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De-Yue Yan^a; Cui-Ming Yuan^a

^a Department of Applied Chemistry, Shanghai Jiao Tong University, Shanghai, People's Republic of China

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Influence of Termination and Transfer on Molecular Weight Distribution of Polymers. IV. Impurity Termination

DE-YUE YAN and CUI-MING YUAN

Department of Applied Chemistry
Shanghai Jiao Tong University
Shanghai, People's Republic of China

ABSTRACT

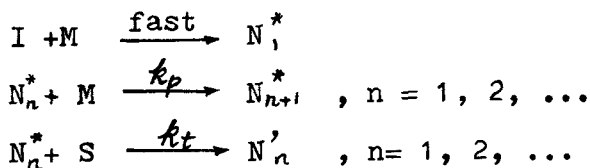
The effect of impurity termination on molecular size distribution for anionic polymerization with instantaneous initiation is discussed. In order to derive rigorous expressions for the molecular size distribution function and other molecular parameters, this paper follows a mathematical procedure which has proved to be useful for the theoretical treatment of the kinetics of polymerizations in the previous parts of this series. The variation of all molecular parameters with the extent of polymerization is illustrated.

In general, disproportionation and combination terminations are absent in anionic polymerization because the active centers with the same electrical charge repel one another. In actual fact, the agents used are never absolutely pure, and the reaction system cannot be kept completely clean. The trace impurities may kill some of the active centers and broaden the molecular size distribution of the resultant polymer to varying degrees. Therefore, the study of impurity termination has much theoretical and practical significance. This

topic has been studied by several authors [1-4]. However, rigorous expressions for the molecular size distribution function and other molecular parameters have not been reported. In this paper, as in previous parts of this series [5], we solve the set of kinetic differential equations for an anionic polymerization with instantaneous initiation and impurity termination by a nonsteady-state method, and develop a method for calculating all molecular parameters from the reaction conditions.

1. SOLUTION OF THE KINETIC DIFFERENTIAL EQUATIONS

We assume anionic polymerization initiated instantaneously and terminated by impurities. Then the reaction scheme may be written as



where M is the residual monomer concentration, N_n^* is the active n -mer concentration, N'_n is the inactive n -mer concentration, k_t is the rate constant for impurity termination, and k_p is the rate constant for chain propagation.

The differential equations for the above reaction scheme are

$$\frac{dN_1^*}{dt} = -(k_p M + k_t S) N_1^* \quad (1)$$

$$\frac{dN_n^*}{dt} = k_p M N_{n-1}^* - (k_p M + k_t S) N_n^* \quad , n = 2, 3, \dots \quad (2)$$

$$\frac{dN'_n}{dt} = k_t S N_n^* \quad , n = 1, 2, \dots \quad (3)$$

$$\frac{dS}{dt} = -k_t S \sum_n N_n^* \quad (4)$$

$$\frac{dM}{dt} = -k_p M \sum_n N_n^* \quad (5)$$

$$\frac{d \sum_n N_n^*}{dt} = -k_t S \sum_n N_n^* \quad (6)$$

The initial conditions of these differential equations are

$$M|_{t=0} = M_0 - I_0 ; S|_{t=0} = S_0 ; N_1^*|_{t=0} = I_0 ; N_{n \geq 2}^*|_{t=0} = N_n^*|_{t=0} = 0$$

where I_0 , M_0 , and S_0 are, respectively, the concentrations of initiator, monomer, and impurity present at the beginning.

The concentration of deactivated polymer, x , is given by

$$x = k_t \int_0^t S \sum_n N_n^* dt \tag{7}$$

or

$$\frac{dx}{dt} = k_t S \sum_n N_n^* \tag{8}$$

With $a = k_p/k_t$, Eqs. (4)-(6) can be transformed into the following forms:

$$\frac{dS}{dx} = -1 \tag{9}$$

$$\frac{dM}{dx} = -\frac{aM}{S} \tag{10}$$

$$\frac{d \sum_n N_n^*}{dt} = -1 \tag{11}$$

Solving Eqs. (9)-(11), we obtain

$$S = S_0 - x \tag{12}$$

$$M = (M_0 - I_0) \left(1 - \frac{x}{S_0}\right)^a \tag{13}$$

$$\sum_n N_n^* = I_0 - x \tag{14}$$

On combining Eqs. (1)-(3) with Eqs. (8) and (12)-(14), the set of differential equations becomes

