Kinetics of free-radical copolymerization: the pseudo-kinetic rate constant method

Hidetaka Tobita*
Process Technology Institute, Kao Corporation, 1334 Minato, Wakayama-Shi, Wakayama, 640 Japan

and Archie E. Hamielec
McMaster Institute for Polymer Production Technology, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7
(*Received 31 July 1990; accepted 7 September 1990*)

The pseudo-kinetic rate constant method in which the kinetic treatment of a multicomponent polymerization reduces to that of a homopolymerization is a useful tool to analyse the kinetics of copolymerization. This method is applicable not only for the systems described by the terminal model for copolymerization but also for those described by the higher order Markov chain statistics such as the penultimate model. It has also been clarified that this method can practically be applicable even when the effect of the chain length dependent bimolecular termination reaction is significant.

(Keywords: copolymerization; kinetics; free-radical polymerization; multicomponent; diffusion-controlled termination; molecular weight distribution)

INTRODUCTION

Conventionally, copolymer composition has been the main interest in the study of the kinetics of copolymerization. However, in order to synthesize superior quality polymers, control of the molecular weight distribution (*MWD*) as well as that of the copolymer composition distribution is important. It is well known that free-radical copolymerization involves various elementary reactions and that as the number of components increases the kinetic expressions become fairly complicated. In order to avoid such complications, the pseudo-kinetic rate constant method has been developed.

The pseudo-kinetic rate constant method has been applied to some copolymerization kinetic studies[1–3], and recently a kinetic model for non-linear copolymerization has also been developed[4–7] based on this method. It is important to clarify where specific approximations are made and where these approximations are acceptable. Furthermore, it is of great interest to know whether this method is applicable when chain length dependent bimolecular termination of polymer radicals is significant.

In this paper, after clarifying the meaning of the pseudo-kinetic rate constant method, it is extended to the systems with chain length dependent bimolecular termination, multicomponent polymerization and to those described by the penultimate model for copolymerization.

THE PSEUDO-KINETIC RATE CONSTANT METHOD

Based on the terminal model for copolymerization, the pseudo-kinetic rate constants for propagation reaction, k_p, chain transfer to monomer, k_{fm}, chain transfer to small molecule (T), k_{fT}, termination by disproportionation, k_{td}, and termination by combination, k_{tc}, are given by the following equations[1–7]:

$$k_p = \sum_{i=1}^{N} \sum_{j=1}^{N} k_{ij} \phi_i^{\cdot} f_j \tag{1}$$

$$k_{fm} = \sum_{i=1}^{N} \sum_{j=1}^{N} k_{f_{ij}} \phi_i^{\cdot} f_j \tag{2}$$

$$k_{fT} = \sum_{i=1}^{N} k_{fT_i} \phi_i^{\cdot} \tag{3}$$

$$k_{td} = \sum_{i=1}^{N} \sum_{j=1}^{N} k_{td_{ij}} \phi_i^{\cdot} \phi_j^{\cdot} \tag{4}$$

$$k_{tc} = \sum_{i=1}^{N} \sum_{j=1}^{N} k_{tc_{ij}} \phi_i^{\cdot} \phi_j^{\cdot} \tag{5}$$

where N is the number of components, and k_{ij} and $k_{f_{ij}}$ are the kinetic rate constants for propagation and chain transfer to monomer, respectively, and the subscripts i and j are used to designate the type of polymer radical and monomer, respectively. The kinetic rate constant, k_{fT_i} is used for chain transfer to small molecule (T), and $k_{td_{ij}}$ and $k_{tc_{ij}}$ are for termination reactions by disproportionation and combination, respectively. The mole fraction of radical of type i is $\phi_i^{\cdot}$, namely:

$$\phi_i^{\cdot} = [R_i^{\cdot}] \Big/ \sum_{i=1}^{N} [R_i^{\cdot}] = [R_i^{\cdot}]/[R^{\cdot}] \tag{6}$$

where $[R_i^{\cdot}]$ is the polymer radical concentration whose radical centre is located on monomer unit i.

The mole fraction of monomer j in the monomer mixture is f_j, namely:

$$f_j = [M_j] \Big/ \sum_{j=1}^{N} [M_j] = [M_j]/[M] \tag{7}$$

---

* To whom correspondence should be addressed. Present address: Department of Materials Science and Engineering, Fukui University, Fukui, 910 Japan

0032-3861/91/142641-07

(In the bimolecular termination reactions, chemically controlled termination reactions are assumed. However, since termination reactions in free-radical polymerization are controlled by diffusion even from the start of the polymerization[8–11], equations (4) and (5) must be modified using an appropriate model which accounts for the diffusion-controlled termination reactions[12–14]. However, such modification is not essential in the context of this paper.)

By application of the pseudo-kinetic rate constants defined by equations (1)–(5), the rate expressions for each type of reaction reduce to those of homopolymerization. For example, the polymerization rate (propagation rate), R_p, and the termination rate, R_t, are given by:

$$R_p = \mathrm{k}_p[\mathrm{R}^\cdot][\mathrm{M}] \tag{8}$$

$$R_t = (\mathrm{k}_{td} + \mathrm{k}_{tc})[\mathrm{R}^\cdot]^2 \tag{9}$$

where $[\mathrm{R}^\cdot]$ is the total polymer radical concentration and $[\mathrm{M}]$ is the total monomer concentration.

These rate expressions are exact, however, it is not self-evident whether these pseudo-kinetic rate constants can be used for the calculation of the *MWD* of copolymers. In the appendix of an earlier paper[4], the necessary condition for the pseudo-kinetic rate constants to be used to calculate the chain length distribution was shown to be that the mole fraction of the polymer radical type is independent of chain length, namely:

$$\phi_1^\cdot = \phi_{1,1}^\cdot = \phi_{2,1}^\cdot = \cdots = \phi_{r,1}^\cdot = \cdots \tag{10a}$$

$$\phi_2^\cdot = \phi_{1,2}^\cdot = \phi_{2,2}^\cdot = \cdots = \phi_{r,2}^\cdot = \cdots \tag{10b}$$

$$\phi_3^\cdot = \phi_{1,3}^\cdot = \phi_{2,3}^\cdot = \cdots = \phi_{r,3}^\cdot = \cdots \tag{10c}$$

$$\vdots$$

where $\phi_{r,1}^\cdot$ is the mole fraction of the polymer radicals of type 1 with chain length r, namely:

$$\phi_{r,1}^\cdot = [\mathrm{R}_{r,1}^\cdot] \Big/ \sum_{i=1}^{N} [\mathrm{R}_{r,i}^\cdot] = [\mathrm{R}_{r,1}^\cdot]/[\mathrm{R}_{r,*}^\cdot] \tag{11}$$

It is obvious that if $\phi_{1,1}^\cdot \neq \phi_1^\cdot$, equation (10a) is mathematically incorrect. However, if $\phi_{r,1}^\cdot$ converges rapidly enough to its overall value, $\phi_1^\cdot$, equation (10a) may be practically satisfied. It is expected that the effect of initial transients of the type of polymer radicals with respect to their chain lengths is negligibly small for very long polymer chains[15,16]. Previously, the necessary condition for equation (10a) to be practically satisfied was stated to be that the variance of copolymer composition distribution for copolymers produced instantaneously (in a very small time interval) is negligibly small[4]. However, as shown by the Stockmayer bivariate distribution of chain length and composition[17], it may take chain lengths greater than several hundred for the variance of copolymer composition distribution to be negligible (see, for example, Figure 1 of ref. 4). It may have been considered that the pseudo-kinetic rate constant method is just an approximation, and may be applicable only for copolymers with very high molecular weights. However, in terms of the chain length distribution, the applicability of this method may be higher than expected previously. Let us clarify how fast $\phi_{r,1}^\cdot$ reaches the steady state.

