Influence of termination and transfer on molecular weight distribution of polymers: 9. Chain transfer to monomer and spontaneous transfer

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A non-steady state kinetic treatment is rigorously performed for cationic polymerization with instantaneous initiation, monomer chain transfer and spontaneous transfer. The molecular weight distribution function and expressions for other molecular parameters are provided. The effect of the reaction conditions on the molecular parameters is illustrated by numerical examples.

(Keywords: monomer transfer; spontaneous transfer; MWD; non-steady state kinetics)

INTRODUCTION

Cationic polymerization frequently involves spontaneous transfer and chain transfer to monomer[1,2]. Although the theoretical aspects of this kind of polymerization have been studied by Nanda and Jain[3], there is still a lack of satisfactory results on this topic, because the assumption of stationary state is not valid for many cationic polymerization systems[4,5]. In Part 8 of this series[6], we dealt with the effect of spontaneous transfer on molecular weight distribution for cationic polymerization with instantaneous initiation. Since, as mentioned above, both spontaneous transfer and chain transfer to monomer frequently happen simultaneously in cationic polymerization, this paper applies the theoretical technique given in reference 7 to derive rigorous expressions for the molecular weight distribution function and the other molecular parameters for cationic polymerization with instantaneous initiation and the two sorts of chain transfer.

MOLECULAR SIZE DISTRIBUTION

If cationic polymerization with instantaneous initiation involves spontaneous transfer and chain transfer to monomer, the reaction scheme is as follows:

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

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

$$N_n^* \xrightarrow{k_{trs}} N'_n+I, \qquad n=1,2,\ldots$$

$$N_n^*+M \xrightarrow{k_{trm}} N'_n+N_1^*, \qquad n=1,2,\ldots$$

where I, M, N_n^* and N'_n denote, respectively, the concentrations of the initiator, the residual monomer, the active n-mers and the inactive n-mers, while k_p, k_{trs} and k_{trm} represent the rate constants of propagation, spontaneous transfer and chain transfer to monomer.

In accordance with the material balance and instantaneous initiation, we have

$$\sum_{n=1}^{\infty} N_n^* = I_0$$

where I_0 is the initial concentration of the initiator.

The kinetic differential equations adapted to the reaction scheme are

$$\frac{\mathrm{d}N_1^*}{\mathrm{d}t}=(k_{trm}M+k_{trs})I_0-[(k_p+k_{trm})M+k_{trs}]N_1^* \tag{1}$$

$$\frac{\mathrm{d}N_n^*}{\mathrm{d}t}=k_pMN_{n-1}^*-[(k_p+k_{trm})M+k_{trs}]N_n^*, \qquad n=2,3,\ldots \tag{2}$$

$$\frac{\mathrm{d}N'_n}{\mathrm{d}t}=(k_{trm}M+k_{trs})N_n^*, \qquad n=1,2,\ldots \tag{3}$$

$$\frac{\mathrm{d}M}{\mathrm{d}t}=-[(k_p+k_{trm})M+k_{trs}]I_0 \tag{4}$$

The initial conditions of these differential equations are:

$$M|_{t=0}=M_0-I_0, \qquad N_1^*|_{t=0}=I_0, \qquad N_{n>1}^*|_{t=0}=N'_{n\geq 1}|_{t=0}=0$$

where M_0 is the initial concentration of the monomer.

For convenience of derivation, we introduce the following parametric variable x:

$$x=\int_0^t [k_{trs}+(k_p+k_{trm})M]\mathrm{d}t \tag{5}$$

or

$$\frac{\mathrm{d}x}{\mathrm{d}t}=k_{trs}+(k_p+k_{trm})M \tag{6}$$

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By putting $a=k_{trm}/k_p$ and $b=k_{trs}/k_p$ equations (1)–(4) can be transformed into the following forms:

$$\frac{dN_1^*}{dx}=\frac{aM+b}{(1+a)M+b}I_0-N_1^* \qquad (7)$$

$$\frac{dN_n^*}{dx}=\frac{M}{(1+a)M+b}N_{n-1}^*-N_n^*, \qquad n=2,3,.. \qquad (8)$$

