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# Graphical Method for Polymerization Kinetics. II. Influence of Monomer Transfer on Molecular Weight Distribution for Anionic Polymerization Initiated by Multifunctional Initiator

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# Graphical Method for Polymerization Kinetics. II. Influence of Monomer Transfer on Molecular Weight Distribution for Anionic Polymerization Initiated by Multifunctional Initiator

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ABSTRACT

This work deals with the kinetics of multifunctional polymerization with instantaneous initiation and monomer transfer. The set of very complicated kinetic differential equations is rigorously solved by a graphical method. Then, the expressions of the molecular weight distribution function, the number- and weight-average degree of polymerization, the distribution of functionality, the average functionality, etc. are obtained. Furthermore, a procedure is proposed for calculating the molecular weight distribution curve and the values of the other molecular parameters mentioned from the initial conditions of the polymerization.

The influence of monomer transfer on the molecular weight distribution of the polymers generated by anionic polymerization initiated by monofunctional initiator has been studied theoretically by several authors [1-6]. Recently, anionic polymerization initiated by multifunctional initiator has also been reported [7]. It is therefore im-



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portant to explore the kinetics of multifunctional polymerization with monomer transfer. In order to simplify the mathematical derivation, the initiation is assumed to be complete instantaneously. A set of linear differential equations as complicated as those treated in this paper is best solved by way of the graphical theory reported previously [8, 9]. Because this work involves a graph with two original vertices, a supplement to the graphical rule is given in the Appendix. After deriving the expressions of the molecular weight distribution function and some molecular parameters of the resultant polymer, these parameters are related to the polymerization conditions, such as the initiator functionality, the initial concentrations of initiator and monomer, constants $k_p$ and $k_{tr}$, and monomer conversion or reaction time, so that this kind of polymerization may be regulated and controlled in accordance with this theory.

## I. DERIVATION OF MOLECULAR WEIGHT DISTRIBUTION FUNCTION

It is assumed that M is the remaining concentration of monomer, r is the functionality of initiator $I_0$, and $N_n^{[r-\ell]}$ is the concentration of the species with $[r - \ell]$ active sites and n monomer units. Because the initiation is accomplished instantaneously, the reaction scheme of the multifunctional polymerization with monomer transfer is as shown. The set of kinetic equations corresponding to this reaction scheme is as follows:

$$\frac{dN_r^{[r]}}{dt} = -r(k_p + k_{tr})MN_r^{[r]} \tag{1}$$

$$\frac{dN_n^{[r]}}{dt} = rk_pMN_{n-1}^{[r]} - r(k_p + k_{tr})MN_n^{[r]}, \quad n > r \tag{2}$$

$$\frac{dN_r^{[r-\ell]}}{dt} = (r-\ell+1)k_{tr}MN_r^{[r-\ell+1]} - (r-\ell)(k_p + k_{tr})MN_r^{[r-\ell]}, \quad \ell = 1, 2, \cdots, (r-2) \tag{3}$$

$$\frac{dN_n^{[r-\ell]}}{dt} = (r-\ell)k_pMN_{n-1}^{[r-\ell]} + (r-\ell+1)k_{tr}MN_n^{[r-\ell+1]} - (r-\ell)(k_p + k_{tr})MN_n^{[r-\ell]}, \quad \ell = 1, 2, \cdots, (r-2) \tag{4}$$

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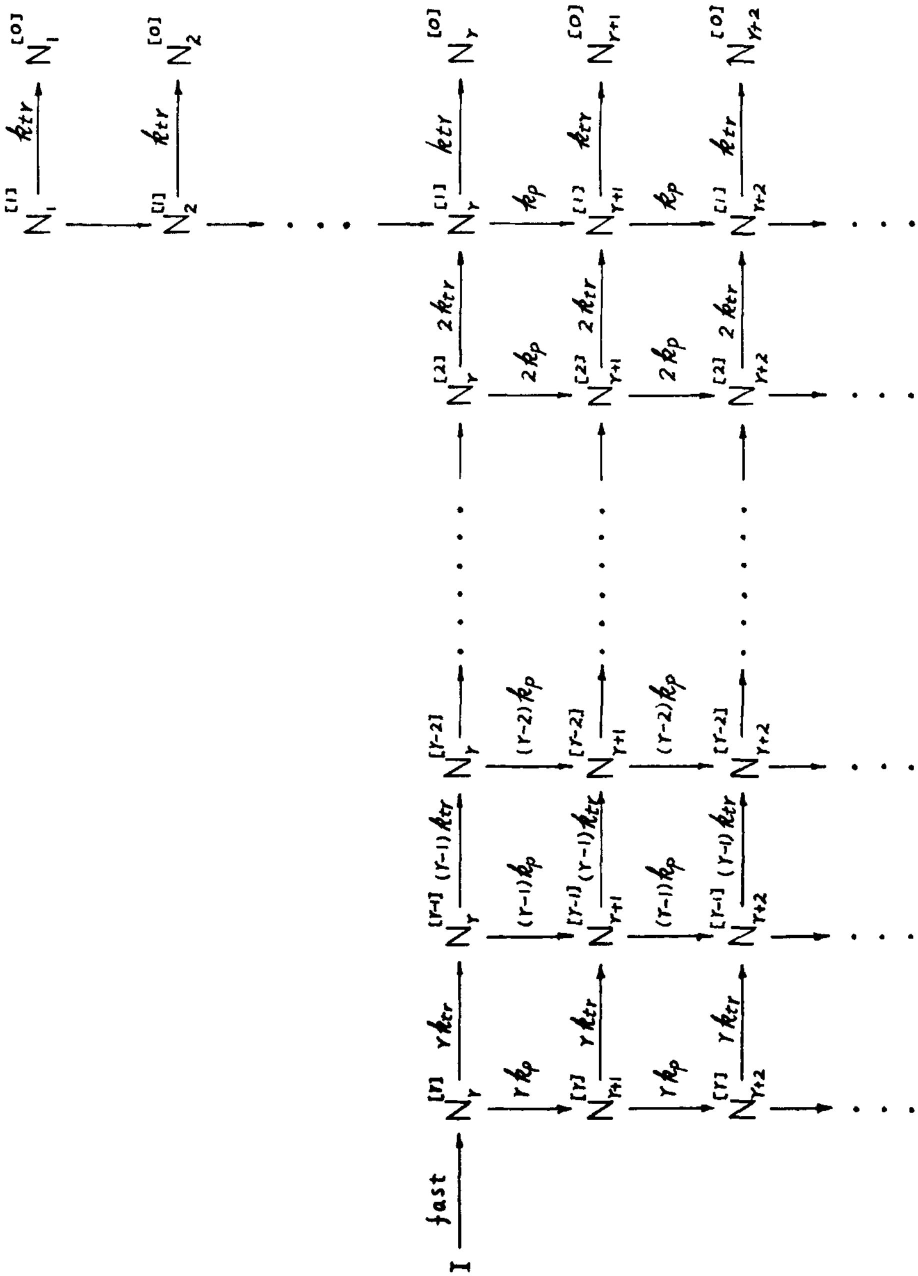

