A theoretical model for anionic polymerization of polar monomers initiated by electron transfer

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The kinetic differential equations for the anionic polymerization of polar monomers initiated by electron transfer with monomer termination are solved rigorously by the linear operator technique. A theoretical method is established by which all the molecular parameters of the polymer, such as the MWD function, average molecular weights, dispersity, distributions of functionality, and average functionality, can be calculated from the reaction constants, the initial conditions and the monomer conversion. The model has not yet been tested experimentally because of the lack of appropriate data.

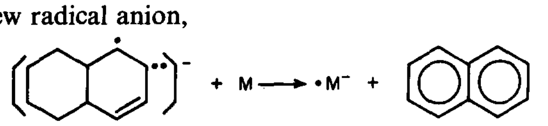
(Keywords: kinetics; MWD; polymerization; theoretical model)

INTRODUCTION

Anionic polymerization initiated by electron transfer has been studied comprehensively by Szwarc *et al.*[1] and others[2]. Initiation proceeds by the prior formation of the active initiator, e.g. the naphthalene radical anion:


(1)

The initiator transfers an electron to a monomer to form a new radical anion,


(2)

The radical anion generated from the monomer dimerizes to form the dicarbanion,

$$2 \cdot M^- \rightarrow {}^-MM^- \tag{3}$$

Anionic propagation occurs at both carbanion ends of the dianion. Experimental data on the reaction kinetics clearly show that more than 99% of the propagation occurs through the dianion[3]. This means that the combination of the radical anion, $\cdot M^-$, is rapid, and the rate of initiation mainly depends on electron transfer from the naphthalene radical anion to monomer. Pepper[4], Nanda *et al.*[5] and Yan[6-8] have studied the theory of anionic polymerization with monomer transfer initiated by the aromatic radical anions.

Polar monomers, such as methyl methacrylate, methyl vinyl ketone, and acrylonitrile, contain substituents that are reactive toward nucleophiles. This leads to termination of the active species and side reactions of the initiator, which are competitive with both propagation and initiation. Fortunately, the side reaction can be avoided to a large extent by using a less nucleophilic initiator in polar solvents at low temperatures. Some authors[9-12] have reported the kinetic theory on anionic polymerization with monomer termination initiated by a monofunctional initiator. This paper deals with the molecular weight distribution function and other molecular parameters of the polymers produced in the anionic polymerization of polar monomers initiated by electron transfer. For convenience of derivation, low reaction temperature and polar solvent are presumed, so that the side reaction of the initiator can be ignored, and the monomer termination of the active species is taken into account below.

MOLECULAR WEIGHT DISTRIBUTION

In accordance with the reaction mechanism mentioned, the set of reaction equations for the anionic polymerization of polar monomers initiated by electron transfer can be given by:

$$I + M \xrightarrow{k_i} \cdot M^- \tag{4}$$

$$2 \cdot M^- \xrightarrow{\text{fast}} N_2^{**} \tag{5}$$

$$N_n^{**} + M \xrightarrow{2k_p} N_{n+1}^{**} \qquad (n \geqslant 2) \tag{6}$$

$$N_n^{**} + M \xrightarrow{2k_t} N_{n+1}^{*} \qquad (n \geqslant 2) \tag{7}$$

$$N_n^{*} + M \xrightarrow{k_p} N_{n+1}^{*} \qquad (n \geqslant 3) \tag{8}$$

$$N_n^{*} + M \xrightarrow{k_t} N_{n+1}' \qquad (n \geqslant 3) \tag{9}$$

where I denotes the initiator, such as the naphthalene radical anion; M and $\cdot M^-$ were defined in Equation (2); and N_n^{**}, N_n^{*} and N_n' symbolize the resultant n-mers with,

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respectively, two carbanions at both ends, one carbanion at one of the ends, and no carbanions. The set of kinetic differential equations can be listed immediately:

$$dI/dt = -k_i MI \tag{10}$$

$$dN_2^{**}/dt = \tfrac{1}{2}k_i MI - 2(k_p + k_t)MN_2^{**} \tag{11}$$

$$dN_n^{**}/dt = 2k_p MN_{n-1}^{**} - 2(k_p + k_t)MN_n^{**} \quad (n \geqslant 3) \tag{12}$$

$$dN_3^{*}/dt = 2k_t MN_2^{**} - (k_p + k_t)MN_3^{*} \tag{13}$$

$$dN_n^{*}/dt = 2k_t MN_{n-1}^{**} + k_p MN_{n-1}^{*} - (k_p + k_t)MN_n^{*} \quad (n \geqslant 4) \tag{14}$$

$$dN_n'/dt = k_t MN_{n-1}^{*} \qquad (n \geqslant 4) \tag{15}$$

$$dM/dt = -k_i MI + (k_p + k_t)M\left(2\sum_{n=2}^{\infty} N_2^{**} + \sum_{n=3}^{\infty} N_n^{*}\right) \tag{16}$$

If I_0 and M_0 are the initial concentrations of the initiator and monomer, respectively, the initial conditions for Equations (10)–(16) are as follows:

$$I|_{t=0} = I_0, \quad M|_{t=0} = M_0, \quad N_n^{**}|_{t=0} = N_n^{*}|_{t=0} = N_n'|_{t=0} = 0$$

Apparently, the polymerization system under consideration must satisfy the following conservation conditions:

$$I_0 - I = 2\left(\sum_{n=2}^{\infty} N_n^{**} + \sum_{n=3}^{\infty} N_n^{*} + \sum_{n=4}^{\infty} N_n'\right) \tag{17}$$

$$M_0 - M = \sum_{n=2}^{\infty} nN_n^{**} + \sum_{n=3}^{\infty} nN_n^{*} + \sum_{n=4}^{\infty} nN_n' \tag{18}$$