$$\frac{dN_1^*}{dx} = - \left\{ \frac{a(M_0 - I_0) \left(1 - \frac{x}{S_0}\right)^{a-1}}{S_0(I_0 - x)} + \frac{1}{I_0 - x} \right\} N_1^* \quad (15)$$

$$\frac{dN_n^*}{dx} = \frac{a(M_0 - I_0) \left(1 - \frac{x}{S_0}\right)^{a-1}}{S_0(I_0 - x)} N_{n-1}^* - \left\{ \frac{a(M_0 - I_0) \left(1 - \frac{x}{S_0}\right)^{a-1}}{S_0(I_0 - x)} + \frac{1}{I_0 - x} \right\} N_n^* \quad (16)$$

$$\frac{dN_n'}{dx} = \frac{1}{I_0 - x} N_n' \quad (17)$$

The corresponding initial conditions become:

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

If $a \neq 1$, solving Eqs. (15)-(17) gives the following molecular size distribution functions for the active and inactive polymers:

$$N_n^* = \frac{I_0 - x}{(n-1)!} \left[\frac{a(M_0 - I_0)}{S_0} u(x) \right]^{n-1} \exp \left\{ - \frac{a(M_0 - I_0)}{S_0} u(x) \right\} \quad (18)$$

$$N_n' = \frac{1}{(n-1)!} \left[\frac{a(M_0 - I_0)}{S_0} \right]^{n-1} \int_0^x u^{n-1}(x) \exp \left\{ - \frac{a(M_0 - I_0)}{S_0} u(x) \right\} dx \quad (19)$$

where

$$u(x) = \int_0^x \frac{(1 - V/S_0)^{a-1}}{I_0 - V} dV \quad (20)$$

The molecular size distribution function for the total polymers is

$$N_n = N_n^* + N_n' \quad (21)$$

The special case of $a = m$ ($m = 1, 2, 3, \dots$) is studied below.

2. DETERMINATION OF THE VARIABLE x

Because the molecular size distribution function given in the preceding sections varies with x , it is necessary to find the relationship between x and the condition of polymerization. Substituting Eq. (13) into the definition of monomer conversion, $y = (M_0 - M)/M_0$, yields

$$x = S_0 \left\{ 1 - \left[(1 - y) M_0 / (M_0 - I_0) \right]^{1/a} \right\} \quad (22)$$

Obviously, when the monomer conversion reaches 100%, x is equal to S_0 . On the other hand, from Eqs. (8), (12), and (14) we can also obtain the relationships between polymerization time t and x or y:

$$x = \frac{S_0 \{ \exp[(S_0 - I_0)k_t t] - 1 \}}{\frac{S_0}{I_0} \exp[(S_0 - I_0)k_t t] - 1} \quad (23)$$

$$y = 1 - \left(1 - \frac{I_0}{M_0} \right) \left\{ 1 - \frac{\exp[(S_0 - I_0)k_t t] - 1}{\frac{S_0}{I_0} \exp[(S_0 - I_0)k_t t] - 1} \right\}^a \quad (24)$$

3. AVERAGE DEGREE OF POLYMERIZATION AND OTHER MOLECULAR PARAMETERS

Before giving the average degree of polymerization and other molecular parameters, we have to derive the statistical moments of N_n^* , N_n' , and N_n from differential Eqs. (15)-(17) or the corresponding molecular size distribution functions,

$$\sum_n n N_n^* = (I_0 - x) \left[\frac{a(M_0 - I_0)u(x)}{S_0} + 1 \right] \quad (25)$$

$$\sum_n n^2 N_n^* = (I_0 - x) \left\{ u(x) \frac{a(M_0 - I_0)}{S_0} + \left[u(x) \frac{a(M_0 - I_0)}{S_0} + 1 \right]^2 \right\} \quad (26)$$