$$\frac{dN_n'}{dx}=\frac{aM+b}{(1+a)M+b}N_n^*, \qquad n=1,2,3,... \qquad (9)$$

$$\frac{dM}{dx}=-I_0 \qquad (10)$$

On integration of equation (10), under the initial condition that, at $x=0$, $M=M_0-I_0$, the expression for the concentration of the monomer is obtained:

$$M=M_0-I_0-I_0x \qquad (11)$$

Substituting equation (11) into equations (7)–(9), we can derive the molecular size distribution functions of active and inactive polymer chains:

$$N_1^*(x)=I_0e^{-x}\left[1+\int_0^x e^{\tau}\frac{a(M_0-I_0-I_0\tau)+b}{(1+a)(M_0-I_0-I_0\tau)+b}d\tau\right] \qquad (12)$$

$$N_n^*(x)=I_0e^{-x}\int_0^x \frac{[\alpha(x)-\alpha(\xi)]^{n-2}}{(n-2)!}\,\frac{M_0-I_0-I_0\xi}{(M_0-I_0-I_0\xi)(1+a)+b}$$
$$\times\left(1+\int_0^{\xi} e^{\tau}\frac{a(M_0-I_0-I_0\tau)+b}{(1+a)(M_0-I_0-I_0\tau)+b}d\tau\right)d\xi \qquad (13)$$

$$N_n'(x)=\int_0^x \frac{a(M_0-I_0-I_0\tau)+b}{(1+a)(M_0-I_0-I_0\tau)+b}N_n^*(\tau)d\tau \qquad (14)$$

where

$$\alpha(x)=\frac{x}{1+a}+\frac{b}{(1+a)^2I_0}\ln[(1+a)(M_0-I_0-I_0x)+b]$$

Though equations (13) and (14) are complicated, the numeric calculation can easily be carried out by using a computer. The molecular size distribution function for the total polymer is

$$N_n=N_n^*+N_n' \qquad (15)$$

If there is no chain transfer to monomer in the polymerization system, i.e. $a=0$, the expressions for N_n^* and N_n' can be simplified to those reported in reference 6.

AVERAGE DEGREES OF POLYMERIZATION AND OTHER MOLECULAR PARAMETERS

First, we have to derive the statistical moments of N_n^*, N_n' and N_n. From equations (7) and (8), the following differential equation results:

$$\frac{d\sum n^sN_n^*}{dx}+\sum n^sN_n^*=\frac{aM+b}{(1+a)M+b}I_0$$
$$+\frac{aM+b}{(1+a)M+b}\sum(n+1)^sN_n^*, \qquad s=0,1,2 \qquad (16)$$

Substituting equation (11) into equation (16), the first-order moment for N_n^* is derived:

$$\sum_{n=1}^{\infty} nN_n^*=I_0[(1+a)(M_0-I_0-I_0x)+b]^{b/(1+a)^2I_0}e^{ax/(1+a)}$$
$$\times\left\{[(1+a)(M_0-I_0)+b]^{-b/(1+a)^2I_0}+\int_0^x e^{ax/(1+a)}\right.$$
$$\left.\times[(1+a)(M_0-I_0-I_0x)+b]^{-b/(1+a)^2I_0}dx\right\} \qquad (17)$$

Taking account of equation (17), we get the second-order moment for N_n^* as follows:

$$\sum_{n=1}^{\infty} n^2N_n^*=[(1+a)(M_0-I_0-I_0x)+b]^{b/(1+a)^2I_0}e^{-ax/(1+a)}$$
$$\times\left\{I_0[(1+a)(M_0-I_0)+b]^{-b/(1+a)^2I_0}\right.$$
$$+\int_0^x\left[I_0+\frac{2(M_0-I_0-I_0\tau)}{(1+a)(M_0-I_0-I_0\tau)+b}\sum_{n=1}^{\infty} nN_n^*(\tau)\right]$$
$$\left.\times[(1+a)(M_0-I_0-I_0\tau)+b]^{-b/(1+a)^2I_0}e^{a\tau/(1+a)}d\tau\right\} \qquad (18)$$

