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Kinetic Approach of Nonlinear Polymerization with a Multistage Process

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ABSTRACT: An algorithm for calculating the average molecular weight has been developed for nonlinear polymerization by a kinetic approach. This method is very general and also can be applied to the systems with multistage processes and those polymerizations with condensation byproducts. The systems of three components with a two-stage process were analyzed by this generalized kinetic method, and it is shown that the profiles of the weight-average degree of polymerization, with reaction time or conversion, and the critical conversion are dependent on the second-stage time and the ratio of reactivity of the two stages. Then a system with condensation byproducts and a system of stepwise homopolymerization with a substitution effect were calculated, and the results are well consistent with those by other methods.

1. Introduction

There are several theories of network formation, including statistical and kinetic methods, to describe the relations among molecular weight of polymers and conversion or reaction time during cure. The statistical methods were derived by Flory and Stockmayer,[1,2] which were generalized and applied successfully by Gordon, Dusek, Macosko, Miller, and Duran et al. to many curing systems.[3–10]

On the other hand, the kinetic approaches were developed by Stockmayer, Kuchanov, and Povolotskaya et al.,[11–13] which can be used for polyfunctional system with equal reactivities of groups and with no substitution effects (random polymerization) to obtain the analytical solutions, of which the results are identical with those by the statistical method. For the nonrandom cases, for example, considering the first-shell substitution effect (FSSE),[12,14] the infinite rate equation can be transformed into finite ordinary differential equations (ODE) for moments by a generating function. Then this set of equations can be solved by numerical methods, and the average molecular weight of polymers can be obtained from the generating function. Kuchanov et al.[12] showed that the critical conversions at the get point are different between the random case and the nonrandom case. Galina and Szustalewicz have also studied the substitution effect of stepwise homopolymerization of a trifunctional monomer and stepwise copolymerization of 3- and 2-functional monomers before gelation by the kinetic approaches.[15,16]

Those methods mentioned above are used widely in many curing systems, but the deriving procedures are case by case and very complicated. In this work, on the basis of the kinetic approach, a very general method is developed by us, which is easily applied to more complex curing systems before gelation. The polymerization with a multistage process and those systems with condensation byproducts during reaction are taken as examples. The average molecular weight of polymers, which changed with reaction time, and the gel time of the systems of three components with a two-stage process are analyzed by this generalized kinetic method. Then a system, etherification of polyol, in which condensation byproducts (water) form, and a system of stepwise homopolymerization with a first-shell substitution effect, are also calculated, and the results are compared with those by other methods.[7,17]

2. Kinetic Approach

We consider a polymerization system in which m irreversible elementary reactions take place between units of molecules as follows:

$$A_{i1} + A_{i2} \xrightarrow{k_i} A_{i3} + A_{i4} + C_i \qquad \text{for } i\text{th reaction,} \quad i = 1, 2, ..., m \qquad (1)$$

where A_{i1} and A_{i2} are the reacting units, A_{i3} and A_{i4} are the resultant units, C_i is the condensation byproduct, which does not exist if there are no condensation byproducts at the ith reaction, and k_i is the rate constant. First, we only consider the following case:

$$A_{ij} \neq A_{rs}, \quad \text{if } (i,j) \neq (r,s), \quad i,r = 1, 2, ..., m, \quad j,s = 1, ..., 4$$

The other cases, for example, homopolymerization, will be derived in the Appendix.

Define $\langle \mathbf{P} \rangle$ as the structure isomer, in which $\mathbf{P}$ is a matrix used to characterize the weight and the number of units of the molecule $\langle \mathbf{P} \rangle$, and the conformation and configuration of $\langle \mathbf{P} \rangle$ are not taken into account. Then $\mathbf{P}$ is defined as

$$\mathbf{P} = \begin{bmatrix} p_{11} & p_{12} & p_{13} & p_{14} & p_{15} \\ p_{21} & p_{22} & p_{23} & p_{24} & p_{25} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ p_{m1} & p_{m2} & p_{m3} & p_{m4} & p_{m5} \\ p_{\mathrm{w}} & 0 & 0 & 0 & 0 \end{bmatrix} \qquad (2)$$

where p_{ij} ($i = 1, 2, ..., m$; $j = 1, ..., 4$) represents the number of A_{ij}, p_{i5} ($i = 1, 2, ..., m$) is the number of times the ith reaction occurs to form the molecule $\langle \mathbf{P} \rangle$, and p_{w} is the weight of $\langle \mathbf{P} \rangle$ if no condensation byproduct forms. The molecular weight of $\langle \mathbf{P} \rangle$, $W(\mathbf{P})$, can be obtained as follows:

$$W(\mathbf{P}) = p_{\mathrm{w}} - \sum_{i=1}^{m} W_{C_i} p_{i5} \qquad (3)$$

where W_{C_i} is the weight of the condensation byproduct, C_i.