REACTION SCHEME. Monomer has been omitted in every step of the reaction.

$$\frac{dN_1^{[1]}}{dt} = k_{tr}M\sum_{l=0}^{r-2}(r-l)\sum_{n=r}^{\infty}N_n^{[r-l]} + k_{tr}M\sum_{n=1}^{\infty}N_n^{[1]} - (k_p+k_{tr})MN_1^{[1]} \tag{5}$$

$$\frac{dN_K^{[1]}}{dt} = k_pMN_{K-1}^{[1]} - (k_p+k_{tr})MN_K^{[1]}, \qquad 1<K<r \tag{6}$$

$$\frac{dN_n^{[1]}}{dt} = k_pMN_{n-1}^{[1]} + 2k_{tr}MN_n^{[2]} - (k_p+k_{tr})MN_n^{[1]}, \quad n\geq r \tag{7}$$

$$\frac{dN_n^{[0]}}{dt} = k_{tr}MN_n^{[1]} \tag{8}$$

The initial conditions of these differential equations are

$$N_r^{[r]}\Big|_{t=0} = I_0, \quad N_{n>r}^{[r]}\Big|_{t=0} = N_n^{[r-l]}\Big|_{t=0} = 0, \quad l = 1, 2, \cdots, r$$

It is obvious that the polymerization system must undergo the following conservation condition:

$$\sum_{l=0}^{r-2}(r-l)\sum_{n=r}^{\infty}N_n^{[r-l]} + \sum_{n=1}^{\infty}N_n^{[1]} = rI_0 \tag{9}$$

$$\sum_{l=0}^{r-2}\sum_{n=r}^{\infty}nN_n^{[r-l]} + \sum_{n=1}^{\infty}n(N_n^{[1]} + N_n^{[0]}) = M_0 - M \tag{10}$$

where M denotes the monomer concentration added into the reaction system. Putting

$$x = \int_0^{t} k_pM\,dt \tag{11}$$

$$\frac{k_{tr}}{k_p} = b$$

the set of Eqs. (1)-(8) can be transformed into a linear one:

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$$\frac{dN_r^{[r]}}{dx} = -r(1+b)N_r^{[r]} \tag{12}$$

$$\frac{dN_n^{[r]}}{dx} = rN_{n-1}^{[r]} - r(1+b)N_n^{[r]} \quad , \quad n > r \tag{13}$$

$$\frac{dN_r^{[r-l]}}{dx} = (r-l+1)bN_r^{[r-l+1]} - (r-l)(1+b)N_r^{[r-l]} \quad , \tag{14}$$

$$l = 1, 2, \cdots, (r-2)$$

$$\frac{dN_n^{[r-l]}}{dx} = (r-l)N_{n-1}^{[r-l]} + (r-l+1)bN_n^{[r-l+1]} - (r-l)(1+b)N_n^{[r-l]} , \tag{15}$$

$$l = 1, 2, \cdots, (r-2)$$

$$\frac{dN_1^{[1]}}{dx} = rbI_0 - (1+b)N_1^{[1]} \tag{16}$$

$$\frac{dN_K^{[1]}}{dx} = N_{K-1}^{[1]} - (1+b)N_K^{[1]} \quad , \quad 1 < K < r \tag{17}$$

$$\frac{dN_n^{[1]}}{dx} = N_{n-1}^{[1]} + 2bN_n^{[2]} - (1+b)N_n^{[1]} \quad , \quad n \geqslant r \tag{18}$$

$$\frac{dN_n^{[0]}}{dx} = bN_n^{[1]} \tag{19}$$

The initial conditions must be transformed as well:

$$N_r^{[r]}\Big|_{x=0} = I_0 \, , \quad N_{n>r}^{[r]}\Big|_{x=0} = N_n^{[r-l]}\Big|_{x=0} = 0 \, , \quad l = 1, 2, \cdots, r$$