BINARY SYSTEMS

Initial transition of the mole fraction of polymer radicals ($\phi_{r,1}^\cdot$)

By application of the stationary-state hypothesis (SSH) for polymer radicals with chain length r, the concentration of polymer radicals of type i, $[\mathrm{R}_{r,i}^\cdot]$, is given by[7]:

$$([\mathrm{R}_{1,1}^\cdot], [\mathrm{R}_{1,2}^\cdot]) = (i_1, i_2)\begin{bmatrix} U_1P_{11}/\mathrm{k}_{11} & 0 \\ 0 & U_2P_{22}/\mathrm{k}_{22} \end{bmatrix} \tag{12}$$

$$([\mathrm{R}_{r,1}^\cdot], [\mathrm{R}_{r,2}^\cdot]) = ([\mathrm{R}_{r-1,1}^\cdot], [\mathrm{R}_{r-1,2}^\cdot]) \times \begin{bmatrix} U_1P_{11} & U_2P_{22}\mathrm{k}_{12}/\mathrm{k}_{22} \\ U_1P_{11}\mathrm{k}_{21}/\mathrm{k}_{11} & U_2P_{22} \end{bmatrix} \quad (r \geqslant 2) \tag{13}$$

where $i_1[\mathrm{M}_1]$ and $i_2[\mathrm{M}_2]$ give the formation rate of $\mathrm{R}_{1,1}^\cdot$ and $\mathrm{R}_{1,2}^\cdot$, respectively. For example, i_1 is given by:

$$i_1 = \mathrm{k}_1[\mathrm{R}_{in}^\cdot] + \mathrm{k}_{f_{11}}[\mathrm{R}_1^\cdot] + \mathrm{k}_{f_{21}}[\mathrm{R}_2^\cdot] + \mathrm{k}_{p1}'[\mathrm{T}^\cdot] \tag{14}$$

where $[\mathrm{R}_{in}^\cdot]$ is the initiator radical concentration, k_1 is the rate constant for initiation reaction between $\mathrm{R}_{in}^\cdot$ and M_1, and k_{p1}' is the rate constant for re-initiation between $\mathrm{T}^\cdot$ and M_1. The probabilities of growth for polymer radicals of types 1 and 2, respectively, are U_1 and U_2 and are given by:

$$U_1 = \frac{\mathrm{k}_{11}[\mathrm{M}_1] + \mathrm{k}_{12}[\mathrm{M}_2]}{\mathrm{k}_{11}[\mathrm{M}_1] + \mathrm{k}_{12}[\mathrm{M}_2] + t_1} \tag{15}$$

$$U_2 = \frac{\mathrm{k}_{21}[\mathrm{M}_1] + \mathrm{k}_{22}[\mathrm{M}_2]}{\mathrm{k}_{21}[\mathrm{M}_1] + \mathrm{k}_{22}[\mathrm{M}_2] + t_2} \tag{16}$$

where $t_1[\mathrm{R}_{r,1}^\cdot]$ is the production rate of dead polymers from $\mathrm{R}_{r,1}^\cdot$ and t_1 is given by:

$$t_1 = (\mathrm{k}_{td_{11}} + \mathrm{k}_{tc_{11}})[\mathrm{R}_1^\cdot] + (\mathrm{k}_{td_{12}} + \mathrm{k}_{tc_{12}})[\mathrm{R}_2^\cdot] + \mathrm{k}_{f_{11}}[\mathrm{M}_1] + \mathrm{k}_{f_{12}}[\mathrm{M}_2] + \mathrm{k}_{fT_1}[\mathrm{T}] \tag{17}$$

with a similar definition for t_2. P_{11} is the probability that a growing polymer chain with M_1 end adds another M_1 unit (for a binary system with terminal model, $P_{11} = \mathrm{k}_{11}[\mathrm{M}_1]/(\mathrm{k}_{11}[\mathrm{M}_1] + \mathrm{k}_{12}[\mathrm{M}_2])$), and P_{22} is the probability that a growing polymer chain with M_2 end adds another M_2 unit.

Table 1 shows some of the calculation conditions and their calculated results. In all cases shown in *Table 1*, the mole fraction of radical of type 1 with chain length r ($\phi_{r,1}^\cdot$) reaches its steady state within 10 steps, which is usually negligibly small compared with the whole chain length of a polymer chain. However, it is worth noting that the limiting radical fraction, $\phi_{\infty,1}^\cdot$ must coincide with the overall value, $\phi_1^\cdot$ in order for equation (10a) to be applicable. Next, let us examine the limiting radical fraction, $\phi_{\infty,1}^\cdot$, and the overall (average) mole fraction of radical of type 1, $\phi_1^\cdot$.

Limiting and overall radical fraction

From equation (13), $[\mathrm{R}_{r,1}^\cdot]/[\mathrm{R}_{r,2}^\cdot]$ ($= A_r$) is given by:

$$A_r = \frac{[\mathrm{M}_1]}{[\mathrm{M}_2]} \times \frac{U_1(\mathrm{k}_{22}[\mathrm{M}_2] + \mathrm{k}_{21}[\mathrm{M}_1])}{U_2(\mathrm{k}_{11}[\mathrm{M}_1] + \mathrm{k}_{12}[\mathrm{M}_2])} \times \frac{\mathrm{k}_{11}A_{r-1} + \mathrm{k}_{21}}{\mathrm{k}_{22} + \mathrm{k}_{12}A_{r-1}} \tag{18}$$

If A_r converges to A, A must satisfy the following quadratic equation:

$$A^2 + (\mathrm{k}_{21}/\mathrm{k}_{12})(r_2 - \mu r_1)A - (\mathrm{k}_{21}/\mathrm{k}_{12})^2\mu = 0 \tag{19}$$

Table 1 Calculation conditions and calculated mole fraction of radical of type 1 ($\phi_{r,1}^{\cdot}$)