The zeroth-order moment of N_n^* is identical with Eq. (14). The moments of deactivated chains are

$$\sum_n N_n' = x \quad (27)$$

$$\sum_n n N_n' = I_0 + (M_0 - I_0) \left[1 - \left(1 - \frac{x}{S_0} \right)^a \right] - (I_0 - x) \left[1 + \frac{u(x)a(M_0 - I_0)}{S_0} \right] \quad (28)$$

$$\begin{aligned} \sum_n n^2 N_n' = & x - (I_0 - x) \left[u(x) \frac{a(M_0 - I_0)}{S_0} \right]^2 + \frac{2a(M_0 - I_0)^2}{S_0} \int_0^x \frac{(1 - x/S_0)^{2a-1}}{I_0 - x} dx - \\ & - u(x) \left(1 - \frac{x}{S_0} \right)^a - \frac{3a(M_0 - I_0)}{S_0} u(x)(I_0 - x) + 3(M_0 - I_0) \left[1 - \left(1 - \frac{x}{S_0} \right)^a \right] \end{aligned} \quad (29)$$

Consequently, the statistical moments of the total polymer are

$$\sum_n N_n = I_0 \quad (30)$$

$$\sum_n n N_n = I_0 + (M_0 - I_0) \left[1 - \left(1 - \frac{x}{S_0} \right)^a \right] \quad (31)$$

$$\sum_n n^2 N_n = I_0 + 3(M_0 - I_0) \left[1 - \left(1 - \frac{x}{S_0} \right)^a \right] + \frac{2\alpha(M_0 - I_0)^2}{S_0} \left\{ \int_0^x \frac{\left(1 - \frac{x}{S_0} \right)^{2a-1}}{I_0 - x} dx - \left(1 - \frac{x}{S_0} \right)^a \mathcal{U}(x) \right\} \quad (32)$$

The number- and weight-average degrees of polymerization for the total polymers can be obtained from Eqs. (30)-(32):

$$\bar{P}_n = 1 - \left(1 - \frac{M_0}{I_0} \right) \left[1 - \left(1 - \frac{x}{S_0} \right)^a \right] \quad (33)$$

$$\bar{P}_w = \left\{ I_0 + 3(M_0 - I_0) \left[1 - \left(1 - \frac{x}{S_0} \right)^a \right] + \frac{2\alpha(M_0 - I_0)^2}{S_0} \left[\int_0^x \frac{\left(1 - \frac{x}{S_0} \right)^{2a-1}}{I_0 - x} dx - \mathcal{U}(x) \left(1 - \frac{x}{S_0} \right)^a \right] \right\} / \left\{ I_0 + (M_0 - I_0) \left[1 - \left(1 - \frac{x}{S_0} \right)^a \right] \right\} \quad (34)$$

The polydispersity, defined as \bar{P}_w/\bar{P}_n , is dependent on a , M_0 , I_0 , and S_0 . Figures 1 and 2 show plots of polydispersity vs monomer conversion for various values of a and S_0 . The molecular size distribution broadens with decreasing a (shown in Fig. 1). Figure 2 shows that the curves become flatter with decreasing amount of impurity. Finally, for $S_0 = 1.0 \times 10^{-6}$ mol/L, \bar{P}_w/\bar{P}_n approaches 1.0 with increasing extent of reaction. For living polymerization, the polydispersity decreases with increasing monomer conversion. This phenomenon is rarely observed in experiment. In fact, a little impurity in a polymerization system is unavoidable. As a result, the molecular size distribution deviates from the Gold distribution [6]. Increasing amounts of impurity increase the breadth of the distribution. This trend is marked in Fig. 3, which show \bar{P}_w/\bar{P}_n vs S_0 at $y = 100\%$. Curve 4 in Fig. 3 indicates that the polydispersity may reach more than 2.0.