Applying a Laplace transformation to Eqs. (12)-(19), i.e.,

$$M_n^{[r-l]} = \int_0^\infty e^{-\lambda x} N_n^{[r-l]} dx \quad , \quad l \quad 0, 1, 2, \cdots, r \tag{20}$$

$$\lambda M_n^{[r-l]} - N_n^{[r-l]}(x=0) = \int_0^\infty e^{-\lambda x} \frac{dN_n^{[r-l]}}{dx} dx \quad , \quad l = 0, 1, 2, \cdots, r \tag{21}$$

we obtain

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$$\frac{\lambda+(1+b)r}{I_0}M_r^{[r]}=1. \tag{22}$$

$$[\lambda+r(1+b)]M_n^{[r]}-rM_{n-1}^{[r]}=0, \quad n>r. \tag{23}$$

$$[\lambda+(r-l)(1+b)]M_r^{[r-l]}-(r-l+1)bM_r^{[r-l+1]}=0, \quad l=1,2,\cdots,(r-2) \tag{24}$$

$$[\lambda+(r-l)(1+b)]M_n^{[r-l]}-(r-l)M_{n-1}^{[r-l]}-(r-l+1)bM_n^{[r-l+1]}$$
$$=0, \quad l=1,2,\cdots,(r-2). \tag{25}$$

$$\frac{\lambda[\lambda-(1+b)]}{rbI_0}M_1^{[1]}=1. \tag{26}$$

$$[\lambda+(1+b)]M_k^{[1]}-M_{k-1}=0, \quad 1<k<r. \tag{27}$$

$$[\lambda+(1+b)]M_n^{[1]}-M_{n-1}^{[1]}-2bM_n^{[2]}=0, \quad n\geqslant r. \tag{28}$$

$$\lambda M_n^{[0]}-bM_n^{[1]}=0. \tag{29}$$

This algebraic set belongs to the expanded type of set (A1) (see Appendix), the coefficient matrix of which relates to the topology of the set itself, and can be represented by Graph G. There are two original vertices in Graph G, one of which is symbolized by (r, r) and has a weight of $[\lambda + r(1+b)]/I_0$, another one is marked by (1, 1) and possesses a weight $\lambda[\lambda - (1+b)]/rbI_0$. Each of the other vertices is noted by a pair of indices (i, j), where i corresponds to n and j to $(r - \ell)$. The weight of vertex (i, j) is $\lambda + j(1 + b)$, independent of i. This means that the weights of all vertices in a certain column just equal each other. Similarly, the edges between the vertices (i, j) and (i + 1, j) as well as those between (i, j) and (i, j - 1) have the weight -j and -jb, respectively. It is evident that the weights of edges are still independent of the index i, and all the edges in each column have the same weight. For convenience's sake, only the uppermost vertex in each column of Graph G is labeled with the corresponding weight, as is the uppermost edge of every column.

According to the graphical rule [8, 9] and its supplement (see Appendix), the set of algebraic Eqs. (22)-(29) can be solved immediately from Graph G. Because $M_n^{[r]}$ is determined by the only path from (r, r) to (n, r), it is easy to get

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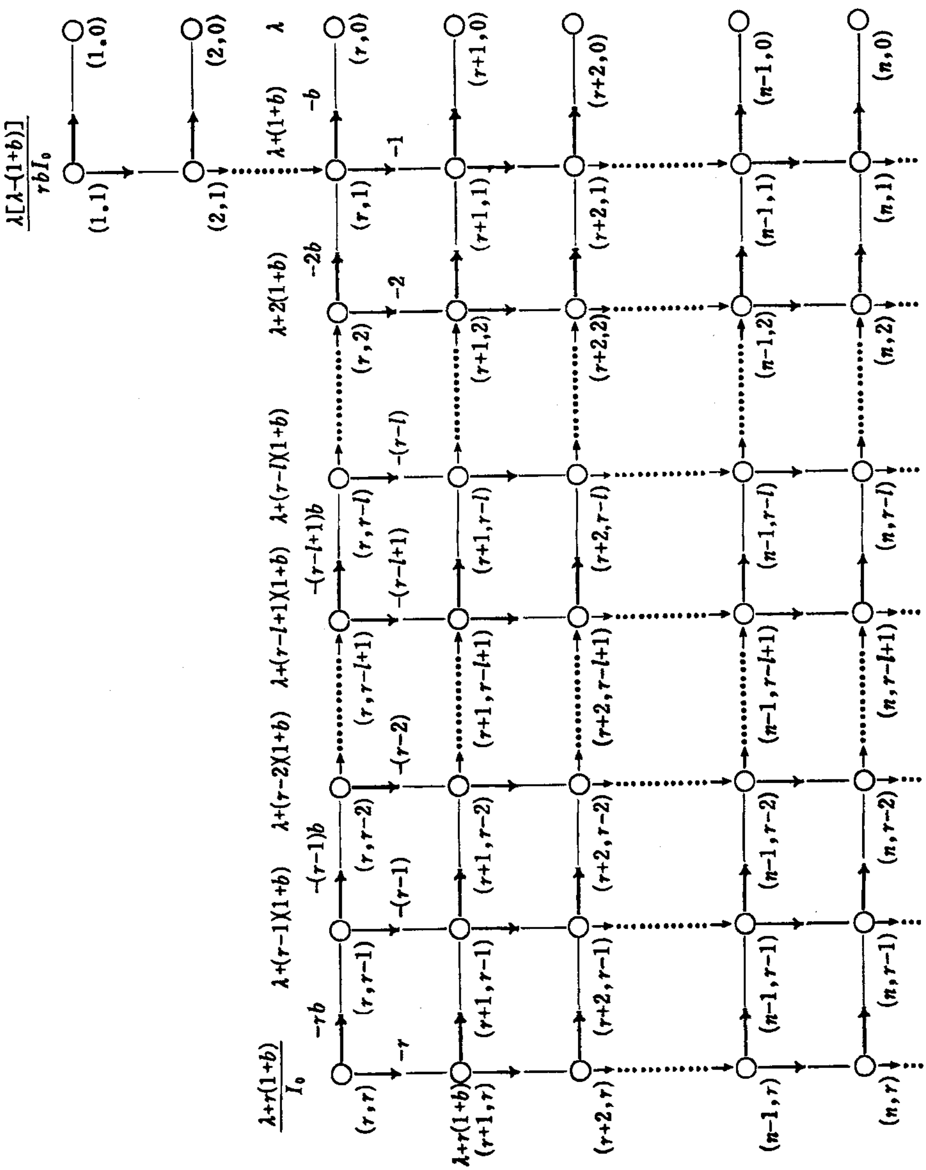


GRAPH G.

$$M_n^{[r]} = \frac{(-1)^{n-r} I_0}{\lambda + r(1+b)} \left\{ \frac{-r}{\lambda + r(1+b)} \right\}^{n-r}. \tag{30}$$