Putting

$$x = \int_0^t k_p M dt \tag{19}$$

and taking D as the differential operator d/dx, the set of Equations (10)–(16) can be transformed into the linear set of equations:

$$[D + a]I = 0 \tag{20}$$

$$[D + 2(1+b)]N_2^{**} = \tfrac{1}{2}aI \tag{21}$$

$$[D + 2(1+b)]N_n^{**} = 2N_{n-1}^{**} \qquad (n \geqslant 3) \tag{22}$$

$$[D + (1+b)]N_3^{*} = 2bN_2^{**} \tag{23}$$

$$[D + (1+b)]N_n^{*} = 2bN_{n-1}^{**} + N_{n-1}^{*} \qquad (n \geqslant 4) \tag{24}$$

$$DN_n' = bN_{n-1}^{*} \qquad (n \geqslant 4) \tag{25}$$

$$DM = -aI - (1+b)\left(2\sum_{n=2}^{\infty} N_n^{**} + \sum_{n=3}^{\infty} N_n^{*}\right) \tag{26}$$

where $a = k_i/k_p$, and $b = k_t/k_p$. The initial conditions of these equations are accordingly transformed into

$$I|_{x=0} = I_0, \quad M|_{x=0} = M_0,$$

$$N_n^{**}|_{x=0} = N_n^{*}|_{x=0} = N_n'|_{x=0} = 0$$

Solving the homogeneous differential equation (20) gives:

$$I = I_0 e^{-ax} \tag{27}$$

From Equation (21), we have

$$N_2^{**} = \frac{I_0 a}{2[2(1+b) - a]}\left(e^{-ax} - e^{-2(1+b)x}\right) \tag{28}$$

Equation (22) results in the recurrence formula:

$$N_n^{**} = \frac{2^{n-2}}{[D + 2(1+b)]^{n-2}} N_2^{**} + \sum_{j=0}^{n-3} \frac{2^j}{[D + 2(1+b)]^j} c_{n-j} e^{-2(1+b)x} \tag{29}$$

where c_{n-j} are constants to be determined. By using the linear differential operator technique, we finally get

$$N_n^{**} = \frac{I_0 2^{n-3} a e^{-2(1+b)x}}{[2(1+b) - a]^{n-1}} \times \sum_{i=n-1}^{\infty} \frac{\{[2(1+b) - a]x\}^i}{i!} \tag{30}$$

Solving Equation (23) gives the following equation:

$$N_3^{*} = \frac{I_0 ab}{2(1+b) - a}\left[\frac{e^{-ax}}{1+b-a} + \frac{e^{-2(1+b)x}}{1+b} + \frac{a - 2(1+b)}{(1+b)(1+b-a)} e^{-(1+b)x}\right] \tag{31}$$

The expression for N_n^{*} is derived from Equation (24) (refer to Appendix):

$$N_n^{*} = I_0 b e^{-(1+b)x}\left\langle \frac{1}{(1+b-a)^{n-2}} \sum_{i=n-2}^{\infty} \frac{[(1+b-a)x]^i}{i!} - \frac{1}{(1+b)^{n-2}} \sum_{i=n-2}^{\infty} \frac{[(1+b)x]^i}{i!} + \frac{e^{-(1+b)x}}{(1+b)^{n-2}} \sum_{i=n-2}^{\infty} \frac{[2(1+b)x]^i}{i!} - \frac{2^{n-2} e^{-(1+b)x}}{[2(1+b) - a]^{n-2}} \sum_{i=n-2}^{\infty} \frac{\{[2(1+b) - a]x\}^i}{i!} \right\rangle \tag{32}$$

Using Equation (32), an expression for N_n' can be obtained by integration:

$$N_n' = I_0 b^2 \left\langle \frac{2^{n-3} e^{-2(1+b)x}}{a[2(1+b) - a]^{n-3}} \sum_{i=n-3}^{\infty} \frac{\{[2(1+b) - a]x\}^i}{i!} + \frac{e^{-2(1+b)x}}{(1+b)^{n-3}}\left[x - \frac{1}{a} - \frac{n-3}{2(1+b)}\right] \sum_{i=n-3}^{\infty} \frac{[2(1+b)x]^i}{i!} + \frac{e^{-(1+b)x}}{(1+b)^{n-3}}\left[\frac{1}{a} - x + \frac{n-3}{1+b}\right] \sum_{i=n-3}^{\infty} \frac{[(1+b)x]^i}{i!} - \frac{e^{-(1+b)x}}{a(1+b-a)^{n-3}} \sum_{i=n-3}^{\infty} \frac{[(1+b-a)x]^i}{i!} + \frac{x}{(1+b)^{n-3}} \times \left\{ \frac{[(1+b)x]^{n-4}}{(n-4)!} e^{-2(1+b)x} - \frac{[(1+b)x]^{n-4}}{(n-4)!} e^{-(1+b)x} \right\} \right\rangle \tag{33}$$

Equations (30), (32) and (33) are the MWD functions for diactive, monoactive and inactive species, respectively. The total number of n-mers is the sum of N_n^{**}, N_n^{*} and N_n':

$$N_n = N_n^{**} + N_n^{*} + N_n' \tag{34}$$

Its concrete expression is omitted here.