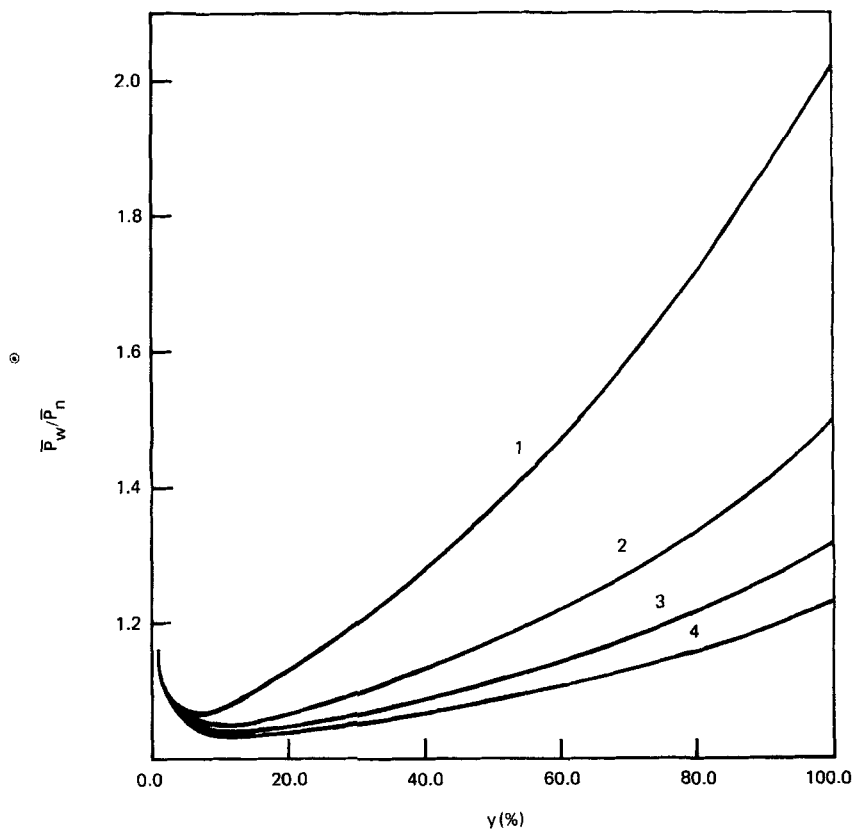


FIG. 1. Plot of \bar{P}_w/\bar{P}_n vs y for various values of a at $S_0 = 1.0 \times 10^{-3}$ mol/L, $I_0 = 2 \times 10^{-3}$ mol/L, $M_0 = 1.0$ mol/L. 1: $a = 0.5$. 2: $a = 1.0$. 3: $a = 1.5$. 4: $a = 2.0$.

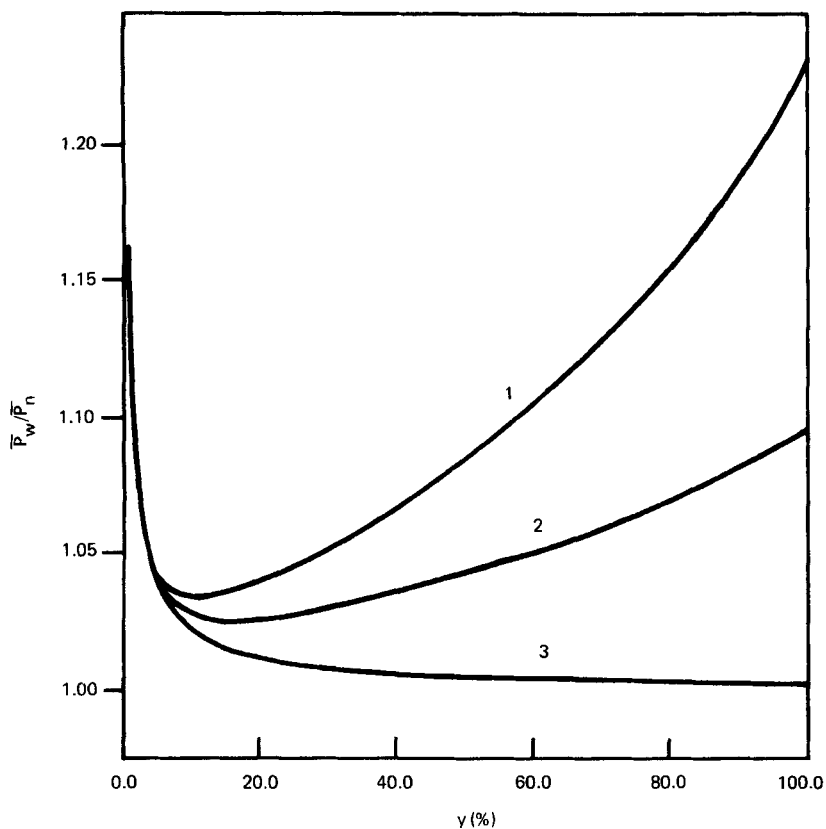


FIG. 2. Plot of \bar{P}_w/\bar{P}_n vs y for various values of S_0 at $M_0 = 1.0$ mol/L, $I_0 = 2 \times 10^{-3}$ mol/L, $a = 2.0$. 1: $S_0 = 1.6 \times 10^{-6}$ mol/L. 2: $S_0 = 0.8 \times 10^{-3}$ mol/L. 3: $S_0 = 1.0 \times 10^{-6}$ mol/L.