Utilizing the Riemann-Mellin formula,

$$N_n^{[r]} = \frac{1}{2\pi i} \int_{s-i\infty}^{s+i\infty} M_n^{[r]} e^{\lambda x} d\lambda = \sum_j res\,[M_n^{[r]} e^{\lambda x}]_{\lambda_j, e} \tag{31}$$

where s is a positive number, $\lambda_j$ is the j-th pole of $M_n^{[r]}e^{\lambda x}$ at the left side of the complex plane, and res represents the residues. As to $M_n^{[r-\ell]}e^{\lambda x}$, there may be several poles in the imaginary axis. From Eq. (30) it is evident that there is only one pole of the $(n - r + 1)$th order for $M_n^{[r]}e^{\lambda x}$, that is, $\lambda_0 = -(1 + b)r$. Consequently we obtain

$$N_n^{[r]} = res\,(M_n^{[r]} e^{\lambda x})_{\lambda_0} = \frac{I_0 (rx)^{n-r} e^{-r(1+b)x}}{(n-r)!}. \tag{32}$$

When $0 < \ell < r - 1$, for the derivation of the general expression of $M_n^{[r-\ell]}$, it is necessary to take account of the total contribution of all the paths between vertices $(r, r)$ and $(n, r - \ell)$. One of these paths is shown in Fig. 1, which includes $(n - r + \ell + 1)$ vertices and $(n - r + \ell)$ edges. There are $(\alpha_0 + 1)$ vertices and $\alpha_0$ edges in Column 1, Fig. 1. The weight of the vertex $(r, r)$ has been given above. Other vertices of Column 1 have the same weight $\lambda + r(1 + b)$. Each of the $\alpha_0$ edges mentioned has the weight $-r$. In Column 2, there are $(\alpha_1 + 1)$ vertices, each of which possesses weight $\lambda + (r - 1)(1 + b)$, and $\alpha_1$ edges, each of which has weight $-(r - 1), \cdots$. Similarly, in column $(\ell + 1)$, there are $(\alpha_\ell + 1)$ vertices with the same weight $\lambda + (r - \ell)\cdot(1 + b)$ and $\alpha_\ell$ edges with the same weight $-(r - \ell)$. Besides, in Fig. 1 there are $\ell$ edges, each of which connects two neighboring columns with each other, and these edges have the respective weights $-rb$, $-(r - 1)b, \cdots, -(r - \ell + 1)b$. Then the contribution of the path shown in Fig. 1 is

$$(-1)^{n-r+\ell} \frac{[-rb][-(r-1)b]\cdots[-(r-\ell+1)b][-r]^{\alpha_0}[-(r-1)]^{\alpha_1}[-(r-2)]^{\alpha_2}\cdots[-(r-\ell)]^{\alpha_\ell}}{\frac{\lambda+r(1+b)}{I_0}[\lambda+r(1+b)]^{\alpha_0}[\lambda+(r-1)(1+b)]^{\alpha_1+1}[\lambda+(r-2)(1+b)]^{\alpha_2+1}\cdots[\lambda+(r-\ell)(1+b)]^{\alpha_\ell+1}}$$

$$= \frac{I_0 b^\ell}{(r-\ell)\prod_{j=0}^{\ell}\left\{\frac{\lambda+(r-j)(1+b)}{r-j}\right\}^{\alpha_j+1}} \tag{33}$$

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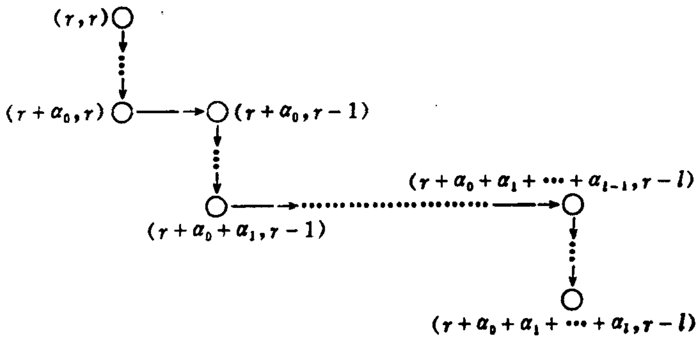


FIG. 1. One of the paths between (r, r) and (n, r - ℓ), $0 < \ell < r - 1$.

Picking up all the contributions of every path from vertex (r, r) to (n, r - ℓ), and putting $\alpha_j + 1 = \beta_j$, we have

$$M_n^{[r-\ell]} = \frac{I_0 b^\ell}{r-\ell} \sum_{\substack{\sum_{j=0}^{\ell}\beta_j = n-r+\ell+1 \\ (n-r+1) \geq \beta_j \geq 1}} \prod_{j=0}^{\ell} \left\{ \frac{\lambda + (r-j)(1+b)}{r-j} \right\}^{-\beta_j} . \tag{34}$$

By the aid of Eq. (21) of Ref. 8, the following equation is derived from Eq. (34):

$$M_n^{[r-\ell]} = I_0 \binom{r}{\ell} \left(\frac{b}{\lambda}\right)^\ell \sum_{j=0}^{\ell} (-1)^j \binom{\ell}{j} (r-j)^{n-r+\ell} \left\{ \lambda + (r-j)(1+b) \right\}^{-(n-r+1)} \tag{35}$$

From Eq. (35) it is known that $M_n^{[r-\ell]} e^{\lambda x}$ has $\ell + 2$ poles, of which $\lambda_0 = 0$ is the $\ell$-th order pole, and $\lambda_j = -(r - j)(1 + b)$ is the $(n - r + 1)$th order pole. We can derive the residue corresponding to every pole separately:

$$\mathrm{res}\,[M_n^{[r-\ell]} e^{\lambda x}]_{\lambda_0} = 0,$$

$$\mathrm{res}\,[M_n^{[r-\ell]} e^{\lambda x}]_{\lambda_j} = I_0 \binom{r}{\ell} \frac{b^\ell}{(1+b)^{n-r+1}} (-1)^{\ell-j} \binom{\ell}{j} \sum_{i=0}^{n-r} \binom{n-r+\ell-i-1}{\ell-1} \frac{[(r-j)(1+b)x]^i e^{-(r-j)(1+b)x}}{i!} \tag{36}$$