Assuming that all the reactions are under chemical control and no intramolecular reaction occurs before gelation, the reactions between molecules can be described

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in the form:

$$\langle \mathbf{P}' \rangle + \langle \mathbf{P}'' \rangle \xrightarrow{k_i} \langle \mathbf{P}' + \mathbf{P}'' + \mathbf{L}_i \rangle + \mathrm{C}_i \tag{4}$$

where $\langle \mathbf{P}' + \mathbf{P}'' + \mathbf{L}_i \rangle$ is the product molecule formed from reactant molecules, $\langle \mathbf{P}' \rangle$ and $\langle \mathbf{P}'' \rangle$, at the ith reaction, and

$$\mathbf{L}_i = \begin{bmatrix} l_{11} & l_{12} & l_{13} & l_{14} & l_{15} \\ l_{21} & l_{22} & l_{23} & l_{24} & l_{25} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ l_{m1} & l_{m2} & l_{m3} & l_{m4} & l_{m5} \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \tag{5}$$

in which $-l_{i1} = -l_{i2} = l_{i3} = l_{i4} = l_{i5} = 1$, and other elements are equal to zero, i.e.,

$$l_{rs}\ (r \neq i, s = 1, 2, ..., 5) = 0$$

Each ith reaction involves the consumption of one unit A_{i1} and one A_{i2} with the formation of one A_{i3}, one A_{i4}, and one condensation byproduct C_i.

Furthermore, we define a dimensionless number fraction, $[\mathbf{P}]$, a ratio of the rate constant, k_i^*, and a scaled time, τ, as follows:

$$[\mathbf{P}] = N(\mathbf{P})/N_0 \tag{6}$$

$$k_i^* = (k_i/k_0)(V_0/V) \tag{7}$$

$$\tau = tN_0k_0/V_0 \tag{8}$$

where $N(\mathbf{P})$ is the number of $\langle \mathbf{P} \rangle$, V is the volume of the system, N_0, k_0, and V_0 are arbitrary reference number, rate constant, and volume, respectively, and t is the reaction time.

If the change of the density of this system is negligible, according to eq 4, the rate equations may be expressed as

$$\frac{\mathrm{d}[\mathbf{P}]}{\mathrm{d}\tau} = \sum_{i=1}^{m} k_i^* \left\{ \sum_{\substack{\text{all } \mathbf{P}',\mathbf{P}'' \\ \text{that } \mathbf{P}=\mathbf{P}'+\mathbf{P}''+\mathbf{L}_i}} [\mathbf{P}'][\mathbf{P}'']p_{i1}'p_{i2}'' - [\mathbf{P}]p_{i1} \sum_{\text{all } \mathbf{P}'''} [\mathbf{P}''']p_{i2}''' - [\mathbf{P}]p_{i2} \sum_{\text{all } \mathbf{P}'''} [\mathbf{P}''']p_{i1}''' \right\} \tag{9}$$

where $\sum_{\text{all } \mathbf{Q}}$ denotes the summation over all possible values of matrix $\mathbf{Q}$.

The positive and two negative terms on the right side of the above equation are the total rate of appearance and disappearance of molecule $\langle \mathbf{P} \rangle$, respectively.

In order to get the relationship between the molecular weight and the reaction time, the generating function method is applied. First, we define a generating function:

$$G[\tau, x_{ij}(i=1,2,...,m;j=1,2,...,5), x_\mathrm{w}] = \sum_{\text{all } \mathbf{P}} \Big(\prod_{\substack{i=1,...,m \\ j=1,...,5}} x_{ij}^{p_{ij}} \Big) x_\mathrm{w}^{p_\mathrm{w}} [\mathbf{P}] \tag{10}$$

where x_{ij} and x_w are dummy variables.