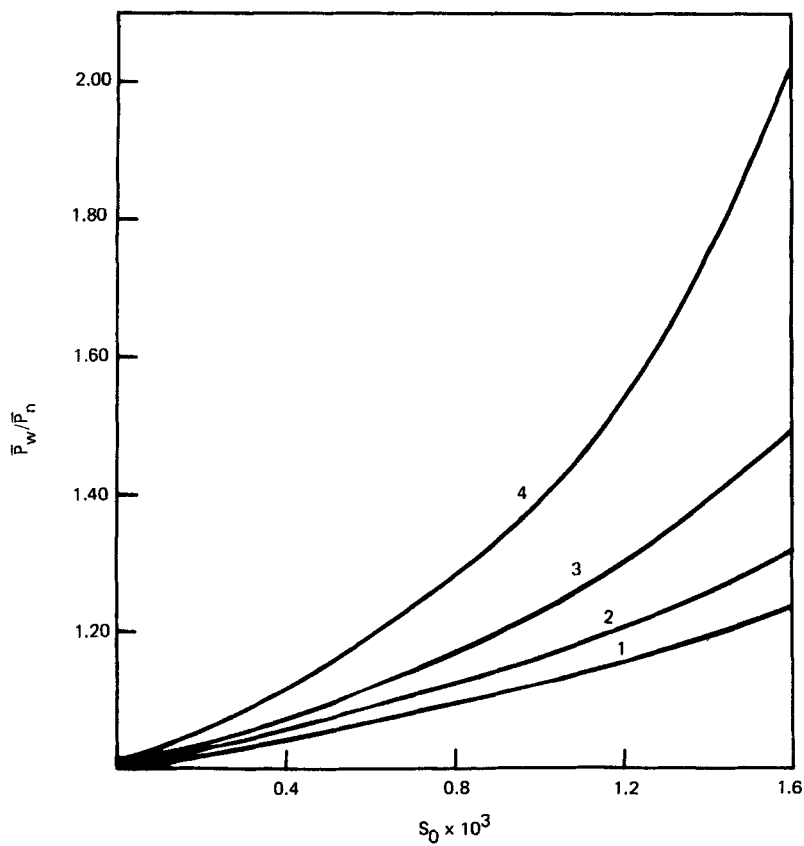


FIG. 3. Plot of \bar{P}_w/\bar{P}_n vs S_0 for various values of a at $M_0 = 1.0$ mol/L, $I_0 = 2 \times 10^{-3}$ mol/L, $y = 100\%$. 1: $a = 2.0$. 2: $a = 1.5$. 3: $a = 1.0$. 4: $a = 0.5$.

4. THE CASE OF a BEING A POSITIVE INTEGER

When $a = 1$, the solution of the set of differential Eqs. (15)-(17) is much simplified. The molecular size distribution functions of active and inactive polymers become

$$N_n^* = \frac{(I_0 - \chi)^\beta I_0^{1-\beta}}{(n-1)!} \left[(\beta-1) \ln \frac{I_0}{I_0 - \chi} \right]^{n-1} \quad (35)$$

$$N_n' = \frac{I_0^{1-\beta}}{(n-1)!} \int_0^\chi (I_0 - \chi)^{\beta-1} \left[(\beta-1) \ln \frac{I_0}{I_0 - \chi} \right]^{n-1} d\chi \quad (36)$$

$$N_n = N_n^* + N_n' \quad (37)$$

where

$$\beta = 1 + \frac{M_0 - I_0}{S_0}$$

The statistical moments of active and inactive polymers are, respectively,

$$\sum_n n N_n^* = (I_0 - \chi) \left\{ 1 + (\beta-1) \ln \frac{I_0}{I_0 - \chi} \right\} \quad (38)$$