OTHER MOLECULAR PARAMETERS

To calculate other molecular parameters, such as the number and weight average degrees of polymerization and the functionality distribution, we have to give the various statistical moments in advance:

$$\sum_{n=2}^{\infty} N_n^{**} = \frac{I_0 a}{2(a-2b)}\left(e^{-2bx} - e^{-ax}\right) \tag{35}$$

$$\begin{aligned}\sum_{n=2}^{\infty} nN_n^{**} = {} & \frac{I_0 a}{(a-2b)^2}\left[(a-2b)xe^{-2bx}\right.\\ & \left. + (1+2b-a)(e^{-ax} - e^{-2bx})\right]\end{aligned} \tag{36}$$

$$\begin{aligned}\sum_{n=2}^{\infty} n^2 N_n^{**} = {} & \frac{I_0 a}{(a-2b)^3}\left\{2(a-2b)^2 x^2 e^{-2bx}\right.\\ & - [4 - 5(a-2b)](a-2b)xe^{-2bx}\\ & \left. + [4 - 5(a-2b) + 2(a-2b)^2](e^{-2bx} - e^{-ax})\right\}\end{aligned} \tag{37}$$

$$\begin{aligned}\sum_{n=3}^{\infty} N_n^{*} = I_0 & \left[\frac{ab}{(a-2b)(a-b)} e^{-ax} + \frac{a}{a-b} e^{-bx}\right.\\ & \left. - \frac{a}{a-2b} e^{-2bx}\right]\end{aligned} \tag{38}$$

$$\begin{aligned}\sum_{n=3}^{\infty} nN_n^{*} = I_0 & \left\{\frac{ab}{(a-2b)(a-b)}\left[3 - \frac{4b-3a}{(a-b)(2b-a)}\right]e^{-ax}\right.\\ & + \frac{a}{a-b}\left[3 + x + \frac{a-2b}{b(a-b)}\right]e^{-bx}\\ & \left. - \frac{a}{a-2b}\left[3 + 2x + \frac{4b-a}{b(2b-a)}\right]e^{-2bx}\right\}\end{aligned} \tag{39}$$

$$\begin{aligned}\sum_{n=3}^{\infty} n^2 N_n^{*} = I_0 & \left\{-\frac{4a}{a-2b} x^2 e^{-2bx}\right.\\ & + \left[-14 - \frac{4}{b} - \frac{28b}{a-2b} + \frac{16b}{(a-2b)^2}\right]xe^{-2bx}\\ & + b\left[-\frac{18}{a-2b} + \frac{28}{(a-2b)^2} + \frac{16}{(2b-a)^3}\right.\\ & \left. - \frac{9}{b} - \frac{7}{b^2} - \frac{2}{b^3}\right]e^{-2bx} + b\left[\frac{18}{a-2b} - \frac{28}{(a-2b)^2}\right.\\ & \left. + \frac{16}{(a-2b)^3} - \frac{9}{a-b} + \frac{7}{(a-b)^2} - \frac{2}{(a-b)^3}\right]e^{-ax}\\ & + b\left[\frac{9}{b} + \frac{7}{b^2} + \frac{2}{b^3} + \frac{9}{a-b} - \frac{7}{(a-b)^2}\right.\\ & \left. + \frac{2}{(a-b)^3}\right]e^{-bx} + b\left[\frac{7}{b} + \frac{2}{b^2} + \frac{7}{a-b} - \frac{2}{(a-b)^2}\right]\\ & \left. \times xe^{-bx} + \frac{a}{a-b} x^2 e^{-bx}\right\}\end{aligned} \tag{40}$$

$$\begin{aligned}\sum_{n=4}^{\infty} N'_n = I_0 & \left[\frac{1}{2} - \frac{a}{a-b} e^{-bx} - \frac{b^2}{(a-2b)(a-b)} e^{-ax}\right.\\ & \left. + \frac{a}{2(a-2b)} e^{-2bx}\right]\end{aligned} \tag{41}$$

$$\begin{aligned}\sum_{n=4}^{\infty} nN'_n = I_0 & \left\{\frac{1+2b}{b} + \frac{b^2}{(a-b)(a-2b)}\left[\frac{3a-4b}{(a-b)(a-2b)} - 4\right]e^{-ax}\right.\\ & - \frac{a}{a-b}\left[4 + x + \frac{2a-3b}{b(a-b)}\right]e^{-bx}\\ & \left. + \frac{a}{a-2b}\left[2 + x + \frac{a-3b}{b(a-2b)}\right]e^{-2bx}\right\}\end{aligned} \tag{42}$$

$$\begin{aligned}\sum_{n=4}^{\infty} n^2 N'_n = I_0 & \left\{\frac{2a}{a-2b} x^2 e^{-2bx} + \frac{a}{a-2b}\left(9 + \frac{4}{b} - \frac{4}{a-2b}\right)\right.\\ & \times xe^{-2bx} + \frac{1}{a-2b}\left[8a + \frac{1}{b}\left(9a - 2 + \frac{3a}{b}\right)\right.\\ & \left. - \frac{1}{a-2b}\left(9a + \frac{2a}{b} - \frac{8b}{a-2b}\right)\right](e^{-2bx} - 1)\\ & + \frac{b^2}{a}\left[\frac{1}{a-b}\left(16 - \frac{9}{a-b} + \frac{2}{(a-b)^2}\right)\right.\\ & \left. - \frac{4}{a-2b}\left(8 - \frac{9}{a-2b} + \frac{4}{(a-2b)^2}\right)\right](e^{-ax} - 1)\\ & - \frac{1}{a-b}\left[16a + \frac{2}{b}\left(9a - 1 + \frac{3a}{b}\right)\right.\\ & \left. - \frac{1}{a-b}\left(9a - \frac{2a}{b} - \frac{2b}{a-b}\right)\right](e^{-bx} - 1)\\ & \left. - \frac{a}{a-b}\left(9 + \frac{4}{b} - \frac{2}{a-b}\right)xe^{-bx} - \frac{a}{a-b} x^2 e^{-bx}\right\}\end{aligned} \tag{43}$$