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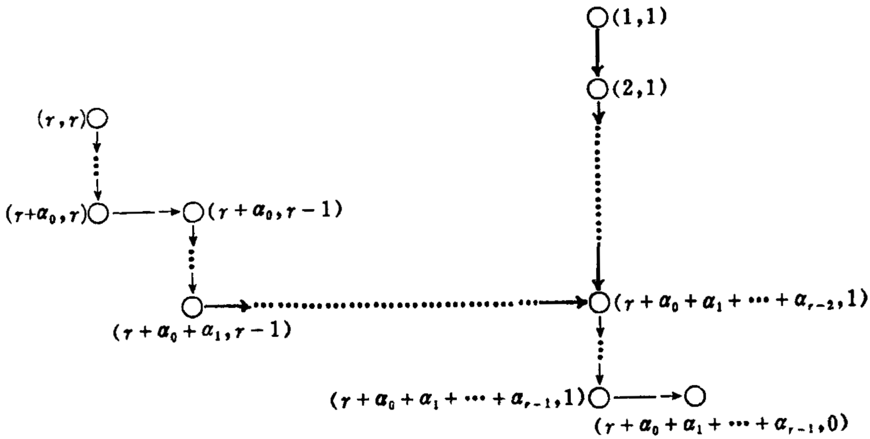


FIG. 2. One of the paths diverting from (r, r) to (n, 0), and the single path from (1, 1) to (n, 0).

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Hence,

$$
\begin{aligned}
N_n^{[r-l]} &= \sum_{j=0}^{l} \operatorname{res}\left[M_n^{[r-l]} e^{\lambda x}\right]_{\lambda_j} \\
&= \frac{I_0 \binom{r}{l} b^l}{(1+b)^{n-r+l}} \sum_{j=0}^{l} (-1)^{l-j} \binom{l}{j} \sum_{i=0}^{n-r} \binom{n-r+l-i-1}{l-1} \frac{[(r-j)(1+b)x]^i e^{-(r-j)(1+b)x}}{i!}
\end{aligned} \tag{37}
$$

For $M_n^{[1]}$ or $M_n^{[0]}$, the contributions of all the paths from (r, r) to (n, 1) or (n, 0) as well as the contribution of the particular path between (1, 1) and (n, 1) or (n, 0) must be taken into account. Figure 2 represents one of the paths from (r, r) to (n, 1) or (n, 0) and the path from (1, 1) to (n, 1) or (n, 0). Such a graph with two vertices as Fig. 2 can be treated according to the theorem given in the Appendix to give the expressions of $M_n^{[1]}$ and $M_n^{[0]}$, then $N_{n\geq r}^{[1]}$ and $N_{n\geq r}^{[0]}$,

$$
\begin{aligned}
N_{n\geq r}^{[1]} &= \frac{I_0 r b}{(1+b)^n}\left\{1 - \sum_{i=0}^{n-1} \frac{[(1+b)x]^i e^{-(1+b)x}}{i!}\right\} + \\
&+ \frac{I_0 \binom{r}{r-1} b^{r-1}}{(1+b)^{n-1}} \sum_{j=0}^{r-1} (-1)^{r-1-j} \binom{r-1}{j} \sum_{i=0}^{n-r} \binom{n-2-i}{r-2} \frac{[(r-j)(1+b)x]^i e^{-(r-j)(1+b)x}}{i!}
\end{aligned} \tag{38}
$$

and

$$N_{n\geq r}^{[0]} = \frac{I_0 r b^2 e^{-(1+b)x}}{(1+b)^{n+1}} \left\{ [(1+b)x - n] \sum_{i=n}^{\infty} \frac{[(1+b)x]^i}{i!} + \frac{[(1+b)x]^n}{(n-1)!} \right\} +$$

$$+ \frac{I_0 b^r}{(1+b)^n} \sum_{j=0}^{r} (-1)^{r-j} \binom{r}{j} \sum_{i=0}^{n-r} \binom{n-1-i}{r-1} \frac{[(r-j)(1+b)x]^i e^{-(r-j)(1+b)x}}{i!} . \tag{39}$$

When $n < r$, only the first term of Eq. (38) or Eq. (39) remains in the expression of $N_n^{[1]}$ or $N_n^{[0]}$. Evidently, the molecular weight distribution function of the total polymers produced in the reaction system is

$$N_n = \sum_{l=0}^{r} N_n^{[r-l]} . \tag{40}$$

So far, the problem given in the title of this paper has been treated rigorously. From the molecular weight distribution function, the expressions for other molecular parameters of the resultant polymer can be derived easily.

## II. SOME MOLECULAR PARAMETERS OF RESULTANT POLYMER

For calculating the number- and weight-average degrees of polymerization, the dispersity, the distribution of functionality, and the average functionality, the various moments of the species with different functionality and the total polymers must first be derived. The following formulas are derived from Eqs. (32), (37), (38), and (39):

$$\sum_{n=1}^{\infty} N_n^{[0]} = I_0 r \left\{ \frac{1}{r} (1 - e^{-bx})^r + bx - (1 - e^{-bx}) \right\} . \tag{41}$$

$$\sum_{n=1}^{\infty} n N_n^{[0]} = I_0 r \left\{ \frac{1+b}{b} (1 - e^{-bx})^r - x e^{-bx} (1 - e^{-bx})^{r-1} + (1+b)x + x e^{-bx} - \left(1 + \frac{2}{b}\right)(1 - e^{-bx}) \right\} . \tag{42}$$