$$\sum_n n^2 N_n^* = (I_0 - \chi) \left\{ \left[(\beta-1) \ln \frac{I_0}{I_0 - \chi} + 1 \right]^2 + (\beta-1) \ln \frac{I_0}{I_0 - \chi} \right\} \quad (39)$$

$$\sum_n n N_n' = \chi + (\beta-1) \left\{ \chi - (I_0 - \chi) \ln \frac{I_0}{I_0 - \chi} \right\} \quad (40)$$

$$\begin{aligned} \sum_n n^2 N_n' = & \chi + 3(\beta-1) \left[\chi - (I_0 - \chi) \ln \frac{I_0}{I_0 - \chi} \right] + (\beta-1)^2 \left\{ 2\chi - \right. \\ & \left. - 2(I_0 - \chi) \ln \frac{I_0}{I_0 - \chi} + (\chi - I_0) \left(\ln \frac{I_0}{I_0 - \chi} \right)^2 \right\} \end{aligned} \quad (41)$$

The zeroth-order moments of active and inactive polymers conform to Eqs. (14) and (17). Thus, the statistical moments of the total polymer are

$$\sum_n n N_n = I_0 + (\beta-1) \chi \quad (42)$$

$$\sum_n n^2 \mathcal{N}_n = I_0 + 3(B-1)\chi + 2(B-1)^2 \left[\chi - (I_0 - \chi) \ln \frac{I_0}{I_0 - \chi} \right] \quad (43)$$

The zeroth-order moment is also in keeping with Eq. (30). If a equals a positive integer other than $a = 1$, integration of Eq. (20) also results in an elementary function:

$$\begin{aligned} \mathcal{U}(\chi) = & (-1)^{m-1} (I_0 - S_0)^{m-1} \ln \frac{I_0}{I_0 - \chi} + \\ & + \sum_{i=0}^{m-2} (-1)^i (I_0 - S_0)^i \frac{S_0^{m-1-i} - (S_0 - \chi)^{m-1-i}}{m-1-i} \end{aligned} \quad (44)$$

Substituting Eq. (44) into Eqs. (18), (19), and (25)-(34) gives the molecular size distribution functions and the statistical moments at $a = m$ ($m = 2, 3, \dots$). But the case of a being equal to a positive integer happens rarely in practice. However, if a is large enough, one can neglect the fractional part of the value of a in numerical calculation without introducing any appreciable error.

5. INFLUENCE OF REACTION CONDITION ON MOLECULAR SIZE DISTRIBUTION

The molecular size distribution functions, Eqs. (18) and (19), include definite integrals $u(x)$, which can be evaluated numerically by computer. Figure 4 shows a plot of molecular size distribution for various y . The influence of a at $y = 100\%$ on molecular size distribution is shown in Fig. 5. The smaller the values of a , the broader the distributions of inactive and total polymer. From the examples of the numerical calculation given above, we know that the variation of all molecular parameters with reaction time t can be derived according to the equations given in this paper.