Equation 9 can be multiplied by $(\prod_{j=1,...,5}^{i=1,...,m} x_{ij}^{p_{ij}}) x_\mathrm{w}^{p_\mathrm{w}}$ and summed over $\mathbf{P}$ to yield

$$\frac{\partial G}{\partial \tau} = \sum_{i=1}^{m} k_i^* [G_{x_{i1}} G_{x_{i2}} x_{i3} x_{i4} x_{i5} - x_{i1} G_{x_{i1}} G_{x_{i2}}^* - x_{i2} G_{x_{i2}} G_{x_{i1}}^*] \tag{11}$$

where

$$G_y = \partial G/\partial y$$

and

$$G_y^* = \partial G/\partial y|_{x_{ij}=x_\mathrm{w}=1\ (i=1,2,...,m;\ j=1,2,...,5)}$$

$$(y = x_{ij} \text{ or } x_\mathrm{w})$$

The ath moment of the molecular weight distribution (MWD) is defined as

$$M_a = \sum_{\text{all } \mathbf{P}} W^a(\mathbf{P})\ [\mathbf{P}] \frac{N_0}{N_\mathrm{T}} \tag{12}$$

where N_T denotes the total number of molecules of the system.

The zeroth, first, and second moment of MWD can be directly related to the generating function given by the following equations:

$$M_0 = \frac{N_0}{N_\mathrm{T}} G|_{x_{ij}=x_\mathrm{w}=1} = \frac{N_0}{N_\mathrm{T}} G^* \tag{13}$$

$$M_1 = \frac{N_0}{N_\mathrm{T}} (G_{x_\mathrm{w}}^* - \sum_{i=1}^{m} W_{\mathrm{C}_i} G_{x_{i5}}^*) \tag{14}$$

$$M_2 = \frac{N_0}{N_\mathrm{T}} [G_{x_\mathrm{w},x_\mathrm{w}}^* + G_{x_\mathrm{w}}^* - 2\sum_{i=1}^{m} W_{\mathrm{C}_i} G_{x_\mathrm{w},x_{i5}}^* + \sum_{\substack{i=1,...,m \\ j=1,...,5 \\ i \neq j}} W_{\mathrm{C}_i} W_{\mathrm{C}_j} G_{x_{i5},x_{j5}}^* + \sum_{i=1}^{m} W_{\mathrm{C}_i}{}^2 (G_{x_{i5},x_{i5}}^* + G_{x_{i5}}^*)] \tag{15}$$

where $G_{y,z}^* = (\partial^2 G/\partial y \partial z)|_{x_{ij}=x_\mathrm{w}=1\ (i=1,2,...,m;\ j=1,2,...,5)}$.

Then we can get the number-average and the weight-average molecular weights as

$$\bar{M}_\mathrm{n} = M_1/M_0 \tag{16}$$

$$\bar{M}_\mathrm{w} = M_2/M_1 \tag{17}$$

The values of M_0, M_1, and M_2 in eqs 13–15 can be calculated by a numerical method, which is described in the Appendix.

3. Results and Discussion

I. Multistage Process. In many cases, networks are formed from monomers by a multistage process rather than a one-stage process. For example, isocynate-terminated prepolymers are formed in a first stage from hydroxyl-terminated monomers reacting with excess diisocyanates and then are cured with diamine or polyol resins to form networks in a second stage.

The model reacting system selected is, in a first stage, excess monomers A2, having two reacting units A, mixing and reacting with monomers B2, which contains two reacting units B. Then, curing agents C4, with four reacting units C, are added at time t_2 to react with the unreacted units A in a second stage. The density of this reacting system is assumed to be constant, and the reactions between units are

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_\mathrm{AB}} \mathrm{A-B} \tag{18}$$

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_\mathrm{AC}} \mathrm{A-C} \tag{19}$$

where A–B and A–C are the resultant units, and k_AB and k_AC are the kinetic rate constants. The parameters of computer modeling are as follows:

$N_0(\mathrm{A2}){:}N_0(\mathrm{B2}){:}N_0(\mathrm{C4}) = 10{:}2{:}4$
(the initial molar ratio of monomers,
in an equal stoichiometric ratio)

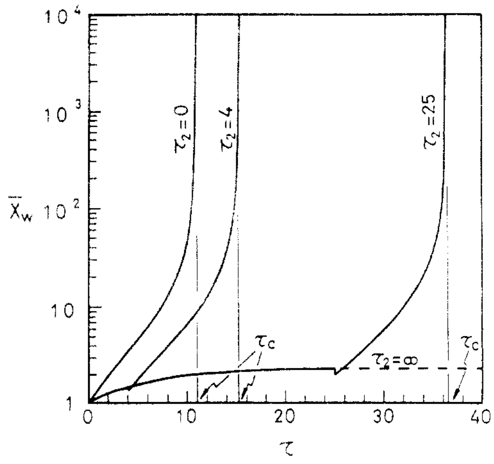

Figure 1. Weight-average degree of polymerization versus reaction time for various second stage times τ_2 (k_{AB}/k_{AC} = 1/1).