Hence

$$\sum_{n=2}^{\infty} N_n = \frac{I_0}{2}(1 - e^{-ax}) = \frac{1}{2}(I_0 - I) \tag{44}$$

$$\sum_{n=2}^{\infty} nN_n = I_0\left[\left(\frac{1+b}{a-b} - 1\right)e^{-ax} - \frac{a(1+b)}{b(a-b)} e^{-bx} + \frac{1+2b}{b}\right] \tag{45}$$

$$\begin{aligned}\sum_{n=2}^{\infty} n^2 N_n = I_0 & \left\{\frac{a}{a-2b}\left(\frac{1+b}{b}\right)^2 (e^{-2bx} - 1)\right.\\ & - \frac{2a}{a-b}\left(1 + \frac{1}{b}\right)xe^{-bx} + \frac{a}{a-b}\left[-7 - \frac{1}{b}\left(11 + \frac{4}{b}\right)\right.\\ & \left. + \frac{2}{a+b}\left(1 + \frac{1}{b}\right)\right](e^{-bx} - 1)\\ & + \left[\frac{b(1+b)}{a(a-b)}\left(7 - \frac{2}{a-b}\right) - \frac{2}{a(a-2b)}\right.\\ & \left.\left. \times (2 + 4b + a^2) + \frac{1}{a}(5 + 9b)\right](e^{-ax} - 1)\right\}\end{aligned} \tag{46}$$

Thus the number and weight average degrees of polymerization for the resultant polymer are easily obtained from Equations (44)–(46):

$$\begin{aligned}\bar{P}_n = {} & 2[a(1+b)(1 - e^{-bx})/(1 - e^{-ax})\\ & - b(1 - a + 2b)]/[b(a-b)]\end{aligned} \tag{47}$$

$$\begin{aligned}\bar{P}_w = & \left\{\frac{a(a-b)(1+b)^2}{b(a-2b)}(1 - e^{-2bx}) + 2a(1+b)xe^{-bx}\right.\\ & - ab\left[7 + \frac{1}{b}\left(11 + \frac{4}{b}\right) - \frac{2}{a-b}\left(1 + \frac{1}{b}\right)\right](1 - e^{-bx})\end{aligned}$$

$$+b(a-b)\left[\frac{b(1+b)}{a(a-b)}\left(7-\frac{2}{a-b}\right)-\frac{2}{a(a-2b)}\right.$$
$$\left.\times(2+4b+a^2)+\frac{1}{a}(5+9b)\right](1-e^{-ax})\Big\}\Big/$$
$$[b(1-a+2b)(1-e^{-ax})-a(1+b)(1-e^{-bx})] \tag{48}$$

The dispersity of the polymer is the ratio of $\bar{P}_w$ to $\bar{P}_n$ – this expression is omitted here. The respective molecular fractions of the diactive, monoactive and inactive species are:

$$f_n^{**}=\sum N_n^{**}/\sum N_n=\frac{a(e^{-2bx}-e^{-ax})}{(a-2b)(1-e^{-ax})} \tag{49}$$

$$f_n^{*}=\sum N_n^{*}/\sum N_n$$
$$=\frac{2a}{(a-2b)(a-b)}$$
$$\times[be^{-ax}+(a-2b)e^{-bx}-(a-b)e^{-2bx}]/(1-e^{-ax}) \tag{50}$$

$$f_n'=\sum N_n'/\sum N_n=1-f_n^{**}-f_n^{*} \tag{51}$$

These equations represent the functionality distribution of the resultant polymer. *Figures 1–3* show plots of f_n^{**}, f_n^* and f_n' as a function of x. The average functionality is:

$$\bar{f}=(2\sum N_n^{**}+\sum N_n^{*})/\sum N_n$$
$$=\frac{2a(e^{-bx}-e^{-ax})}{(a-b)(1-e^{-ax})} \tag{52}$$

The weight fractions of diactive, monoactive, and inactive species are:

$$f_w^{**}=\sum nN_n^{**}/\sum nN_n$$
$$=ab(a-b)[(a-2b)xe^{-2bx}$$
$$+(1+2b-a)(e^{-ax}-e^{-2bx})]/$$
$$\{(a-2b)^2[a(1+b)(1-e^{-bx})$$
$$-b(1+2b-a)(1-e^{-ax})]\} \tag{53}$$