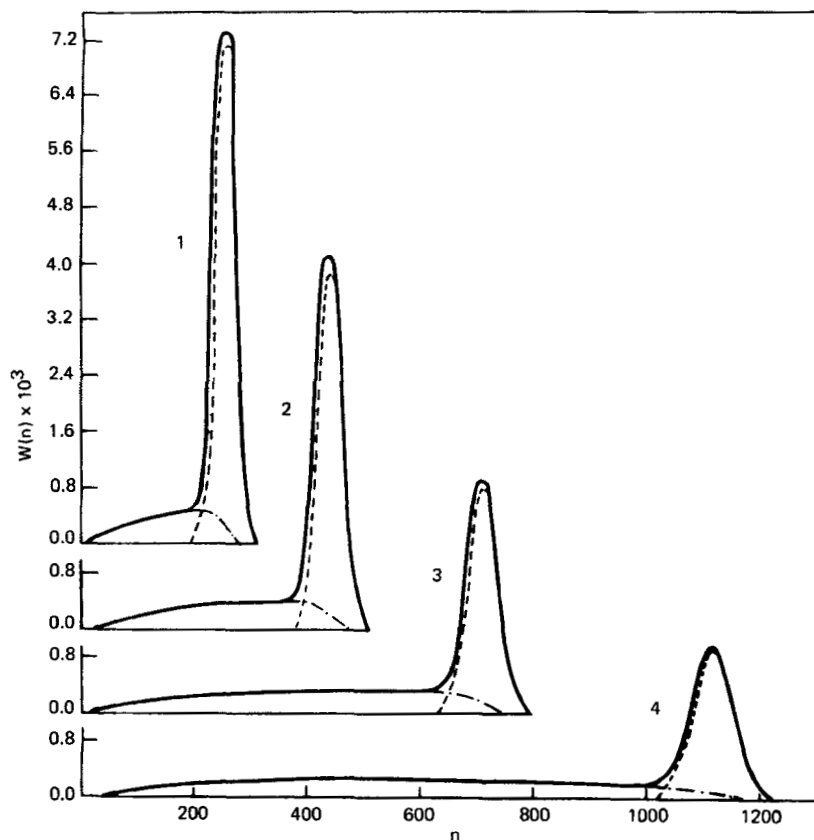


FIG. 4. Plot of molecular size distribution for various values of y at $M_0 = 1.0$ mol/L, $I_0 = 2 \times 10^{-3}$ mol/L, $a = 0.8$. 1: $y = 40\%$. 2: $y = 60\%$. 3: $y = 80\%$. 4: $y = 100\%$. (--) Active polymer. (-·-) inactive polymer, (—) total polymers.

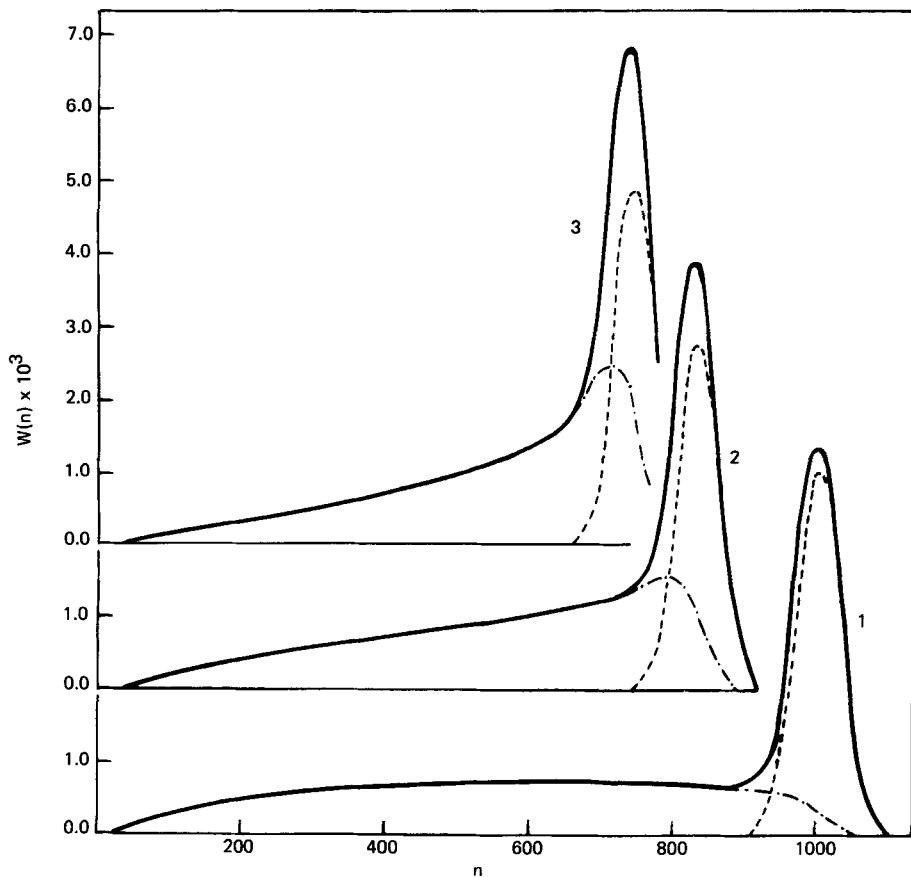


FIG. 5. Plot of molecular size distribution for various values of a at $M_0 = 1.0$ mol/L, $I_0 = 2 \times 10^{-3}$ mol/L, $S_0 = 1.6 \times 10^{-3}$ mol/L, $y = 100\%$. 1: $a = 1.0$. 2: $a = 1.5$. 3: $a = 2.0$.

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