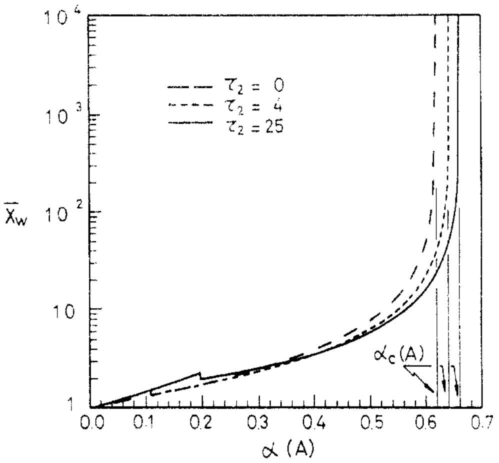

Figure 2. Weight-average degree of polymerization versus conversion of unit A for various second stage times τ_2 (k_{AB}/k_{AC} = 1/1).

$$k_{AB}/k_{AC} = 1/10,\ 1/1,\ \text{or}\ 1/0.1$$

$$\tau = 10k_{AB}C_0(\mathrm{A2})t$$

$$\tau_2 = 10k_{AB}C_0(\mathrm{A2})t_2$$

where t is the reaction time, and C_0(A2) is the initial concentration of monomers A2 in the mixture consisting of monomers A2 and B2.

Figure 1 shows the weight-average degree of polymerization, $\bar{X}_w$, which is obtained by setting molecular weights of monomers equal to 1, versus the scaled time τ, for various second-stage time, τ_2, at which monomers C4 are added to react with the prepolymers of the first stage. As shown in Figure 1, the rising rate of $\bar{X}_w$ decreases with increasing time for the system without curing agent C4 ($\tau < \tau_2$). However, once monomers C4 are added, $\bar{X}_w$ rises sharply and tends to an infinite value as the reaction approaches the gel time, τ_c, of the system. Figures 2–4 give plots of $\bar{X}_w$ versus the conversion of unit A, α(A). Because adding monomers C4 into the reacting system at τ_2 will reduce the average degree of polymerization, there are discontinuous points at τ_2 in Figures 1–4.

In our calculations, the profiles of $\bar{X}_w$ versus α(A) and the critical conversion, α_c, at which gelation occurs, depend on both the time τ_2 and the ratio of reactivity k_{AB}/k_{AC}. On the other hand, in stage 2 ($\tau > \tau_2$), the profiles of $\bar{X}_n$ versus α(A) are independent of either the value of τ_2 or the ratio of k_{AB}/k_{AC} (Figures 5–7), because the decreasing rate of the number of molecules in the reacting system is equal to the decreasing rate of the number of units A.

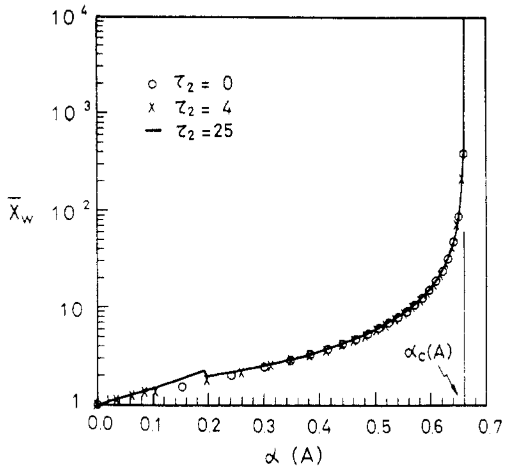

Figure 3. Weight-average degree of polymerization versus conversion of unit A for various second stage times τ_2 (k_{AB}/k_{AC} = 1/0.1).