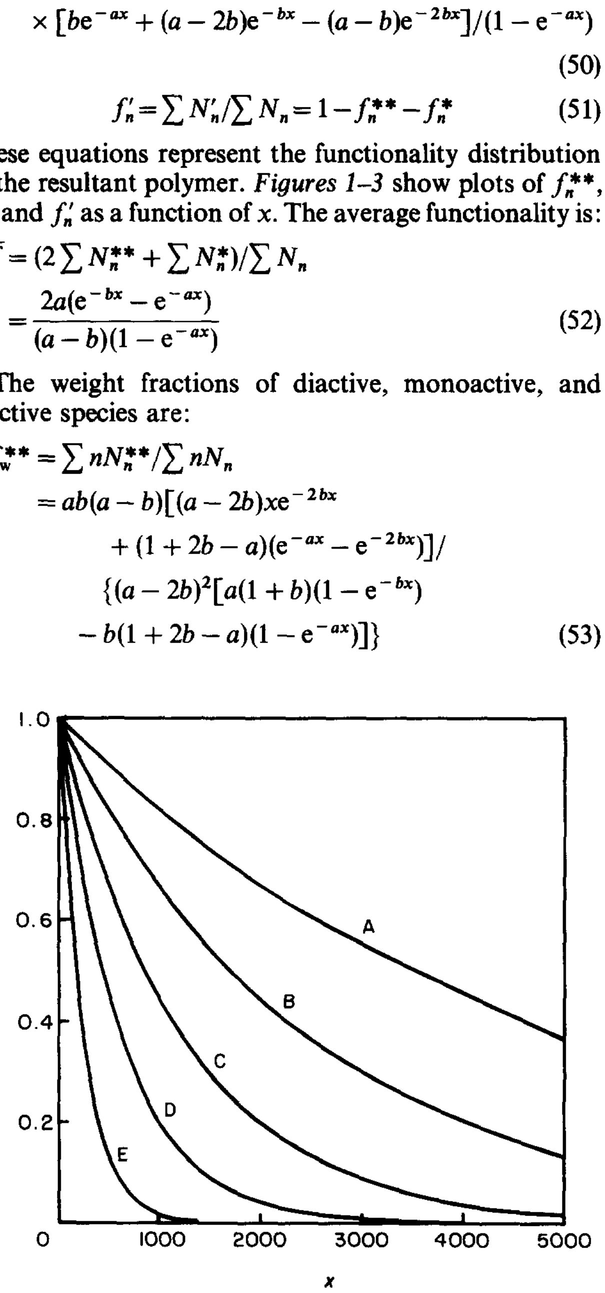

Figure 1 Plot of f_n^* *versus* x for $a=0.5$ and (A) $b=0.0001$; (B) $b=0.0002$; (C) $b=0.0004$; (D) $b=0.0008$; (E) $b=0.002$

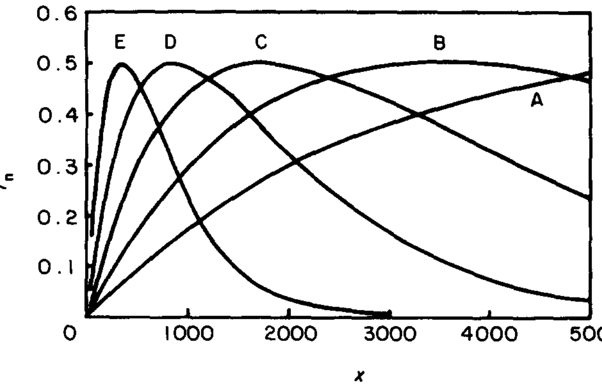

Figure 2 Plot of f_n^* *versus* x for $a=0.5$ and values of b as given in *Figure 1*

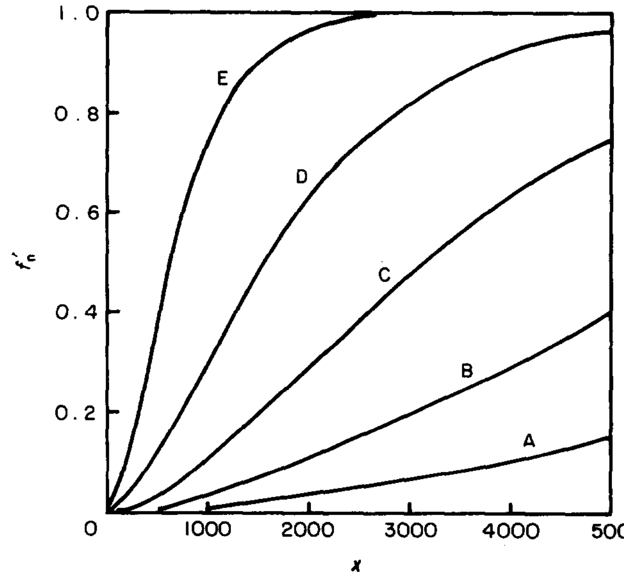

Figure 3 Dependence of f_n' on x for $a=0.5$ and values of b as given in *Figure 1*

$$f_w^{*}=\sum nN_n^{*}/\sum nN_n$$
$$=b(a-b)\left\{\frac{ab}{(a-b)(a-2b)}\left[3-\frac{3a-4b}{(a-b)(a-2b)}\right]e^{-ax}\right.$$
$$+\frac{a}{a-b}\left[3+x+\frac{a-2b}{b(a-b)}\right]e^{-bx}$$
$$\left.-\frac{a}{a-2b}\left[3+2x-\frac{a-4b}{b(a-2b)}\right]e^{-2bx}\right\}\Big/$$
$$[a(1+b)(1-e^{-bx})-b(1+2b-a)(1-e^{-ax})] \tag{54}$$

$$f_w'=\sum nN_n'/\sum nN_n=1-f_w^{**}-f_w^{*} \tag{55}$$

The set of equations (53)–(55) can be considered as the weight distribution function of functionality of the resultant polymer.

DISCUSSION

To discuss the influence of reaction conditions on the molecular parameters of the resultant polymer, it is necessary to clarify the dependence of x on reaction conditions. From Equation (45) the following formula is acquired:

$$Y=\frac{I_0}{M_0}\left[\left(\frac{1+b}{a-b}-1\right)e^{-ax}-\frac{a(1+b)}{b(a-b)}e^{-bx}+\frac{1+2b}{b}\right] \tag{56}$$

where Y denotes monomer conversion. If we substitute constants a, b, initial conditions M_0, I_0 and reaction condition Y into Equation (56), x can be determined by iteration. Therefore, the MWD function, average molecular weights, dispersity, distributions of functionality and average functionality may be theoretically plotted against Y or M_0/I_0, respectively.