Calculation conditions[a]

	I	II	III	IV
U_1/U_2	1	1	0.99	0.9
i_1/i_2	1	2	1	1

Calculated results

	$\phi_{r,1}^{\cdot}$			
r	I	II	III	IV
1	0.35443	0.52336	0.35213	0.33071
2	0.41063	0.36819	0.40872	0.39061
3	0.39744	0.40748	0.39549	0.37719
4	0.40061	0.39820	0.39866	0.38027
5	0.39985	0.40043	0.39791	0.37956
6	0.40004	0.39990	0.39809	0.37973
7	0.39999	0.40002	0.39805	0.37969
8	0.40000	0.39999	0.39806	0.37970
9	0.40000	0.40000	0.39805	0.37970
10	0.40000	0.40000	0.39805	0.37970
∞	0.4	0.4	0.39805	0.37970
$\phi_1^{\cdot}$[b]	0.4	0.4	0.39795	0.37855

[a] $r_1=0.4$, $r_2=0.6$, $f_1=0.25$, $\mathrm{k}_{21}/\mathrm{k}_{12}=2$

[b] $\phi_1^{\cdot}$ changes with the absolute values of U_1 and U_2. Values shown are based on $U_2=1$

where r_1 and r_2 are reactivity ratios, and:

$$\mu=\frac{f_1(r_2f_2+f_1)U_1}{f_2(r_1f_1+f_2)U_2} \tag{20}$$

When $U_1/U_2=1$, $A=\mathrm{k}_{21}f_1/(\mathrm{k}_{12}f_2)$, so that:

$$\phi_{\infty,1}^{\cdot}=\frac{\mathrm{k}_{21}f_1}{\mathrm{k}_{21}f_1+\mathrm{k}_{12}f_2} \qquad (U_1/U_2=1) \tag{21}$$

However, in general, $\phi_{\infty,1}^{\cdot}$ changes with the ratio U_1/U_2.

Next, let us consider the overall polymer radical fraction $\phi_1^{\cdot}$. By application of the SSH for $[\mathrm{R}_1^{\cdot}]$ and $[\mathrm{R}_2^{\cdot}]$, the ratio $[\mathrm{R}_1^{\cdot}]/[\mathrm{R}_2^{\cdot}]$ is given by[7]:

$$\frac{[\mathrm{R}_1^{\cdot}]}{[\mathrm{R}_2^{\cdot}]}=\frac{(\mathrm{k}_{21}/\mathrm{k}_{12})\{I_1[(1-U_2)/U_2](r_2f_2+f_1)+f_1\}}{I_2[(1-U_1)/U_1](r_1f_1+f_2)+f_2} \tag{22}$$

where $I_1=i_1[\mathrm{M}_1]/(i_1[\mathrm{M}_1]+i_2[\mathrm{M}_2])$ and $I_2=1-I_1$.

Therefore, the overall radical fraction $\phi_1^{\cdot}$ is dependent on the absolute value of U_1 and U_2. If U_1 and U_2 are very close to unity, equation (22) can be approximated by:

$$\phi_1^{\cdot}=\frac{\mathrm{k}_{21}f_1}{\mathrm{k}_{21}f_1+\mathrm{k}_{12}f_2} \tag{23}$$

As shown in equations (21) and (23), if U_1 and U_2 are very close to unity, $\phi_{\infty,1}^{\cdot}$ is practically equal to $\phi_1^{\cdot}$. The calculated results for $\phi_{\infty,1}^{\cdot}$ and $\phi_1^{\cdot}$ are also shown in *Table 1*. *Figure 1* shows the change in the difference between $\phi_{\infty,1}^{\cdot}$ and $\phi_1^{\cdot}$, and that of the number-average chain length of polymer radicals, $\bar{P}_\mathrm{N}^{\cdot}$, as a function of U_1 under the condition of $U_2=1.0$. When $\bar{P}_\mathrm{N}^{\cdot}$ is larger than a few hundred, the assumption that $\phi_{\infty,1}^{\cdot}=\phi_1^{\cdot}$ may be practically acceptable as shown in *Figure 1*. Furthermore, when $\bar{P}_\mathrm{N}^{\cdot}$ is larger than a few hundred, the contribution of polymer radicals with chain length smaller than 10 in which the fluctuation in radical fraction is significant may be negligible with respect to the chain length distribution.

Note, $\bar{P}_\mathrm{N}^{\cdot}$ is equal to that of dead polymers $\bar{P}_\mathrm{N}$, if termination reactions by combination do not occur. Roughly speaking, the necessary condition for the application of the pseudo-kinetic rate constant method to the calculation of the chain length distribution is that $\bar{P}_\mathrm{N}$ is larger than a few hundred. Incidentally, it is worth noting that the usual copolymer composition equation based on the terminal model[18–20], which is sometimes called the Mayo–Lewis equation, assumes that equation (23) is valid, and therefore, the condition that $\bar{P}_\mathrm{N}$ is larger than a few hundred is also necessary for the application of the usual copolymer composition equation.

A comparison of the chain length distribution of the polymer radicals is shown in *Figure 2*. The prediction by the pseudo-kinetic rate constant method agrees satisfactorily for $r \geqslant 5$. Even when $\bar{P}_\mathrm{N}^{\cdot}$ is as low as 31.3, the error caused by the use of the pseudo-kinetic rate constant method may be small as shown in *Figure 3a*

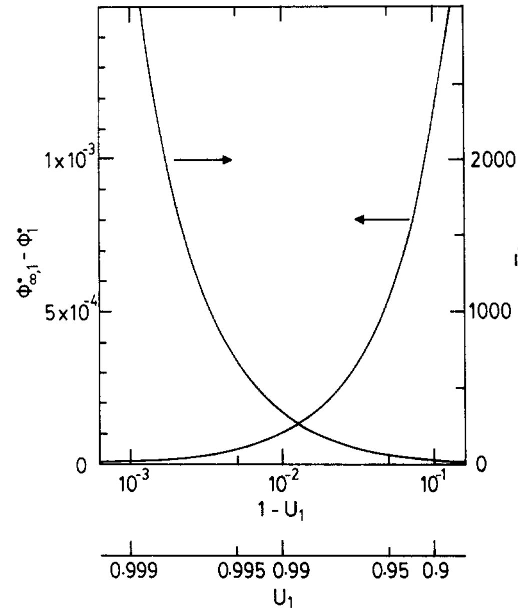

Figure 1 Differences of $\phi_{\infty,1}^{\cdot}$ and $\phi_1^{\cdot}$ and the number-average chain length of polymer radicals, $\bar{P}_\mathrm{N}^{\cdot}$, as a function of U_1 ($U_2=1.0$, $r_1=0.4$, $r_2=0.6$, $f_1=0.25$, $\mathrm{k}_{21}/\mathrm{k}_{12}=2$, $i_1/i_2=1.0$)