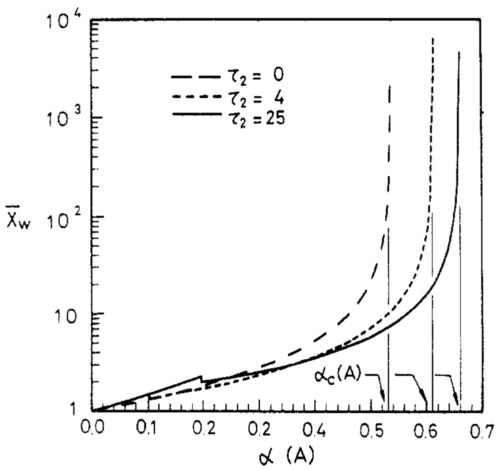

Figure 4. Weight-average degree of polymerization versus conversion of unit A for various second stage times τ_2 (k_{AB}/k_{AC} = 1/10).

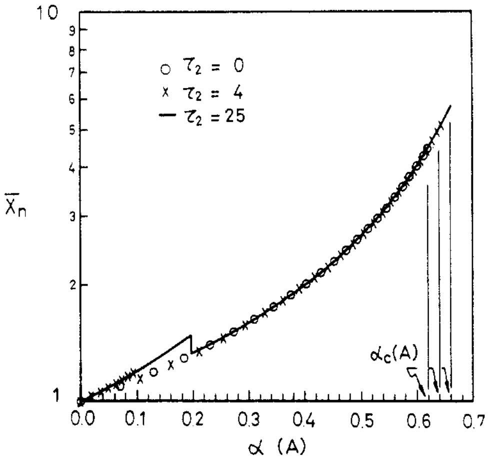

Figure 5. Number-average degree of polymerization versus conversion of unit A for various second stage times τ_2 (k_{AB}/k_{AC} = 1/1).

Table I shows the dependence of critical conversion on τ_2 and the ratio of reactivity. The difference of critical conversion between various τ_2 decreases with increasing of the ratio of k_{AB}/k_{AC}. If the reaction between units A and B is rather faster than that of units A and C, for example, k_{AB}/k_{AC} = 1/0.1 in this system, whether the C4 is added at time zero (τ_2 = 0) or later (τ_2 = 25), the $\bar{X}_w$ profiles are very close to each other in stage 2 (Figure 3). In such a case, both the differences of the conversions of units B and C between τ_2 = 0 and τ_2 = 25 tend to be zero

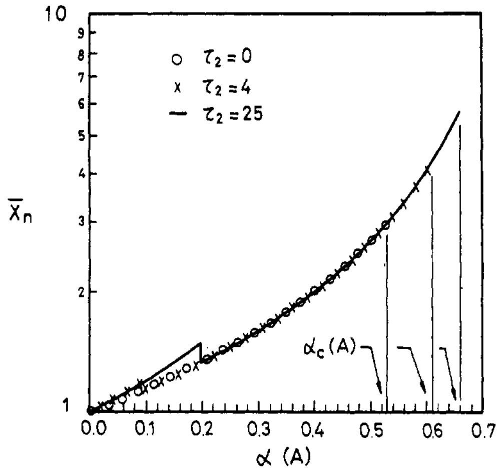

Figure 6. Number-average degree of polymerization versus conversion of unit A for various second stage times τ_2 (k_{AB}/k_{AC} = 1/10).

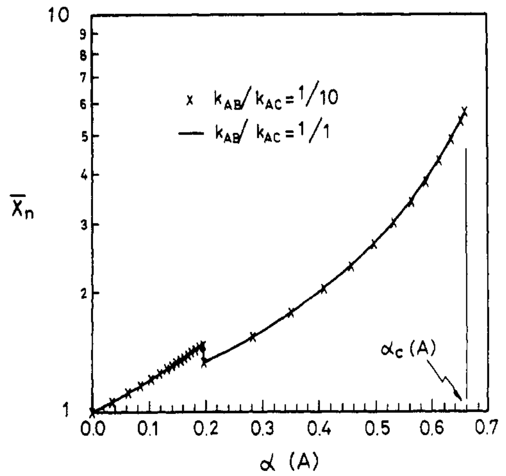

Figure 7. Number-average degree of polymerization versus conversion of unit A for k_{AB}/k_{AC} = 1/1 or 1/10 (τ_2 = 25).