Figures 4–9 plot the differential MWD curves of diactive, monoactive, inactive and total polymer for various values of Y, where $W_n^{**} = nN_n^{**}/\sum nN_n$, $W_n^* = nN_n^*/\sum nN_n$, $W_n' = nN_n'/\sum nN_n$, $W_n = W_n^{**} + W_n^* + W_n'$.

During the initial period of polymerization (*Figures 4* and *5*), there are mainly diactive species and a small proportion of monoactive species in the total polymer. Therefore, the MWD curves appear unimodal. With increasing conversion, termination becomes more and more important, and the MWD curves appear bimodal (*Figures 6* and *7*). Finally, the MWD curves (*Figures 8* and *9*) appear unimodal again, with the active species exhausted.

In anionic polymerization of methyl methacrylate in THF, the side reaction plays an important role if the reaction temperature is high. As a result, the molecular

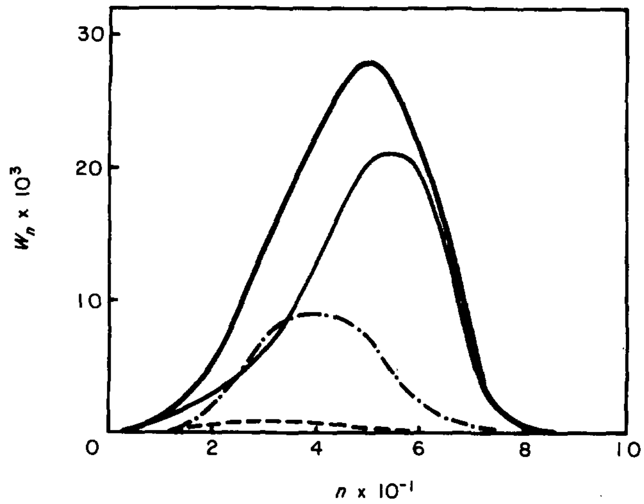

Figure 4 MWD of total polymer and the various polymer species with different functionalities for $a = 0.1$, $b = 0.01$, $M_0/I_0 = 300$, $Y = 6.5\%$; (——) diactive polymer (W_n^{**}); (–·–·–) monoactive polymer (W_n^*); (– – –) inactive polymer (W_n'); (——) total polymer (W_n)

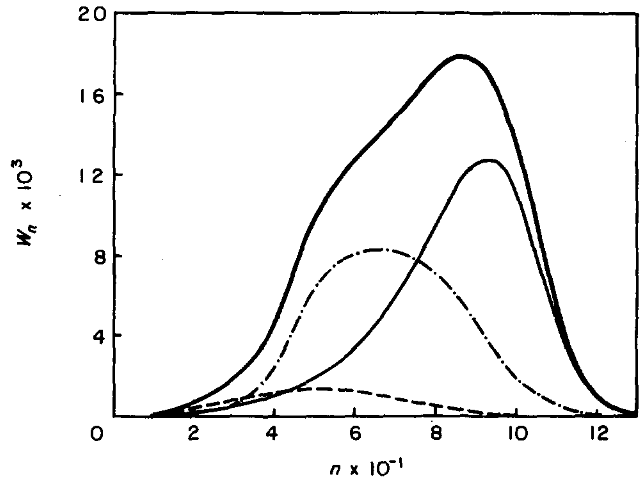

Figure 5 MWD of total polymer and the various polymer species with different functionalities, $Y = 11.3\%$. Other parameters are identical to those of *Figure 4*

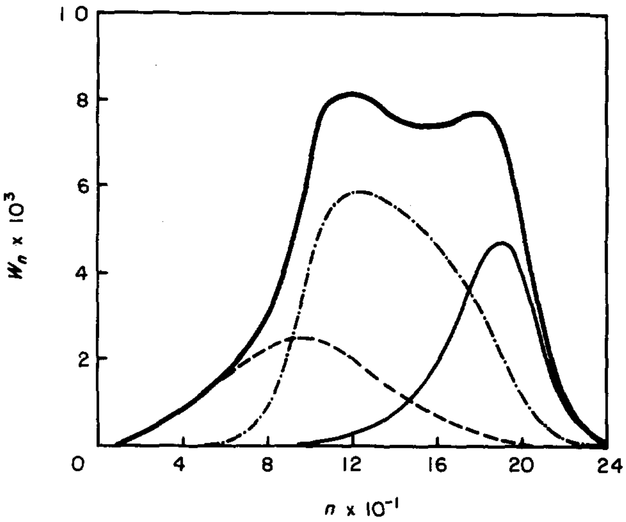

Figure 6 MWD of total polymer and the various polymer species with different functionalities, for $Y = 20.2\%$. Other parameters are identical to those of *Figure 4*

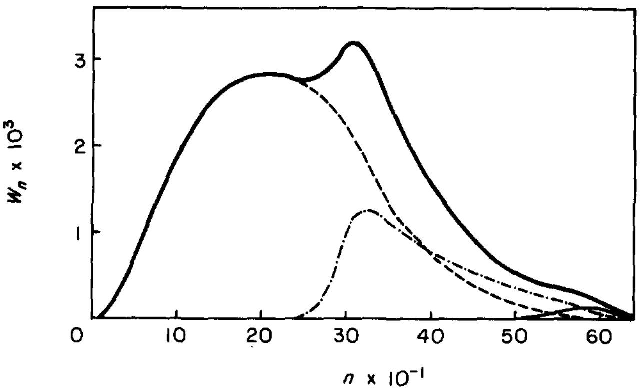

Figure 7 MWD of total polymer and the various polymer species with different functionalities for $Y = 32.1\%$. Other parameters are identical to those of *Figure 4*