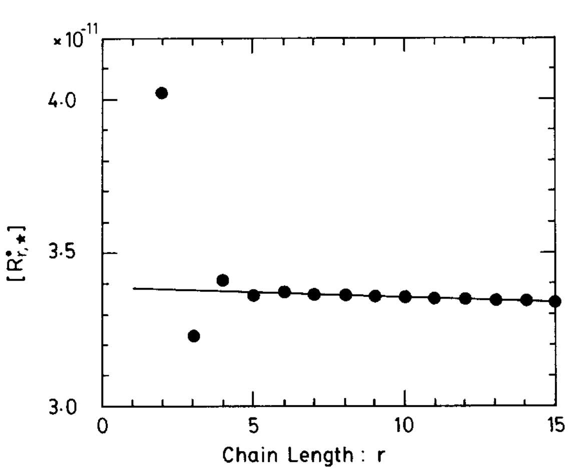

Figure 2 Polymer radical concentration, $[\mathrm{R}_{r,*}^{\cdot}]$, as a function of chain length, r ($\bar{P}_\mathrm{N}^{\cdot}=933$, $\mathrm{k}_{11}=400$, $\mathrm{k}_{12}=1000$, $\mathrm{k}_{21}=200$, $\mathrm{k}_{22}=120$, $[\mathrm{M}_1]=2$, $[\mathrm{M}_2]=6$, $\phi_{1,1}^{\cdot}=1.0$, $R_\mathrm{I}=5\times10^{-8}$, $\mathrm{k}_\mathrm{t}=5\times10^{7}$). ●, Exact solution; ——, pseudo-kinetic rate constant method

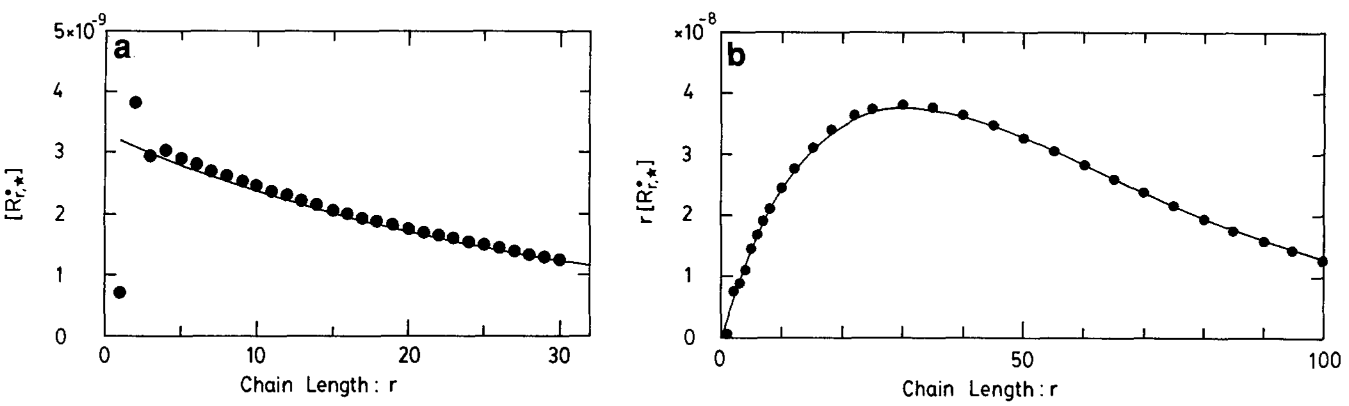

Figure 3 (a) Polymer radical concentration, $[\mathrm{R}_{r,*}^{\bullet}]$, as a function of chain length, r ($\bar{P}_{\mathrm{N}}^{\bullet}=31.3$, $R_{\mathrm{I}}=5\times10^{-6}$, $\mathrm{k_t}=5\times10^{8}$. Other conditions are the same as in *Figure 2*). (b) Polymer radical concentration by weight, $r\,[\mathrm{R}_{r,*}^{\bullet}]$, as a function of chain length, r. Calculation conditions are the same as in (a). Even when the number-average chain length is as low as 31.3, the difference between the exact solution and the pseudo-kinetic rate constant method may be small. ●, Exact solution; ——, pseudo-kinetic rate constant method

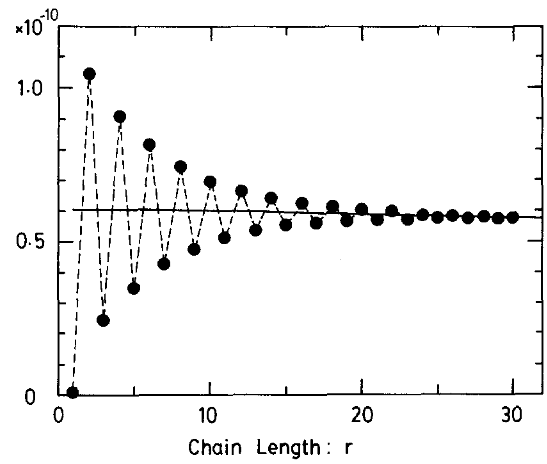

Figure 4 Polymer radial concentration, $[\mathrm{R}_{r,*}^{\bullet}]$, as a function of chain length, r (strong alternating tendency, $\bar{P}_{\mathrm{N}}^{\bullet}=520$, $\mathrm{k}_{11}=40$, $\mathrm{k}_{12}=1000$, $\mathrm{k}_{21}=200$, $\mathrm{k}_{22}=12$. Other conditions are the same as in *Figure 2*). - - ● - -, Exact solution; ——, pseudo-kinetic rate constant method

and *b*. (Please note that the distribution of $[\mathrm{R}_{r,*}^{\bullet}]$ and $r[\mathrm{R}_{r,*}^{\bullet}]$ is equivalent to the instantaneous number- and weight-chain length distribution of dead polymers, if the effect of termination reaction by combination is negligible.) Another example in which the alternating tendency is strong is shown in *Figure 4*. It may take longer to reach the steady state when the alternating tendency or block character is strong, however, it may be considered that the pseudo-kinetic rate constant method is valid for the most statistical copolymerization systems. The weight-chain length distribution, $W^*(r)$, is therefore given by (see Appendix):

$$W^*(r)=(\tau+\beta)[\tau+(\beta/2)(\tau+\beta)(r-1)]r\Phi^{r+1} \tag{24}$$

where

$$\tau=(R_{\mathrm{f}}+R_{\mathrm{td}})/R_{\mathrm{p}} \tag{25}$$

$$\beta=R_{\mathrm{tc}}/R_{\mathrm{p}} \tag{26}$$

$$\Phi=1/(1+\tau+\beta) \tag{27}$$

and R_{p} = propagation rate ($=\mathrm{k_p}[\mathrm{R}^{\bullet}][\mathrm{M}]$), R_{f} = rate of chain transfer ($=\{\mathrm{k_{fm}}[\mathrm{M}]+\mathrm{k_{fT}}[\mathrm{T}]\}[\mathrm{R}^{\bullet}]$), R_{td} = rate of termination by disproportionation ($=\mathrm{k_{td}}[\mathrm{R}^{\bullet}]^2$) and R_{tc} = rate of termination by combination ($=\mathrm{k_{tc}}[\mathrm{R}^{\bullet}]^2$).