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$$\sum_{n=1}^{\infty} n^2 N_n^{[0]} = I_0 r\{(r-1)x^2 e^{-2bx}(1-e^{-bx})^{r-2} - (\frac{2r}{b}+2r+1+x)xe^{-bx}\cdot$$
$$\cdot(1-e^{-bx})^{r-1} + (\frac{1}{b}+\frac{r+1}{b^2}+\frac{2r}{b}+r)(1-e^{-bx})^r +$$
$$+(1+b)(1+\frac{2}{b})x + x^2 e^{-bx} + (3+\frac{4}{b})xe^{-bx} - (1+\frac{6}{b}+\frac{6}{b^2})(1-e^{-bx})\}. \quad (43)$$

$$\sum_{n=1}^{\infty} N_n^{[1]} = I_0 r\{1 + e^{-bx}(1-e^{-bx})^{r-2}\}(1-e^{-bx}). \quad (44)$$

$$\sum_{n=1}^{\infty} nN_n^{[1]} = I_0 r\{(1+\frac{1}{b})(1-e^{-bx}) - xe^{-bx} + [(1+x+\frac{(r-1)(1+b)}{b})$$

$$(e^{bx}-1) - (r-1)x]e^{-2bx}(1-e^{-bx})^{r-2}\}. \quad (45)$$

$$\sum_{n=1}^{\infty} n^2 N_n^{[1]} = I_0 r\{(1+\frac{3}{b}+\frac{2}{b^2})(1-e^{-bx}) - x^2e^{-bx} - (3+\frac{2}{b})xe^{-bx} + [(r-1)(r-2)x^2 -$$
$$-(r-1)\left(\frac{2(r-1)}{b}+2r+1+3x\right)x(e^{-bx}-1) + \left(\frac{(r-1)}{b}+\frac{r(r-1)}{b^2}+\right.$$
$$\left.+2(r+x)\frac{r-1}{b}+r^2+(2r+1)x+x^2\right)(e^{-bx}-1)^2]e^{-3bx}(1-e^{-bx})^{r-3}\}. \quad (46)$$

For $0 \leq \ell \leq r-2$,

$$\sum_{n=r}^{\infty} N_n^{[r-l]} = I_0\binom{r}{l}e^{-rbx}(e^{bx}-1)^{\ell}. \quad (47)$$

$$\sum_{n=r}^{\infty} nN_n^{[r-l]} = I_0\binom{r}{l}e^{-rbx}(e^{bx}-1)^{l-1}\{[\frac{l(1+b)}{b}+(r-l)(1+x)](e^{bx}-1) - lx\}. \quad (48)$$

$$\sum_{n=r}^{\infty} n^2 N_n^{[r-l]} = I_0\binom{r}{l}e^{-rbx}(e^{bx}-1)^{l-2}\{l(l-1)x^2 - l[\frac{2l}{b}+(2r+1)+$$
$$+(2(r-l)+1)x]x(e^{bx}-1) + [\frac{l}{b}+\frac{l(l+1)}{b^2}+$$
$$+2(r+(r-l)x)\frac{l}{b}+r^2+(2r+1)(r-l)x+(r-l)^2x^2](e^{bx}-1)^2\}. \quad (49)$$

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The moments of the total polymers are:

$$\sum_{n=1}^{\infty} N_n = I_0 \{1 + rbx\}. \tag{50}$$

$$\sum_{n=1}^{\infty} nN_n = I_0 r\{1 + (1+b)x\}. \tag{51}$$

$$\sum_{n=1}^{\infty} n^2 N_n = I_0 r\{r + (1+b)(1+\tfrac{2}{b})x + \tfrac{2}{b}(r-1+\tfrac{r-2}{b})(1-e^{-bx}) - \tfrac{r-1}{b^2}(1-e^{-2bx})\}. \tag{52}$$

According to the definitions, the number- and weight-average degrees of polymerization of the species with various functionalities can be calculated directly (omitted here). Those of total polymers are as follows:

$$\bar{P}_n = r\{1 + (1+b)x\}/\{1 + rbx\}. \tag{53}$$

$$\bar{P}_w = \{r + (1+b)(1+\tfrac{2}{b})x + \tfrac{2}{b}(r-1+\tfrac{r-2}{b})(1-e^{-bx}) - \tfrac{r-1}{b^2}(1-e^{-2bx})\}/\{1+(1+b)x\}. \tag{54}$$

The dispersity of the resultant polymer is determined by the number- and weight-average degrees of polymerization, also omitted. The functionality distribution is given by

$$f_{[r-l]} = \binom{r}{l} e^{-brx}(e^{bx}-1)^l/(1+rbx). \tag{55}$$

$$f_{[1]} = r\{1 + e^{-bx}(1-e^{-bx})^{r-2}\}(1-e^{-bx})/(1+rbx). \tag{56}$$

$$f_{[0]} = r\{\tfrac{1}{r}(1-e^{-bx})^r + bx - (1-e^{-bx})\}/(1+rbx). \tag{57}$$

The average functionality is

$$\bar{f} = 1/(1 + rbx).$$

The weight distribution of functionality can also be obtained from the first-order moments of the species and total polymers when necessary.

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## III. CALCULATION OF MOLECULAR PARAMETERS FROM POLYMERIZATION CONDITION

Even though the expressions of the various molecular parameters were derived in the previous sections, all of them can only be utilized in practice to predict the character of the polymer formed until the value of x is determined. Fortunately, we can relate x to the reaction time or the monomer conversion.