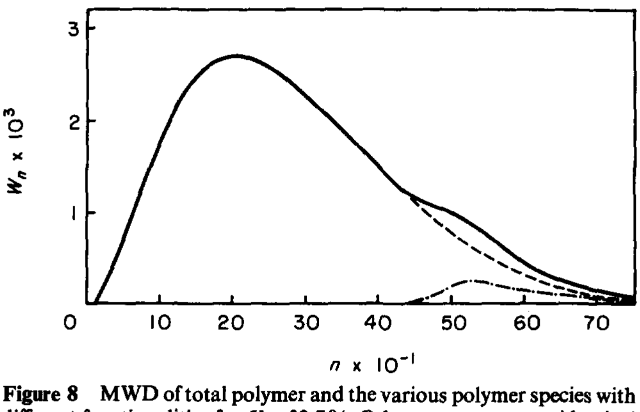

Figure 8 MWD of total polymer and the various polymer species with different functionalities for $Y = 33.7\%$. Other parameters are identical to those of *Figure 4*

weight distribution broadens, and the polymerization does not reach complete conversion[13]. The limit of monomer conversion can be obtained from Equation (56) when $x \to \infty$, i.e.

$$\lim_{x\to\infty} Y = \frac{I_0}{M_0}\left(2 + \frac{1}{b}\right) \tag{57}$$

Apparently, our theoretical results agree qualitatively with the experimental phenomena reported in the past.

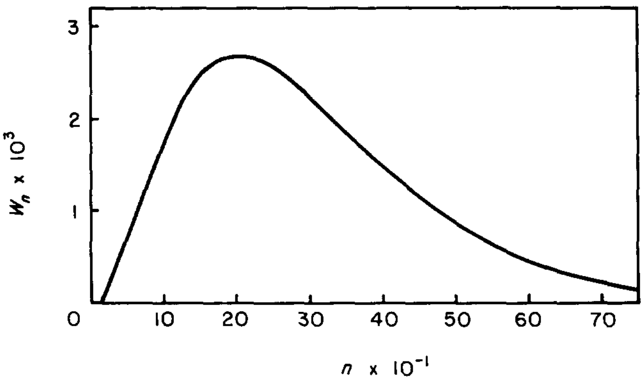

Figure 9 MWD of total polymer and the various polymer species with different functionalities for $Y = 34.0\%$. Other parameters are identical to those of *Figure 4*

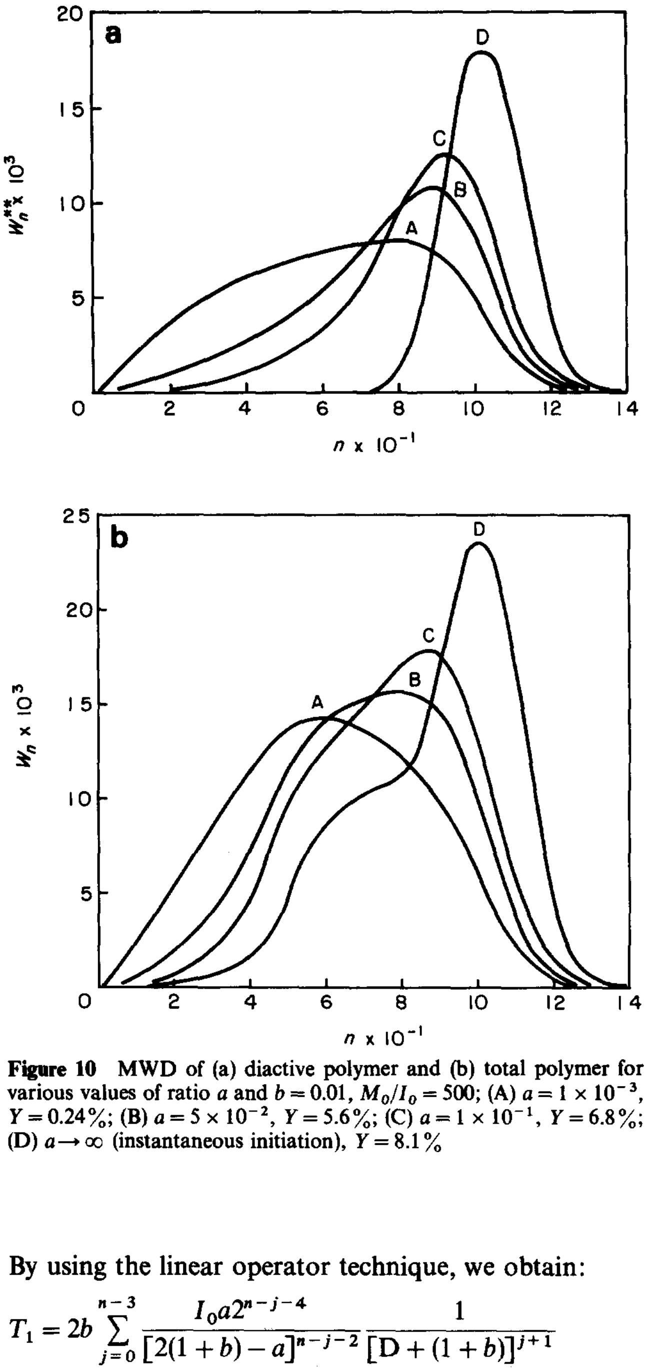

Figure 10 MWD of (a) diactive polymer and (b) total polymer for various values of ratio a and $b = 0.01$, $M_0/I_0 = 500$; (A) $a = 1 \times 10^{-3}$, $Y = 0.24\%$; (B) $a = 5 \times 10^{-2}$, $Y = 5.6\%$; (C) $a = 1 \times 10^{-1}$, $Y = 6.8\%$; (D) $a \to \infty$ (instantaneous initiation), $Y = 8.1\%$

The relation between the MWD function of the diactive and total polymer and ratio a and conversion Y is shown in *Figure 10*, where ratio a increases with curve number. In fact, the data of *Figure 10* were calculated at $x = 50$, which means an initial reaction period. With the help of Equation (56), the conversion Y can be obtained from the value of a. Because $Y \leqslant 10\%$, we may assume that the monomer concentration M keeps constant. According to the definition of x (Equation (19)), the physical significance of *Figure 10* is that the curves are MWD curves at the same reaction time t. We have not plotted the MWD curves for monoactive and inactive polymer in this case, because the major contribution to the variation of the MWD function in the initial period of polymerization is made by diactive polymer species.