Summation of equation (9) leads to

$$\frac{d\sum_{n=1}^{\infty} n^sN_n'}{dx}=\frac{a(M_0-I_0-I_0x)+b}{(1+a)(M_0-I_0-I_0x)+b}\sum_{n=1}^{\infty} n^sN_n^*, \qquad s=0,\ 1,2 \qquad (19)$$

Combination of equations (16) and (19) gives:

$$\frac{d\sum_{n=1}^{\infty} n^sN_n}{dx}=\frac{aM+b}{(1+a)M+b}I_0+\frac{M}{(1+a)M+b}$$
$$\times\left\{\sum_{n=1}^{\infty}(n+1)^sN_n^*-\sum_{n=1}^{\infty} n^sN_n^*\right\}, \qquad s=0,1,2 \qquad (20)$$

The statistical moments of the total polymers resulting from equation (20) are

$$\sum_{n=1}^{\infty} N_n=\frac{I_0}{1+a}[1+(1+x)a]$$
$$+\frac{b}{(1+a)^2}\ln\frac{(1+a)(M_0-I_0)+b}{(1+a)(M_0-I_0-I_0x)+b} \qquad (21)$$

$$\sum_{n=1}^{\infty} nN_n=I_0(1+x) \qquad (22)$$

$$\sum_{n=1}^{\infty} n^2 N_n = I_0(1+x) + 2\int_0^x \frac{M_0 - I_0 - I_0\tau}{(1+a)(M_0 - I_0 - I_0\tau) + b} \times \sum_{n=1}^{\infty} nN_n^*(\tau)\,\mathrm{d}\tau \qquad (23)$$

The statistical moments for the inactive polymer can be deduced from the following equation:

$$\sum_{n=1}^{\infty} n^s N'_n = \sum_{n=1}^{\infty} n^s (N_n - N_n^*), \qquad s = 0,1,2 \qquad (24)$$

From equations (21)–(23), we obtain the formulae for the number- and weight-average degrees of polymerization for all the polymers generated in the pertinent polymerization system:

$$\bar{P}_n = I_0(1+x) \Bigg/ \left\{ \frac{I_0}{1+a}[1 + a(1+x)] + \frac{b}{(1+a)^2} \ln \frac{(1+a)(M_0 - I_0) + b}{(1+a)(M_0 - I_0 - I_0 x) + b} \right\} \qquad (25)$$

$$\bar{P}_w = 1 + \frac{2}{I_0(1+x)} \int_0^x \frac{M_0 - I_0 - I_0\tau}{(1+a)(M_0 - I_0 - I_0\tau) + b} \times \sum_{n=1}^{\infty} nN_n^*(\tau)\,\mathrm{d}\tau \qquad (26)$$

The molar and weight fractions of the active polymer chains are as follows:

$$f_n^* = I_0 \Bigg/ \left\{ \frac{I_0}{1+a}[1 + (1+x)a] + \frac{b}{(1+a)^2} \ln \frac{(1+a)(M_0 - I_0) + b}{(1+a)(M_0 - I_0 - I_0 x) + b} \right\} \qquad (27)$$

$$f_w^* = [(1+a)(M_0 - I_0 - I_0 x) + b]^{b/(1+a)^2 I_0} \frac{e^{ax/(1+a)}}{1+x} \times \left\{ [(1+a)(M_0 - I_0) + b]^{-b/(1+a)^2 I_0} + \int_0^x e^{a\tau/(1+a)} [(1+a)(M_0 - I_0 - I_0\tau) + b] e^{-b/(1+a)^2 I_0} \mathrm{d}\tau \right\} \qquad (28)$$

The molar and weight fractions of the inactive polymer chains are:

$$f'_n = 1 - f_n^* \qquad (29)$$

$$f'_w = 1 - f_w^* \qquad (30)$$

The value of the parametric variable x involved in the above formulae may be determined, as in reference 6, by integrating equation (6). The relationship between x and the time of the polymerization, t, is

$$x = \frac{(1+a)(M_0 - I_0) + b}{(1+a)I_0} [1 - e^{-I_0(k_p + k_{trm})t}] \qquad (31)$$