Equation (11) combined with Eq. (51) results in

$$\frac{dx}{dt} = k_p\{M_0 - I_0 r[1+(1+b)x]\}. \tag{59}$$

Solving Eq. (59), we have

$$x = \frac{M_0 - rI_0}{r(1+b)I_0}\left(1 - e^{-k_p r(1+b)I_0 t}\right). \tag{60}$$

On the other hand, another important relation is obtained from Eqs. (10) and (51):

$$x = \frac{M_0 y - rI_0}{r(1+b)I_0}, \tag{61}$$

where

$$y = \frac{M_0 - M}{M_0}, \tag{62}$$

which is the monomer conversion. The relation between the conversion and the reaction time is

$$y = \frac{rI_0 + (M_0 - rI_0)(1 - e^{-k_p r(1+b)I_0 t})}{M_0}. \tag{63}$$

By substituting Eq. (60) or (61) into the appropriate expressions, the dependence of various molecular parameters on time or conversion can be made clear. We have a program by which all the molecular parameters given above can be computed from the polymerization condition in a short time. A few examples are listed below.

### (A). r = 2

In the case of r = 2, there are three species within the polymerization system, i.e., bifunctional, monofunctional, and nonfunctional polymers. Substituting 2 for r in Eqs. (37), (38), and (39), we get the

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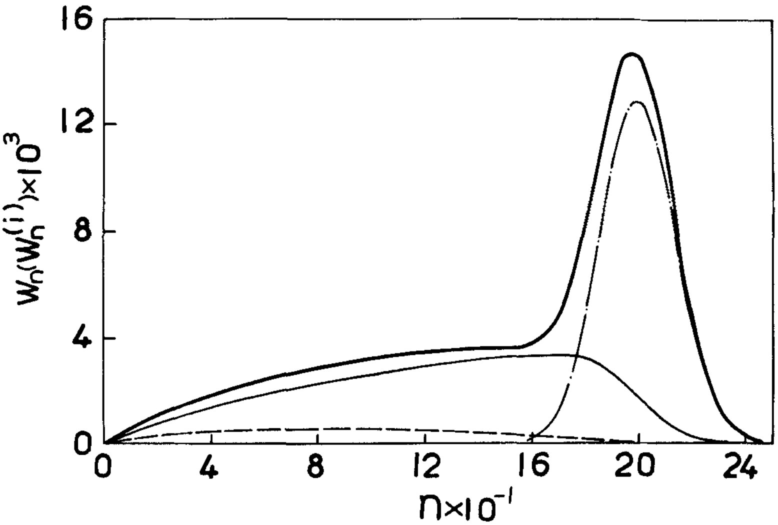


FIG. 3. The plot of the molecular weight distribution of the polymer produced in a bifunctional polymerization with monomer transfer, y = 20%; i = 0, 1, 2; i.e., (–·) $W_n^{[2]} \sim n$, (—) $W_n^{[1]} \sim n$, (- -) $W_n^{[0]} \sim n$, (—) $W_n \sim n$.

expressions of $N_n^{[2]}$, $N_n^{[1]}$, and $N_n^{[0]}$ at once. For $b = 4 \times 10^{-3}$, $I/M = 1 \times 10^{-3}$, and y = 20 and 70%, the molecular weight distribution curves of the total polymer and each species are shown in Figs. 3 and 4, where $W_n^{[2]} = nN_n^{[2]}/\sum_n nN_n$, $W_n^{[1]} = nN_n^{[1]}/\sum_n nN_n$, $W_n^{[0]} = nN_n^{[0]}/\sum_n nN_n$, and $W_n = nN_n/\sum_n nN_n$.

(B). r = 3

Similar to Case (A), four species have been forming during the polymerization. Substituting 3 for r in the related equations, all of the molecular parameters are determined. When $b = 4 \times 10^{-3}$ and $I/M = 1 \times 10^{-3}$, the dependence of the functionality distribution on monomer conversion is illustrated by Fig. 5. For y = 70% and the other conditions the same as those of Fig. 5, the molecular weight distribution curves are given in Fig. 6, where $W_n^{[3]} = nN_n^{[3]}/\sum_n nN_n$. Comparing Fig. 6 with Fig. 4, it is clear that the more functions the initiator has, the more complicated is the plot.

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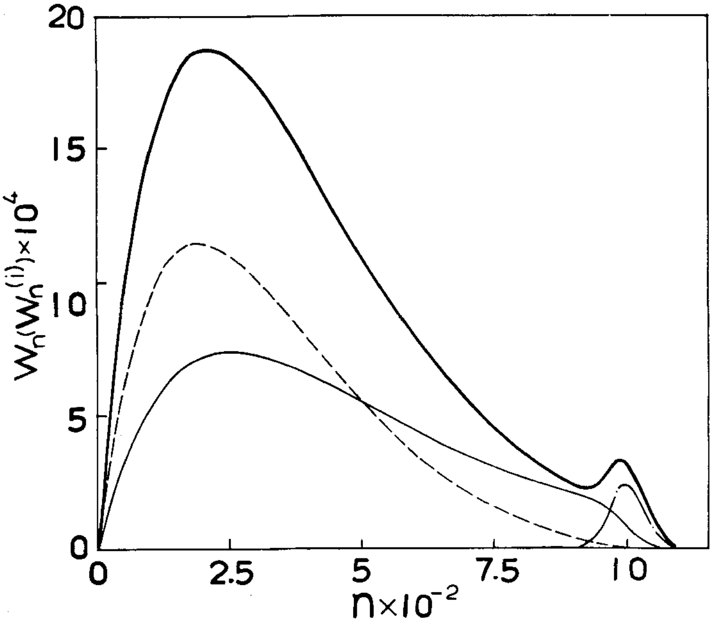


FIG. 4. y = 70%; the other values and symbols are identical with those in Fig. 3.

