}(I_0 - x) + I_0 \tag{25}$$

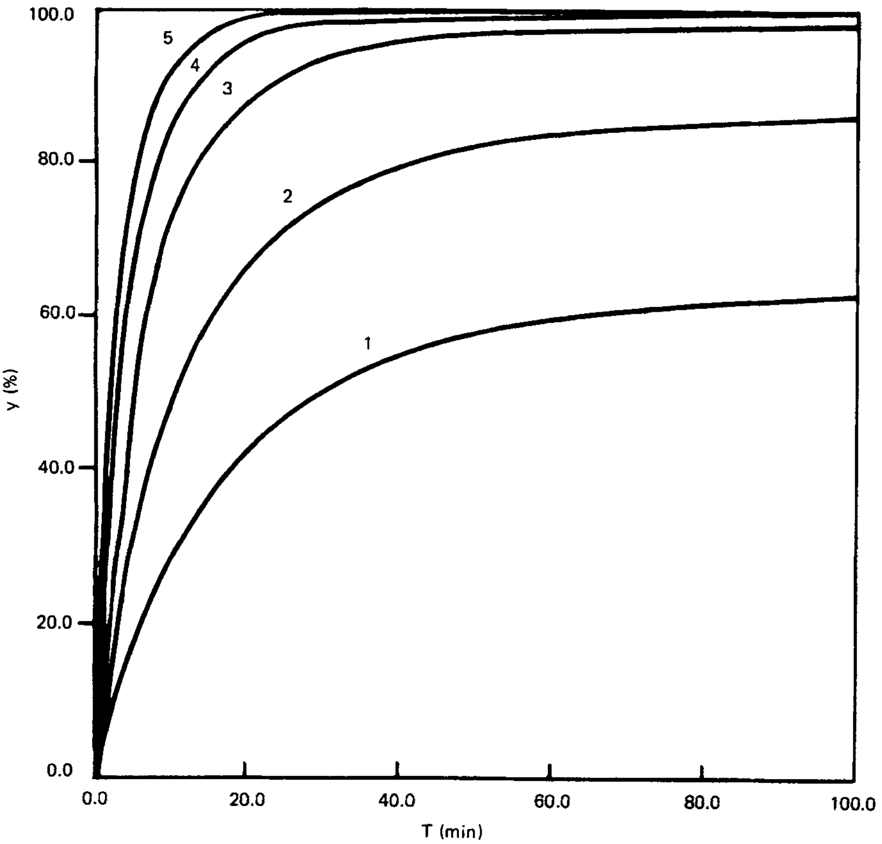

FIG. 1. Monomer conversion vs polymerization time, $k_t = 0.04$ min^{-1}, $I_0 = 2 \times 10^{-3}$ mol/L, $M_0 = 1$ mol/L. 1: a = 500 L/mol. 2: a = 1 000 L/mol. 3: a = 2 000 L/mol. 4: a = 3 000 L/mol. 5: a = 5 000 L/mol.

$$\sum_n n^2 N_n' = I_0 + 3(M_0 - I_0)(1 - e^{-ax}) - (I_0 - x)\{A[Ei(aI_0) - Ei(aI_0 - ax)] + [A\,Ei(aI_0) - A\,Ei(aI_0 - ax) + 1]^2\} + \frac{2A^2}{a}\{Ei(2aI_0) - Ei(2aI_0 - 2ax) - e^{a(I_0 - x)}[Ei(aI_0) - Ei(aI_0 - ax)]\} \tag{26}$$

Thus, the statistical moments of the total polymer are

$$\sum_n N_n = I_0 \tag{27}$$

$$\sum_n nN_n = I_0 + (M_0 - I_0)(1 - e^{-ax}) \tag{28}$$

$$\sum_n n^2 N_n = I_0 + 3(M_0 - I_0)(1 - e^{-ax}) + \frac{2A^2}{a}\{Ei(2aI_0) - Ei(2aI_0 - 2ax) - e^{a(I_0 - x)}[Ei(aI_0) - Ei(aI_0 - ax)]\} \tag{29}$$