Substituting equation (31) into equation (11), the concentration of residual monomer is obtained:

$$M = \left(M_0 - I_0 + \frac{b}{1+a} \right) e^{-I_0(k_p + k_{trm})t} - \frac{b}{1+a} \qquad (32)$$

When the monomer is completely consumed, the time of polymerization is given by

$$t_{max} = \frac{1}{I_0(k_p + k_{trm})} \ln\left(1 + \frac{(M_0 - I_0)(1+a)}{b} \right) \qquad (33)$$

According to equation (31), when $t = 0$, $x =$ zero; when $t \to t_{max}$, which means at the completion of the polymerization, $x_{max} = (M_0 - I_0)/I_0$. Therefore the variable range of x is

$$0 \leqslant x \leqslant (M_0 - I_0)/I_0$$

On the other hand, from equation (11) or equation (31) we can also obtain the relationship between monomer conversion y and x or t:

$$y = \frac{I_0(1+x)}{M_0} \qquad (34)$$

or

$$y = 1 + \frac{b}{(1+a)M_0} - \left(1 - \frac{I_0}{M_0} + \frac{b}{(1+a)M_0} \right) e^{-I_0(k_p + k_{trm})t} \qquad (35)$$

We can then relate the molecular parameters given above to the polymerization variables, such as the initial concentrations of initiator and monomer, and reaction time or monomer conversion.

NUMERICAL RESULTS AND DISCUSSION

From equations (12)–(15) and (22), we can obtain the differential molecular weight distribution functions for the active, inactive and total polymer:

$$W^*(n) = nN_n^* \Bigg/ \sum_{n=1}^{\infty} nN_n$$

$$W'(n) = nN'_n \Bigg/ \sum_{n=1}^{\infty} nN_n \qquad (36)$$

$$W(n) = nN_n \Bigg/ \sum_{n=1}^{\infty} nN_n$$

Although the molecular weight distribution function obtained contains a definite integral, numerical calculation can easily be performed by computer. *Figure 1* shows a plot of the molecular weight distributions of the resultant polymers for $M_0 = 1.0\,\mathrm{mol\,l^{-1}}$, $I_0 = 5 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$, $a(k_{trm}/k_p) = 1.0 \times 10^{-4}$, $b(k_{trs}/k_p) = 4.0 \times 10^{-4}\,\mathrm{l\,mol^{-1}}$ and $y = 100\%$. To gain insight into the effect of spontaneous transfer and chain transfer to monomer on the molecular weight distribution, we calculated the molecular weight distribution curves at various monomer conversions, as shown in *Figures 2* and *3*. We conclude from *Figures 2* and *3* that during polymerization the concentration of inactive polymer formed increases with increasing

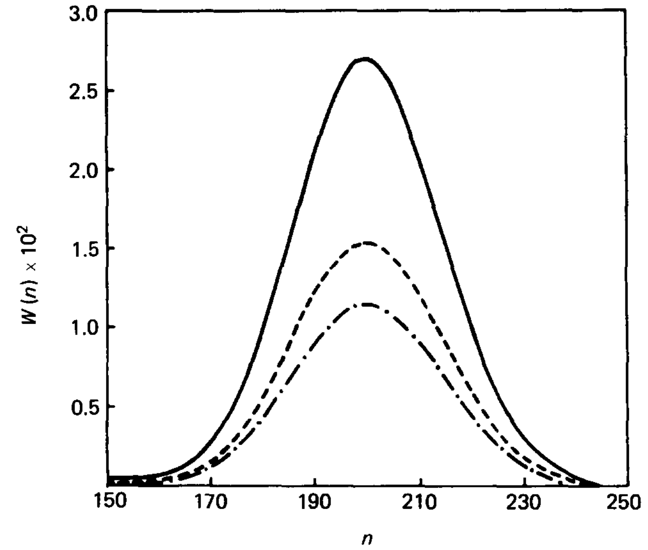

Figure 1 Molecular weight distribution $W(n)$ of polymer obtained in polymerization with chain transfer to monomer and spontaneous transfer. $M_0=1\,\mathrm{mol\,l^{-1}}$; $I_0=5\times10^{-3}\,\mathrm{mol\,l^{-1}}$; $a=1\times10^{-4}$; $b=4\times10^{-4}\,\mathrm{l\,mol^{-1}}$; $y=100\%$. ---, Active polymer chains; -·-·-, inactive polymer chains; ———, total polymer chains