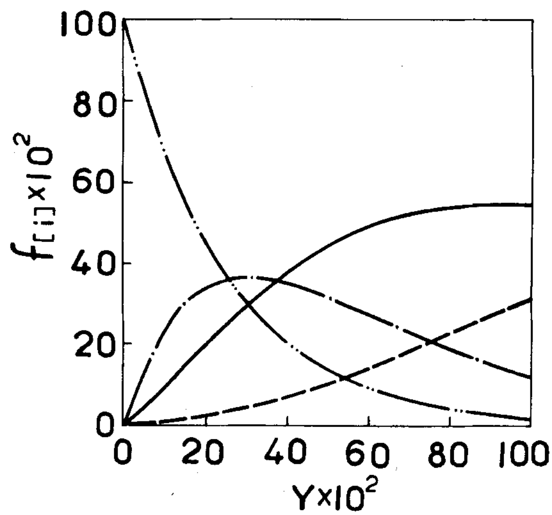


FIG. 5. The functionality varying with conversion, i = 0, 1, 2, 3; i.e., (–·) $f_{[2]} \sim y$, (—) $f_{[1]} \sim y$, (- -) $f_{[0]} \sim y$, (–··) $f_{[3]} \sim y$.

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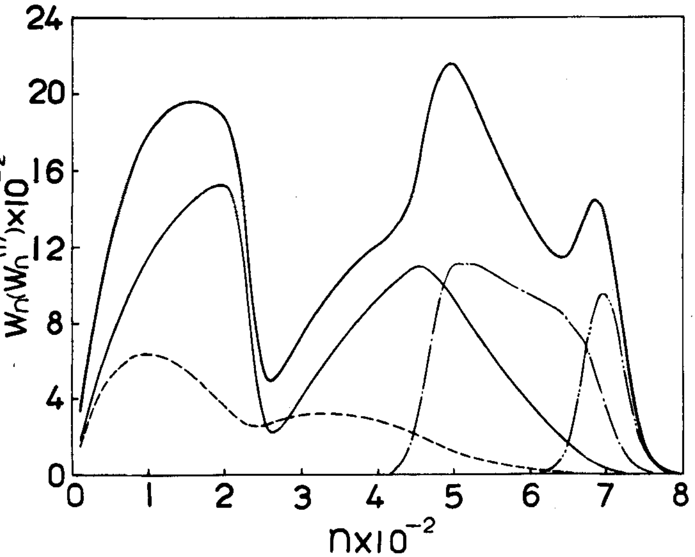


FIG. 6. The plot of the molecular weight distribution of the polymer generated in a trifunctional polymerization with monomer transfer, y = 70%; (—··) $W_n^{[3]} \sim n$. The other lines have the same meanings as those in Fig. 3.

When r = 1, the results obtained are identical with those reported before [6]. If r > 3, we can follow the examples of (A) and (B) to estimate the value of any molecular parameter from the related polymerization condition.

## APPENDIX

There is a linear set of algebraic equations, for instance,

$$\begin{pmatrix} a_{11} & & & & & & & \\ a_{12} & a_{22} & & & & & 0 & \\ a_{13} & a_{23} & a_{33} & & & & & \\ 0 & \cdots & 0 & a_{44} & & & & \\ \vdots & & \vdots & a_{45} & a_{55} & & & \\ 0 & \cdots & 0 & 0 & a_{56} & a_{66} & & \\ a_{17} & a_{27} & a_{37} & \vdots & \ddots & a_{67} & a_{77} & \\ a_{18} & a_{28} & a_{38} & 0 & \cdots & 0 & a_{78} & a_{88} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ x_8 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \\ 0 \\ \vdots \\ \vdots \\ 0 \end{pmatrix} \tag{A1}$$

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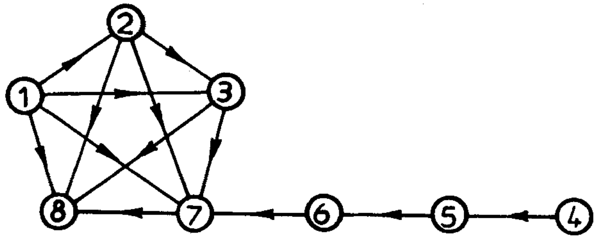


GRAPH $G_8$. A graph with a pair of original vertices.

The triangle matrix relates to the topology of algebraic set (A1) which is represented by the graph with two original vertices, i.e., $G_8$. Vertex i (= 1, 2, ..., 8) in Graph G has weight $a_{ii}$ and the edge diverting from vertex i to j (> i) has weight $a_{ij}$. Both vertices 1 and 4 are defined as the original vertices.

Every root $x_i$ of set (A1) can be derived from $G_8$ in terms of the graphical rule. Our previous work [8] gives the method for finding $x_1$, $x_2$, $x_3$, as well as $x_4$, $x_5$, $x_6$. As for $x_7$ and $x_8$, the whole contribution of all the paths diverting from both original vertices to vertex 7 or 8 must be taken into account. For example, the derivation of $x_7$ is as follows:

| | |
|---|---|
| $1 \to 2 \to 3 \to 7$ | $(-1)^3 \dfrac{a_{12}\,a_{23}\,a_{37}}{a_{11}\,a_{22}\,a_{33}\,a_{77}}$ |
| $1 \to 2 \to 7$ | $(-1)^2 \dfrac{a_{12}\,a_{27}}{a_{11}\,a_{22}\,a_{77}}$ |
| $1 \to 3 \to 7$ | $(-1)^2 \dfrac{a_{13}\,a_{37}}{a_{11}\,a_{33}\,a_{77}}$ |
| $1 \to 7$ | $(-1) \dfrac{a_{17}}{a_{11}\,a_{77}}$ |
| $4 \to 5 \to 6 \to 7$ | $(-1)^3 \dfrac{a_{45}\,a_{56}\,a_{67}}{a_{44}\,a_{55}\,a_{66}\,a_{77}}$ |

then

$$x = -\frac{a_{12}a_{23}a_{37}}{a_{11}a_{22}a_{33}a_{77}} + \frac{a_{12}a_{27}}{a_{11}a_{22}a_{77}} + \frac{a_{13}a_{37}}{a_{11}a_{33}a_{77}} - \frac{a_{17}}{a_{11}a_{77}} - \frac{a_{45}a_{56}a_{67}}{a_{44}a_{55}a_{66}a_{77}} \quad \text{(A2)}$$

The expression of root $x_8$ can be obtained by analogy.

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