Equation (24) is not the *MWD*, however, since the variance of copolymer composition distribution is negligibly small when the chain length r is larger than a few hundred[17]. Equation (24) can easily be transformed into the *MWD* by the use of the average molecular weight of comonomers ($M_{\mathrm{av}}=M_{\mathrm{w1}}\bar{F}_1+M_{\mathrm{w2}}\bar{F}_2$) for such chain lengths. Furthermore, if the difference in the molecular weights of comonomers is small, the use of M_{av} would be a good approximation to calculate the *MWD* from equation (24).

The bivariate distribution of chain length and composition, $W(r, y)\,\mathrm{d}r\,\mathrm{d}y$, which is the weight fraction of copolymer whose chain length is r to $r+\mathrm{d}r$ and composition deviation y to $y+\mathrm{d}y$, is given by (see Appendix):

$$W(r, y)\,\mathrm{d}r\,\mathrm{d}y=\frac{M_{\mathrm{w_1}}F_1+M_{\mathrm{w_2}}F_2}{M_{\mathrm{w_1}}\bar{F}_1+M_{\mathrm{w_2}}\bar{F}_2}\,[W^*(r)\,\mathrm{d}r][N(0,\sigma^2)\,\mathrm{d}y] \tag{28}$$

where $\bar{F}_1$ and $\bar{F}_2$ are the average copolymer composition for polymers produced instantaneously, and F_1 and F_2 are the instantaneous copolymer composition of the specific polymer chain. The independent variable y is the composition deviation which is defined by $y=F_1-\bar{F}_1$ and $N(0, \sigma^2)$ is the copolymer composition distribution which is given by a normal distribution with mean zero and variance σ^2.

$$\sigma^2=\bar{F}_1\bar{F}_2K/r \tag{29}$$

$$K=[1+4\bar{F}_1\bar{F}_2(r_1r_2-1)]^{0.5} \tag{30}$$

If the number-average chain length is large enough, the polymer radical fraction, $\phi_i^{\bullet}$, which is necessary to calculate the pseudo-kinetic rate constants, would be obtained by using the SSH for each type of polymer radical instead of using equation (22), namely:

$$R_{12}=R_{21} \tag{31}$$

where R_{12} is the rate of propagation in which M_2 follows M_1 with similar definition for R_{21}.

Up to this point, it has been assumed that the termination rate constants are not chain length dependent. It is of great interest to know whether the pseudo-kinetic rate constant method is applicable even when the effect of the chain length dependent termination reaction is significant. In this case, t_1 and t_2 are functions of chain length, namely, $t_1(r)$ and $t_2(r)$, and therefore $U_1(r)$ and

$U_2(r)$. Equation (13) must be modified as follows:

$$([R_{r,1}^{\cdot}],[R_{r,2}^{\cdot}])=U_2(r)([R_{r-1,1}^{\cdot}],[R_{r-1,2}^{\cdot}])\times\begin{bmatrix}[U_1(r)/U_2(r)]P_{11} & P_{22}k_{12}/k_{22}\\ [U_1(r)/U_2(r)]P_{11}k_{21}/k_{11} & P_{22}\end{bmatrix}\tag{32}$$

Therefore, even though $U_1(r)$ and $U_2(r)$ change with chain length, the mole fraction, $\phi_{r,1}^{\cdot}$, does not change if the ratio $U_1(r)/U_2(r)$ is independent of chain length. Since the probability of growth, U, is very close to unity, the assumption that $U_1(r)/U_2(r)$ is independent of chain length may be a good approximation. The chain length distribution is, therefore, given by (see Appendix):

$$W^*(r)=r(\bar{\tau}+\bar{\beta})\tau(r)\left[\prod_{m=1}^{r}\Phi(m)\right]+(r/2)(\bar{\tau}+\bar{\beta})^2\left\{\sum_{s=1}^{r-1}\beta(s,r-s)\left[\prod_{m=1}^{s}\Phi(m)\right]\left[\prod_{m=1}^{r-s}\Phi(m)\right]\right\}\tag{33}$$

where

$$\tau(r)=(R_{\mathrm{td}}(r)+R_{\mathrm{f}})/R_{\mathrm{p}}\tag{34}$$

$$\beta(r)=R_{\mathrm{tc}}(r)/R_{\mathrm{p}}\tag{35}$$

$$\Phi(r)=1/[1+\tau(r)+\beta(r)]\tag{36}$$

$\bar{\tau}$ and $\bar{\beta}$ are the average values over all chain lengths.

When the effect of chain length dependent termination is significant, the necessary conditions for the application of the pseudo-kinetic rate constant method are: that $\bar{P}_{\mathrm{N}}$ is larger than a few hundred; and the ratio of the probability of growth of the polymer radical with chain length r, $U_1(r)/U_2(r)$, is independent of chain length.

MULTICOMPONENT POLYMERIZATION

The extension of the pseudo-kinetic rate constant method to a multicomponent polymerization is straightforward. Equations (12) and (13) can be written as follows:

$$([R_{1,1}^{\cdot}],[R_{1,2}^{\cdot}],[R_{1,3}^{\cdot}],\ldots)=(i_1,i_2,i_3,\ldots)\begin{bmatrix}U_1P_{11}/k_{11} & 0 & 0 & 0 & \cdots\\ 0 & U_2P_{22}/k_{22} & 0 & 0 & \cdots\\ 0 & 0 & U_3P_{33}/k_{33} & 0 & \cdots\\ \vdots & \vdots & \vdots & \vdots & \cdots\\ \vdots & \vdots & \vdots & \vdots & \cdots\end{bmatrix}\tag{37}$$

$$([R_{r,1}^{\cdot}],[R_{r,2}^{\cdot}],[R_{r,3}^{\cdot}],\ldots)=([R_{r-1,1}^{\cdot}],[R_{r-1,2}^{\cdot}],[R_{r-1,3}^{\cdot}]\ldots)\begin{bmatrix}U_1P_{11} & U_2P_{22}k_{12}/k_{22} & U_3P_{33}k_{13}/k_{33} & \cdots\\ U_1P_{11}k_{21}/k_{11} & U_2P_{22} & U_3P_{33}k_{23}/k_{33} & \cdots\\ U_1P_{11}k_{31}/k_{11} & U_2P_{22}k_{32}/k_{22} & U_3P_{33} & \cdots\\ \vdots & \vdots & \vdots & \cdots\\ \vdots & \vdots & \vdots & \cdots\end{bmatrix}\quad(r\geqslant 2)\tag{38}$$