The number- and weight-average degrees of polymerization for the total polymer are obtained, respectively, from Eqs. (27)-(29):

$$\overline{P}_n = 1 + \frac{M_0 - I_0}{I_0}(1 - e^{-ax}) \tag{30}$$

$$\overline{P}_w = \{I_0 + 3(M_0 - I_0)(1 - e^{-ax}) + \frac{2A^2}{a}[Ei(2aI_0) - Ei(2aI_0 - 2ax) - e^{a(I_0 - x)}(Ei(aI_0) - Ei(aI_0 - ax))]\} / \{I_0 + (M_0 - I_0)(1 - e^{-ax})\} \tag{31}$$

It is easy to obtain the polydispersity. Figure 2 shows the relation between the polydispersity and the polymerization time for several values of a. It is seen that the polydispersity increases with decreasing a. Figure 3 shows a plot of $\overline{P}_w/\overline{P}_n$ vs t for various values of k_t at a = 1 000 L/mol.

The mole fractions of the active and inactive polymers in the polymerization system are

$$f_n^* = \sum_n N_n^* \Big/ \sum_n N_n = 1 - \frac{x}{I_0} \tag{32}$$

$$f_n' = 1 - f_n^* = \frac{x}{I_0} \tag{33}$$

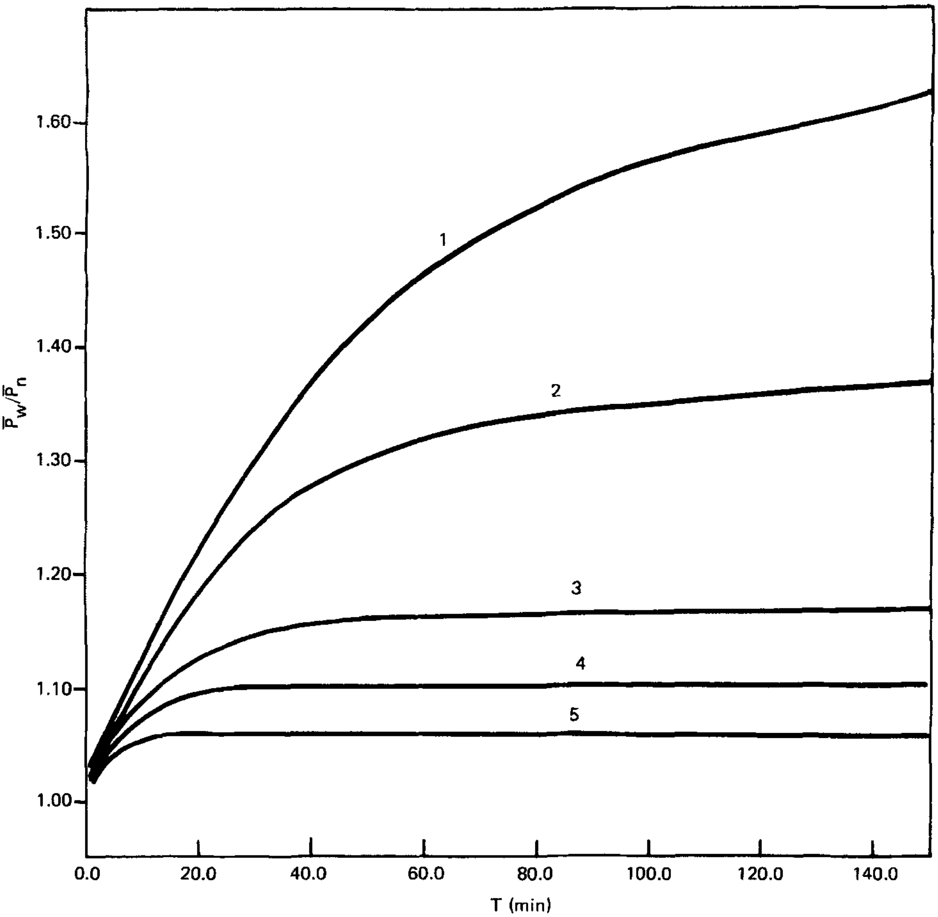

FIG. 2. $\overline{P}_w/\overline{P}_n$ vs t for various values of a. Other conditions as in Fig. 4.