As may be seen from the figures, the smaller the ratio a, the broader the relative MWD curve. In other words, fast initiation leads to a narrow molecular weight distribution.

Evidently, it is the monomer termination that complicates the molecular weight distribution of the polymer generated in such a system at limiting conversion (Equation (57)). But if the polymerization is stopped before it reaches limiting conversion, both initiation and termination may influence the molecular weight distribution obtained from the resultant polymer.

Attempts to test this experimentally have failed because a suitable apparatus is not yet available, and appropriate kinetic data have not yet been published, to our knowledge.

APPENDIX

From Equation (24) we get the recurrence formula for N_n^*:

$$N_n^* = 2b\sum_{j=0}^{n-3}\frac{1}{[\mathrm{D}+(1+b)]^{j+1}}N_{n-j-1}^{**} - 2b\frac{1}{[\mathrm{D}+(1+b)]^{n-2}}N_2^{**} + \frac{1}{[\mathrm{D}+(1+b)]^{n-3}}N_3^* + \sum_{j=0}^{n-4}\frac{1}{[\mathrm{D}+(1+b)]^{j}}\mathrm{e}^{-(1+b)x} = T_1 + T_2 + T_3 + T_4 \tag{A1}$$

By using the linear operator technique, we obtain:

$$T_1 = 2b\sum_{j=0}^{n-3}\frac{I_0 a 2^{n-j-4}}{[2(1+b)-a]^{n-j-2}}\frac{1}{[\mathrm{D}+(1+b)]^{j+1}} \times\left\{\mathrm{e}^{-ax} - \sum_{s=0}^{n-j-3}\frac{\{[2(1+b)-a]x\}^s}{s!}\mathrm{e}^{-2(1+b)x}\right\} = T_{11} + T_{12} \tag{A2}$$

$$T_{11} = I_0 b\mathrm{e}^{-ax}\left\{\frac{1}{(1+b-a)^{n-2}} - \frac{2^{n-2}}{[2(1+b)-a]^{n-2}}\right\} \tag{A3}$$

$$T_{12} = -\frac{2^{n-3}abI_0}{[2(1+b)-a]^{n-2}}\sum_{j=0}^{n-3}\sum_{s=0}^{n-j-3}\sum_{k=0}^{s} \times\left\{(-1)^{j+1}\left(\frac{1}{1+b}\right)\left[\frac{2(1+b)-a}{2(1+b)}\right]^j \times\left[\frac{2(1+b)-a}{1+b}\right]^k \times\binom{j+k}{k}\frac{\{[2(1+b)-a]x\}^{s-k}}{(s-k)!}\mathrm{e}^{-2(1+b)x}\right\} \tag{A4}$$

Let $i = s - k$, then

$$T_{12} = \frac{I_0 ab 2^{n-3} e^{-2(1+b)x}}{(1+b)[2(1+b)-a]^{n-2}} \sum_{i=0}^{n-3} \sum_{j=0}^{n-i-3} \sum_{s=i}^{n-j-3} \times \left\{ \left[-\frac{2(1+b)-a}{2(1+b)} \right]^j \left[\frac{2(1+b)-a}{1+b} \right]^{s-i} \times \binom{j+s-i}{s-i} \frac{\{[2(1+b)-a]x\}^i}{i!} \right\}$$

$$= I_0 b e^{-2(1+b)x} \left\{ \frac{2^{n-2}}{[2(1+b)-a]^{n-2}} \sum_{i=0}^{n-3} \frac{\{[2(1+b)-a]x\}^i}{i!} - \frac{1}{(1+b)^{n-2}} \sum_{i=0}^{n-3} \frac{[2(1+b)x]^i}{i!} \right\} \quad (A5)$$

$$T_2 = \frac{I_0 ab}{2(1+b)-a} \left\{ \frac{e^{-2(1+b)x}}{[-(1+b)]^{n-2}} - \frac{e^{-ax}}{(1+b-a)^{n-2}} \right\} \quad (A6)$$

$$T_3 = \frac{I_0 ab}{2(1+b)-a} \left\{ \frac{e^{-ax}}{(1+b-a)^{n-2}} - \frac{e^{-2(1+b)x}}{[-(1+b)]^{n-2}} \right\} - \frac{I_0 ab}{(1+b)(1+b-a)} \frac{e^{-(1+b)x} x^{n-3}}{(n-3)!} \quad (A7)$$

$$T_4 = \sum_{i=0}^{n-4} c_{n-i} \frac{x^i e^{-(1+b)x}}{i!} \quad (A8)$$

Hence

$$N_n^* = T_{11} + T_{12} + T_2 + T_3 + T_4 \quad (A9)$$

If the initial conditions are substituted into Equation (A9), the integral constants can be ascertained:

$$c_{n-i} = I_0 b \left\{ \frac{1}{(1+b)^{n-i-2}} + \frac{1}{(1+b-a)^{n-i-2}} \right\} \quad (A10)$$

Thus, we obtain Equation (32).

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