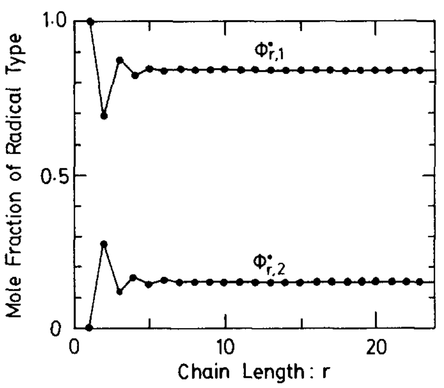

Figure 5 Mole fraction of radical type as a function of chain length, r (terpolymerization, $k_{11}/k_{12}=0.6$, $k_{11}/k_{13}=0.4$, $k_{22}/k_{21}=0.4$, $k_{22}/k_{23}=1.25$, $k_{33}/k_{31}=0.1$, $k_{33}/k_{32}=0.2$, $U_2/U_1=U_3/U_1=1.0$, $f_1=0.4$, $f_2=0.3$, $\phi_{1,1}^{\cdot}=1.0$). The mole fraction of radical type reaches its steady state (=overall value) within 10 steps

An example of the calculated results for terpolymerization is shown in *Figure 5*. The necessary conditions for the applicaton of the pseudo-kinetic rate constant method is the same as those for a binary system, and equations (24) and (33) [and (A7) and (A8) in the Appendix] are also applicable for a multicomponent polymerization by application of the pseudo-kinetic rate constant defined by equations (1)–(5).

PENULTIMATE MODEL

A prevailing view of copolymerization kinetics is that the propagation step is, in most cases, correctly described by the terminal model, whereas the termination process is more complex and still to be elucidated. However, it has recently been speculated that it is the propagation step that needs to be examined, and the penultimate effect on the propagation reactions is being tested from the point of view of its effect on copolymerization rate[21–28]. According to these recent investigations, it may be necessary to re-investigate the penultimate effect on the propagation step for many copolymerization systems whose cross-termination factor proposed by Walling[29] deviates greatly from unity. The sequence length distribution may, in some cases, not be effective for establishing the validity of the terminal model[27].

The pseudo-kinetic rate constants based on the penultimate model for copolymerization are as follows:

$$k_{\mathrm{p}}=\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}k_{ijk}\phi_{ij}^{\cdot}f_k\tag{39}$$

$$k_{\mathrm{fm}}=\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}k_{\mathrm{f}_{ijk}}\phi_{ij}^{\cdot}f_k\tag{40}$$

$$k_{\mathrm{fT}}=\sum_{i=1}^{N}\sum_{j=1}^{N}k_{\mathrm{fT}_{ij}}\phi_{ij}^{\cdot}\tag{41}$$

$$k_{\mathrm{td}}=\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}k_{\mathrm{td}_{ijkl}}\phi_{ij}^{\cdot}\phi_{kl}^{\cdot}\tag{42}$$

$$k_{\mathrm{tc}}=\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}k_{\mathrm{tc}_{ijkl}}\phi_{ij}^{\cdot}\phi_{kl}^{\cdot}\tag{43}$$

These pseudo-kinetic rate constants give the exact reaction rate. For example, the propagation rate, R_{p}, and the rate of termination, R_{t} are given by equations (8) and (9), respectively. It is straightforward to show that the necessary condition for the application of these pseudo-kinetic rate constants for the calculation of the *MWD* is that the mole fraction of radical type is independent of

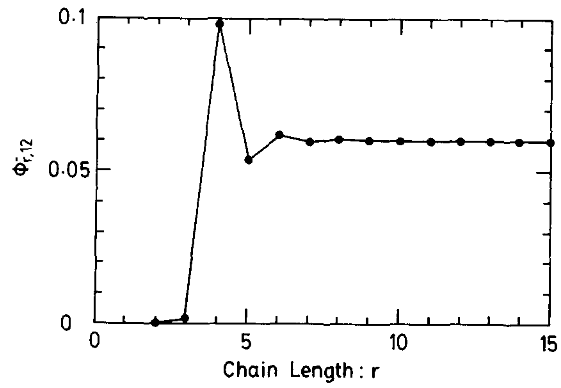

Figure 6 Mole fraction of radical type as a function of chain length, *r* (penultimate model, $k_{111}/k_{112}=k_{211}/k_{212}=0.4$, $k_{222}/k_{221}=k_{122}/k_{121}=0.6$, $k_{211}/k_{111}=0.5$, $k_{122}/k_{222}=0.3$, $k_{222}/k_{111}=0.3$, $U_{12}/U_{11}=U_{21}/U_{11}=U_{22}/U_{11}=1.0$, $f_1=0.25$, $\phi_{2,11}^{\bullet}=1.0$). The mole fraction of radical type reaches its steady state (=overall value) within 10 steps

chain length, namely:

$$\phi_{11}^{\bullet}=\phi_{2,11}^{\bullet}=\cdots=\phi_{r,11}^{\bullet}=\cdots \tag{44a}$$

$$\phi_{12}^{\bullet}=\phi_{2,12}^{\bullet}=\cdots=\phi_{r,12}^{\bullet}=\cdots \tag{44b}$$

$$\phi_{13}^{\bullet}=\phi_{2,13}^{\bullet}=\cdots=\phi_{r,13}^{\bullet}=\cdots \tag{44c}$$

$$\vdots$$

$$\phi_{ij}^{\bullet}=\phi_{2,ij}^{\bullet}=\cdots=\phi_{r,ij}^{\bullet}=\cdots$$

$$\vdots$$

As an example, let us consider a binary copolymerization system. By application of the SSH for each type of polymer radical with chain length *r*, $[R_{r,ij}^{\bullet}]$ is given by:

$$([R_{r,11}^{\bullet}],[R_{r,12}^{\bullet}],[R_{r,21}^{\bullet}],[R_{r,22}^{\bullet}]) = ([R_{r-1,11}^{\bullet}],[R_{r-1,12}^{\bullet}],[R_{r-1,21}^{\bullet}],[R_{r,22}^{\bullet}]) \begin{bmatrix} U_{11}P_{111} & U_{12}P_{122}k_{112}/k_{122} & 0 & 0 \\ 0 & 0 & U_{21}P_{211}k_{121}/k_{211} & U_{22}P_{222}k_{122}/k_{222} \\ U_{11}P_{111}k_{211}/k_{111} & U_{12}P_{122}k_{212}/k_{122} & 0 & 0 \\ 0 & 0 & U_{21}P_{211}k_{221}/k_{211} & U_{22}P_{222} \end{bmatrix} \quad (r\geqslant 3) \tag{45}$$

One of the calculated results is shown in *Figure 6*. In the figure, $\phi_{2,11}^{\bullet}=1$ was assumed. The fundamental argument is the same as previously discussed, and the necessary condition for the application of the pseudo-kinetic rate constant method is that $\bar{P}_N$ is larger than a few hundred.