Similarly, the weight fractions of the active and inactive polymers are obtained from Eqs. (22), (25), and (28):

$$f_w^* = (I_0 - x)\left\{A\left[Ei(aI_0) - Ei(aI_0 - ax)\right] + 1\right\} \Big/ \left\{I_0 + (M_0 - I_0)(1 - e^{-ax})\right\} \tag{34}$$

$$f_w' = 1 - f_w^* \tag{35}$$

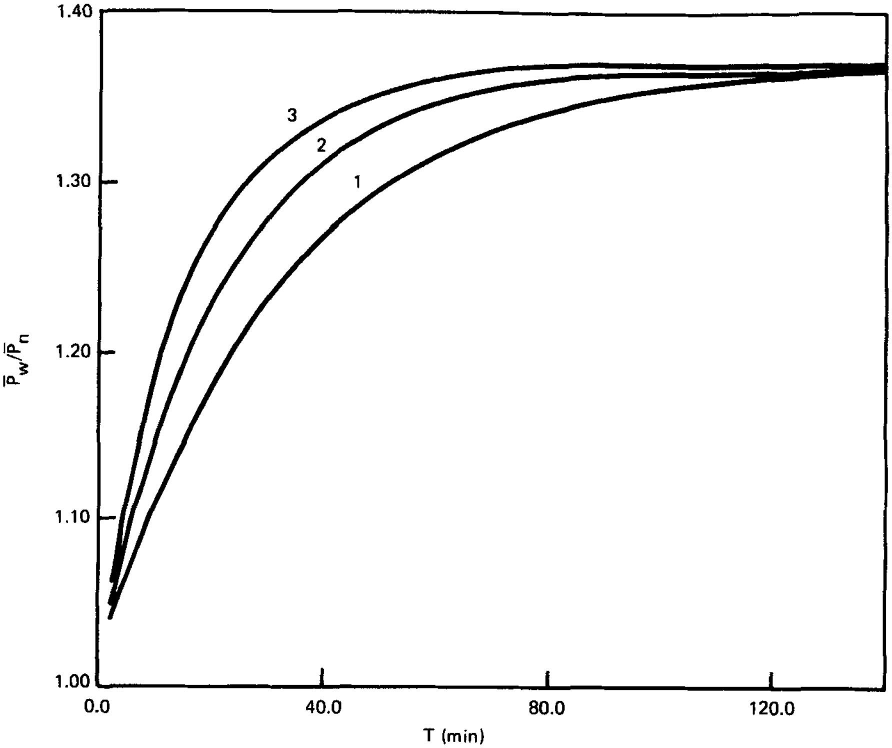

FIG. 3. $\overline{P}_w/\overline{P}_n$ vs t for the various values of k_t. a = 1 000 L/mol, $I_0 = 2 \times 10^{-3}$ mol/L, $M_0 = 1$ mol/L. 1: $k_t = 0.04$ min^{-1}. 2: $k_t = 0.06$ min^{-1}. 3: $k_t = 0.08$ min^{-1}.

Up to now all molecular parameters have been derived theoretically. In the next section we study the relationship between molecular size distribution and reaction conditions.