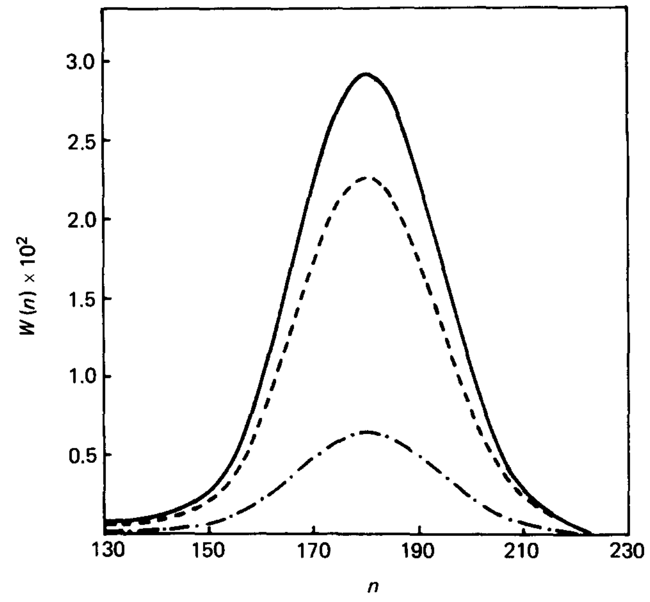

Figure 2 Molecular weight distribution $W(n)$ of polymer obtained in polymerization with chain transfer to monomer and spontaneous transfer. $M_0=1\,\mathrm{mol\,l^{-1}}$; $I_0=5\times10^{-3}\,\mathrm{mol\,l^{-1}}$; $a=6\times10^{-4}$; $b=4\times10^{-4}\,\mathrm{l\,mol^{-1}}$; $y=90\%$. Curves are explained in *Figure 1*

monomer conversion. On the other hand, these figures also demonstrate that, with increasing monomer conversion, the average molecular weight increases and the molecular weight distribution of the polymers becomes wider.

The polydispersity index of the resultant polymer is defined as the ratio of the weight-average degree of polymerization to the number-average degree, which can be calculated from equations (25), (26) and (34). *Figure 4* shows the relationship between the polydispersity index and monomer conversion for several values of a at $b=0.4\times10^{-3}\,\mathrm{l\,mol^{-1}}$. The curves of *Figure 4* indicate that the polydispersity index increases with increasing a at constant b, and is larger than that formed without chain transfer to monomer, which was shown in reference 6. This is a very significant characteristic of chain transfer

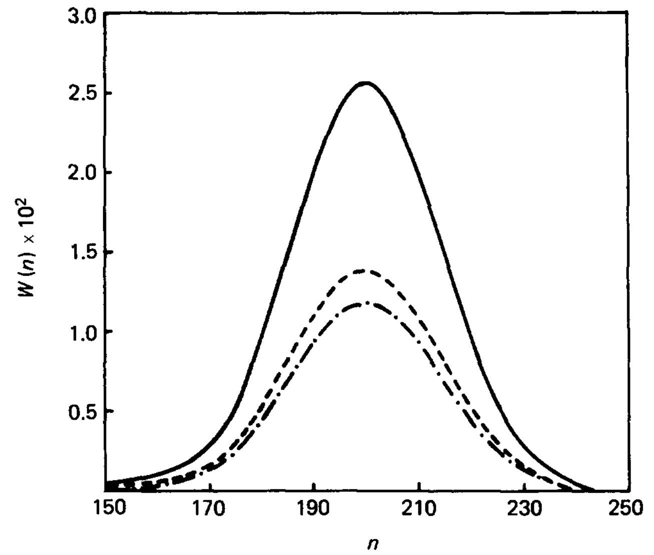

Figure 3 Molecular weight distribution $W(n)$ of polymer obtained in polymerization with chain transfer to monomer and spontaneous transfer. $y=100\%$; other quantities as in *Figure 2*. Curves are explained in *Figure 1*