Even when the effect of chain length dependent termination is significant, it is straightforward to show that the pseudo-kinetic rate constant method is applicable if the ratio of the probability of chain growth, $U_{ij}(r)/U_{11}(r)=B_{ij}$, is independent of chain length.

CONCLUSIONS

By application of the pseudo-kinetic rate constant method, the kinetic treatment of a multicomponent polymerization reduces to that of a homopolymerization, and therefore, this method is a powerful tool to analyse the kinetics and the *MWD* of a multicomponent polymerization. This method is applicable for any order of Markov chains, and is applicable for the calculation of chain length distribution if the number-average chain length is larger than a few hundred. Even when the effect of chain length dependent bimolecular termination is significant, the pseudo-kinetic rate constant method is practically applicable, if the change in the ratio of the probability of chain growth with chain length is negligible.

REFERENCES

1 Hamielec, A. E. and MacGregor, J. F. in 'Polymer Reaction Engineering' (Eds K. H. Reichert and W. Geiseler), Hanser Publishers, New York, 1983, p. 21
2 Broadhead, T. O., Hamielec, A. E. and MacGregor, J. F. *Makromol. Chem. Suppl.* 1985, **10/11**, 105
3 Hamielec, A. E., MacGregor, J. F. and Penlidis, A. *Makromol. Chem., Macromol. Symp.* 1987, **10/11**, 521
4 Tobita, H. and Hamielec, A. E. *Makromol. Chem., Macromol. Symp.* 1988, **20/21**, 501
5 Tobita, H. and Hamielec, A. E. *Macromolecules* 1989, **22**, 3098
6 Tobita, H. and Hamielec, A. E. in 'Polymer Reaction Engineering' (Eds K. H. Reichert and W. Geiseler), VCH Verlagsgesellschaft, New York, 1989, p. 43
7 Tobita, H. *PhD Thesis* McMaster University, 1990
8 North, A. M. in 'Reactivity, Mechanism and Structure in Polymer Chemistry' (Eds A. D. Jenkins and A. Ledwith), Wiley-Interscience, New York, 1974, Ch. 5
9 O'Driscoll, K. F. *Pure Appl. Chem.* 1981, **53**, 617
10 Mita, I. and Horie, K. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* 1987, **C27**, 91
11 Wittmer, P. *Makromol. Chem. Suppl.* 1979, **3**, 129
12 Atherton, J. N. and North, A. M. *Trans. Faraday Soc.* 1962, **58**, 2049
13 North, A. M. 'The Kinetics of Free-Radical Polymerization', Pergamon, London, 1966, p. 94
14 Russo, S. and Munari, S. *J. Macromol. Sci.* 1968, **A2**, 1321
15 Fueno, T. and Furukawa, J. *J. Polym. Sci.* 1964, **A2**, 3681
16 Price, F. P. in 'Markov Chains and Monte Carlo Calculations in Polymer Science' (Ed. G. G. Lowry), Marcel Dekker, New York, 1970, p. 187
17 Stockmayer, W. H. *J. Chem. Phys.* 1945, **13**, 199
18 Mayo, F. R. and Lewis, F. M. *J. Am. Chem. Soc.* 1944, **66**, 1594
19 Alfrey, T. and Goldfinger, G. *J. Chem. Phys.* 1944, **12**, 205
20 Wall, F. T. *J. Am. Chem. Soc.* 1944, **66**, 2050
21 Fukuda, T., Ma, Y.-D. and Inagaki, H. *Polym. J.* 1982, **14**, 705
22 Fukuda, T., Ma, Y.-D. and Inagaki, H. *Macromolecules* 1985, **18**, 17
23 Ma, Y.-D., Fukuda, T. and Inagaki, H. *Macromolecules* 1985, **18**, 26
24 Fukuda, T., Ma, Y.-D. and Inagaki, H. *Makromol. Chem. Suppl.* 1985, **12**, 125
25 Fukuda, T., Kubo, K., Ma, Y.-D. and Inagaki, H. *Polym. J.* 1987, **19**, 523
26 Davis, T. P. and O'Driscoll, K. F. *Makromol. Chem., Rapid Commun.* 1989, **10**, 509
27 Davis, T. P. and O'Driscoll, K. F. *J. Polym. Sci., Polym. Lett. Edn.* 1989, **27**, 417
28 Fukuda, T., Ma, Y.-D., Kubo, K. and Takada, A. *Polym. J.* 1989, **21**, 1003
29 Walling, C. *J. Am. Chem. Soc.* 1949, **71**, 1930
30 Simha, R. and Branson, H. *J. Chem. Phys.* 1944, **12**, 253
31 Tacx, J. C. J. F., Lissen, H. N. and German, A. L. *J. Polym. Sci., Polym. Chem. Edn.* 1988, **26**, 61

APPENDIX

Kinetic derivation of the weight-chain length distribution in free-radical homopolymerization

By application of the SSH for polymer radicals with chain length *r*, one obtains:

$$[R_1^{\bullet}]=\frac{R_I+k_{fm}[M][R^{\bullet}]+k_{fT}[T][R^{\bullet}]}{k_p[M]+k_{fm}[M]+k_{fT}[T]+(k_{tc}+k_{td})[R^{\bullet}]} \tag{A1}$$

$$[R_r^{\bullet}]=\frac{{}_p[M][R_{r-1}^{\bullet}]}{k_p[M]+k_{fm}[M]+k_{fT}[T]+(k_{tc}+k_{td})[R^{\bullet}]} \tag{A2}$$

where R_I is the rate of initiation.

Using the ratios that are defined by equations (25) and

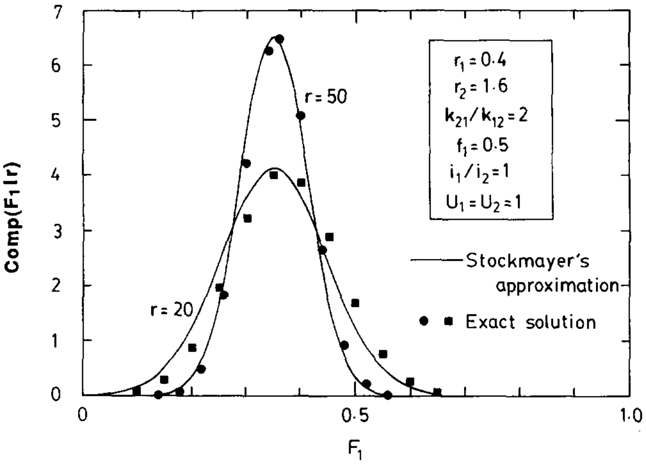

Figure A1 Calculated copolymer composition distribution

(26) in the text, equations (A1) and (A2) reduce to:

$$[\mathrm{R}_1^{\bullet}]=\frac{\tau+\beta}{1+\tau+\beta}[\mathrm{R}^{\bullet}] \qquad \text{(A3)}$$

$$[\mathrm{R}_r^{\bullet}]=\frac{1}{1+\tau+\beta}[\mathrm{R}_{r-1}^{\bullet}] \qquad \text{(A4)}$$

therefore,

$$[\mathrm{R}_r^{\bullet}]=[\mathrm{R}^{\bullet}](\tau+\beta)\Phi^r \qquad \text{(A5)}$$

where Φ was defined by equation (27) in the text.