4. EFFECT OF REACTION CONDITIONS ON MOLECULAR SIZE DISTRIBUTION

According to Eqs. (15)-(18) and (28), we can calculate the curves of the variation of molecular size distributions with monomer conversion. It is shown in Fig. 4 that the distributions of the active polymer are quite narrow, but those of the inactive polymer are very broad. The higher the monomer conversion, the broader the distribution of the inactive polymer. Finally, if the polymerization time is long

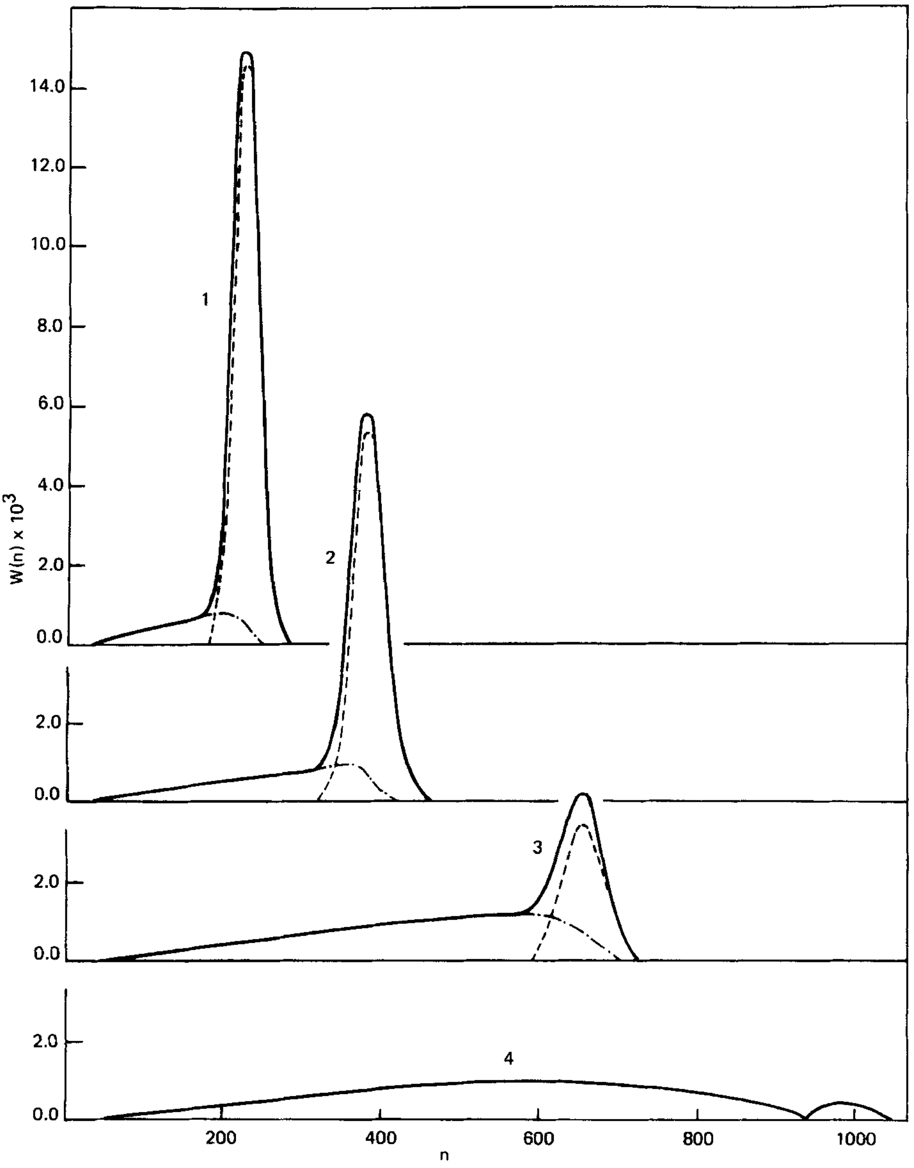

FIG. 4. Plot of molecular size distribution for various values of y. a = 1 000 L/mol, k_t = min^{-1}, $I_0 = 2 \times 10^{-3}$ mol/L, M_0 = 1 mol/L.

1: y = 40%. 2: y = 60%. 3: y = 80%. 4: Y (t = ∞) = 86.49%. (- -) Active polymer, (— ·) inactive polymer, (—) total polymers.