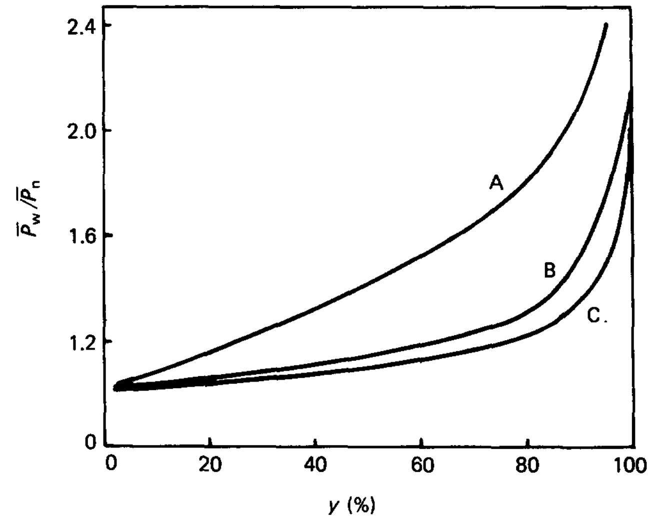

Figure 4 Plot of polydispersity index $\bar{P}_w/\bar{P}_n$ *versus* monomer conversion y. $M_0=1\,\mathrm{mol\,l^{-1}}$; $I_0=5\times10^{-3}\,\mathrm{mol\,l^{-1}}$; $b=k_{trs}/k_p=4\times10^{-4}\,\mathrm{l\,mol^{-1}}$. Curve A, $a=8\times10^{-4}$; curve B, $a=2\times10^{-4}$; curve C, $a=8\times10^{-5}$

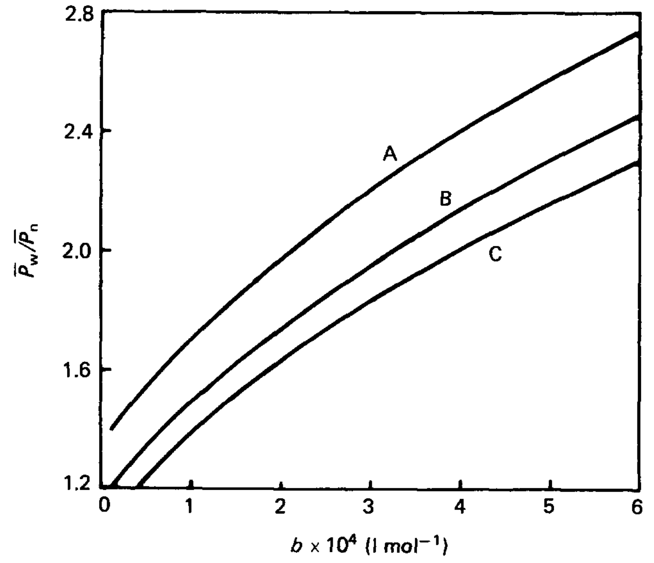

Figure 5 Plot of polydispersity index $\bar{P}_w/\bar{P}_n$ *versus* ratio $b=k_{trs}/k_p$. $M_0=1\,\mathrm{mol\,l^{-1}}$; $I_0=5\times10^{-3}\,\mathrm{mol\,l^{-1}}$; $y=100\%$. Curve A, $a=4\times10^{-4}$; curve B, $a=2\times10^{-4}$; curve C, $a=8\times10^{-5}$

to monomer. Chain transfer to monomer does not affect the rate of polymerization. However, it does affect polydispersity. This effect is seen in *Figure 5* which shows a plot of $\bar{P}_w/\bar{P}_n$ *versus* b for various values of a at $y = 100\%$.

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