The instantaneous weight-chain length distribution, $W^*(r)$ [$=rR_{\mathrm{FP}}(r)/\sum_{r=1}^{\infty} rR_{\mathrm{FP}}(r)$, where $R_{\mathrm{FP}}(r)$ is the production rate of polymer molecules with chain length r], is therefore given by equation (24) in the text. The instantaneous number- and weight-average chain lengths ($\bar{P}_{\mathrm{N}}$ and $\bar{P}_{\mathrm{W}}$, respectively) are given by:

$$\bar{P}_{\mathrm{N}}=\frac{1+\tau+\beta}{\tau+\beta/2}\approx\frac{1}{\tau+\beta/2} \quad (\tau, \beta \ll 1) \qquad \text{(A6)}$$

$$\bar{P}_{\mathrm{W}}=\frac{\tau(2+\tau+\beta)+\beta(3+\tau+\beta)}{(\tau+\beta)^2}\approx\frac{2\tau+3\beta}{(\tau+\beta)^2} \quad (\tau, \beta \ll 1) \qquad \text{(A7)}$$

If r is large enough, equation (24) can be approximated as follows:

$$W^*(r)=(\tau+\beta)[\tau+(\beta/2)(\tau+\beta)(r-1)]r\exp[-r(\tau+\beta)] \qquad \text{(A8)}$$

When the effect of chain length dependent bimolecular termination is significant, equation (A5) must be modified as follows:

$$[\mathrm{R}_r^{\bullet}]=(\bar{\tau}+\beta)\left[\prod_{m=1}^{r}\Phi(m)\right][\mathrm{R}^{\bullet}] \qquad \text{(A9)}$$

Therefore, the weight-chain length distribution is given by equation (33) in the text.

Stockmayer's bivariate distribution of chain length and composition

In statistical copolymerization, the chain length of a copolymer is finite, and therefore, the compositions as well as the chain lengths of the individual chains cannot be identical. Therefore, for copolymer chains produced instantaneously (in a very small time interval) there is a bivariate distribution of composition and chain length.

It was Simha and Branson[30] who proposed a very extensive and rather complete treatment of the statistics of copolymerization by application of the terminal model for copolymerization. However, their results were in fairly complex formulations and therefore difficult to apply directly. Stockmayer[17] proposed a simple expression by replacing summations with integrals and factorials with expressions based on Stirling's approximation. It is straightforward to derive equation (A8) starting from the Stockmayer bivariate distribution[7]. If the molecular weight of monomer 1, M_{w1}, and that of monomer 2, M_{w2}, are equal, the Stockmayer bivariate distribution states that the weight fraction of copolymer whose chain length is r to $r+\mathrm{d}r$ and composition deviation y to $y+\mathrm{d}y$ is given by the following equation:

$$W^*(r, t)\,\mathrm{d}r\,\mathrm{d}y=W^*(r)\,\mathrm{d}r\,\mathrm{Comp}(y|r)\,\mathrm{d}y \qquad \text{(A10)}$$

Namely, the Stockmayer bivariate distribution, $W^*(r, y)$ consists of the product of weight-chain length distribution, $W^*(r)$, and composition distribution, $\mathrm{Comp}(y|r)$, which is given by the conditional probability distribution given the chain length r. [It has also been shown that equation (A10) is practically applicable even when the effect of chain length dependent termination is significant[7].] The composition distribution, $\mathrm{Comp}(y|r)$ is a normal distribution whose variance, σ^2 is given by equations (29) and (30) in the text. Roughly speaking, Stockmayer's composition distribution is a good approximation for chain lengths larger than 50 if the average chain length is large enough ($U_1 \approx 1$ and $U_2 \approx 1$). An example of the calculated results is shown in *Figure A1*.

Recently, a modified Stockmayer equation, which accounts for comonomers with different molecular weights, was proposed by Tacx *et al.*[31]. In their paper, a correction factor was derived and they investigated conditions where this correction factor has significant effect on the bivariate distribution. Unfortunately, the physical meaning of this correction factor as derived by Tacx *et al.* is obscure. We now derive a correction factor whose physical interpretation is clear.

When $M_{\mathrm{w1}} \neq M_{\mathrm{w2}}$, the bivariate distribution which accounts for the different molecular weights of comonomers, $W(r, y)$ is given by:

$$W(r, y)\,\mathrm{d}r\,\mathrm{d}y =\frac{(M_{\mathrm{w1}}F_1+M_{\mathrm{w2}}F_2)[W^*(r)\,\mathrm{d}r][N(0, \sigma^2)\,\mathrm{d}y]}{\int_r\int_y (M_{\mathrm{w1}}F_1+M_{\mathrm{w2}}F_2)W^*(r)N(0, \sigma^2)\,\mathrm{d}y\,\mathrm{d}r} \qquad \text{(A11)}$$

[denominator of equation (A11)]

$$\begin{aligned}
&=\int_r W^*(r)\int_y (M_{\mathrm{w1}}F_1+M_{\mathrm{w2}}F_2)N(0, \sigma^2)\,\mathrm{d}y\,\mathrm{d}r \\
&=(M_{\mathrm{w1}}\bar{F}_1+M_{\mathrm{w2}}\bar{F}_2)\int_{\mathrm{r}} W^*(r)\int_y N(0, \sigma^2)\,\mathrm{d}y\,\mathrm{d}r \\
&\quad+(M_{\mathrm{w1}}-M_{\mathrm{w2}})\int_r W^*(r)\int_y yN(0, \sigma^2)\,\mathrm{d}y\,\mathrm{d}r \\
&=M_{\mathrm{w1}}\bar{F}_1+M_{\mathrm{w2}}\bar{F}_2 \qquad \text{(A12)}
\end{aligned}$$

Therefore, $W(r, y)$ is given by equation (28) in the text, and the meaning of the correction factor [$=(M_{\mathrm{w1}}F_1+M_{\mathrm{w2}}F_2)/(M_{\mathrm{w1}}\bar{F}_1+M_{\mathrm{w2}}\bar{F}_2)$] is obvious.