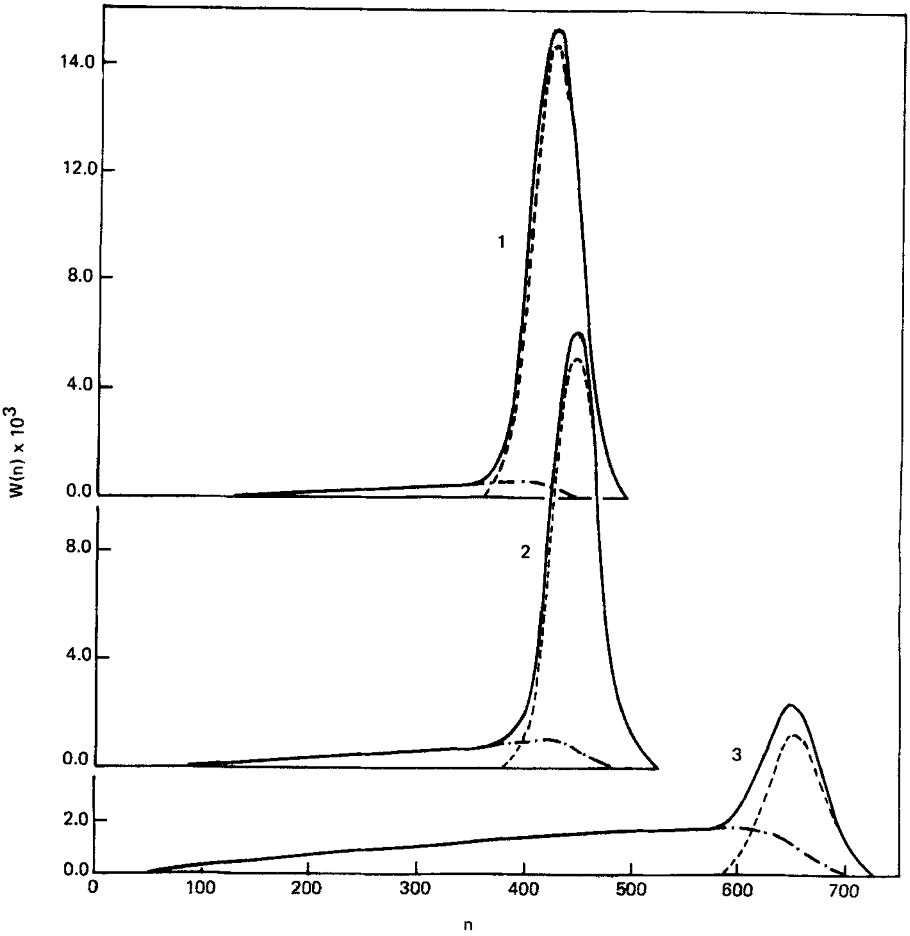

FIG. 5. Plot of the molecular size distribution for various values of a. $k_t = 0.04\ \text{min}^{-1}$, $y = 80\%$, $I_0 = 2 \times 10^{-3}$ mol/L, $M_0 = 1$ mol/L. 1: a = 5 000 L/mol. 2: a = 3 000 L/mol. 3: a = 1 000 L/mol. Other conditions as in Fig. 4.

enough, all of the active polymers become dead ones (see Curve 4). Figure 5 shows the effect of ratio a on the molecular size distribution at $y = 80\%$, $k_t = 0.04\ \text{min}^{-1}$, $I_0 = 2 \times 10^{-3}$ mol/L, and $M_0 = 1$ mol/L. It is evident that the distribution broadens with decreasing a. In a similar way, the influence of other reaction conditions on molecular size distribution can also be given.

During the derivations, this paper has not introduced any approximations. All of the formulas given above are reliable. Some of them, as mentioned above, contain special functions, but they can be calculated without any difficulty by microcomputer. Therefore, the kinetics of ionic polymerization with spontaneous termination and instantaneous initiation has been solved satisfactorily.

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