Table I. Gel Times (τ_c) and Critical Conversions of Units A, B, and C (α_c (A), α_c(B), and α_c(C)) for Various Values of k_{AB}/k_{AC} and τ_2

k_{AB}/k_{AC}	τ_2	τ_c	α_c(A)	α_c(B)	α_c(C)
1/10	0	1.1	0.53	0.10	0.64
1/10	4	5.2	0.61	0.57	0.62
1/10	25	26.1	0.66	0.99	0.58
1/1	0	10.9	0.62	0.62	0.62
1/1	4	15.3	0.64	0.81	0.60
1/1	25	36.4	0.66	0.99	0.58
1/0.1	0	111.5	0.66	1.00	0.58
1/0.1	4	116.7	0.66	1.00	0.58
1/0.1	25	138.8	0.66	1.00	0.58

near gel point as shown in Figure 8. On the contrary, if k_{AB} is less than k_{AC}, for example, k_{AB}/k_{AC} = 1/10, most units B are consumed (about 99%; see Figure 9) in the first stage for the system with τ_2 = 25, but, in the one-stage process, i.e., τ_2 = 0, units B are consumed very slowly, thus, the differences of $\bar{X}_w$ profiles between these two different values of τ_2 are larger than both the systems of k_{AB}/k_{AC} = 1/1 and k_{AB}/k_{AC} = 1/0.1 (Figures 2–4).

II. Polymerization with Condensation Byproducts. There are many cases that condensation byproducts may form during polymerization, for example, synthesis of a polyester from a diol and a diacid, a polyamine from a diamine and a diacid, and a polyether from a polyol.

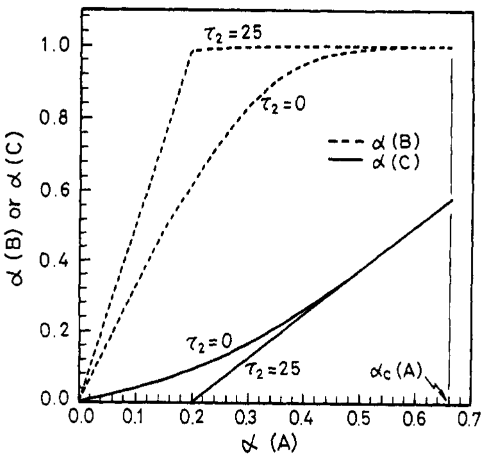

Figure 8. Conversion of unit B or C versus conversion of unit A (k_{AB}/k_{AC} = 1/0.1).

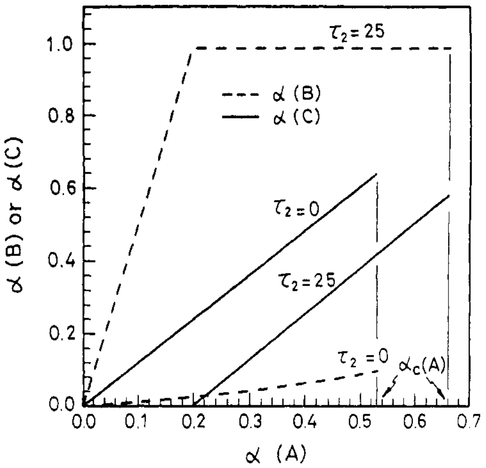

Figure 9. Conversion of unit B or C versus conversion of unit A (k_{AB}/k_{AC} = 1/10).

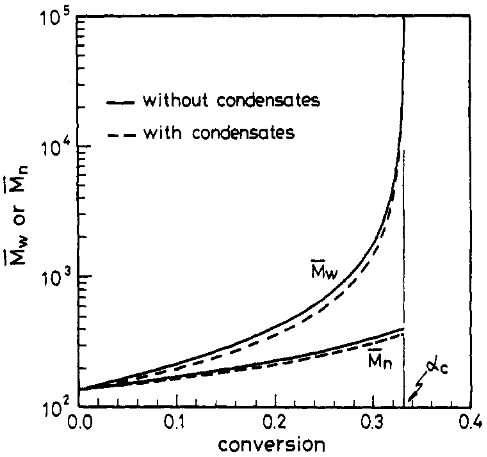

Figure 10. Average molecular weight versus conversion of unit OH for polyetherification.

We select an example, etherification of pentaerythritol, which will produce byproducts, H_2O:

$$C(CH_2OH)_4 \rightarrow \text{polyether} + H_2O \qquad (20)$$

Figure 10 shows the results calculated by the kinetic model, in which parameters are as follows:

molecular weight of pentaerythritol = 136

f (functionality) = 4

weight of H_2O = 18

The reactivities of units –OH are assumed to be of no substitution effects, i.e., random polymerization. It was

Table II. Calculated $\bar{M}_w$ for Polyetherification According to the Kinetic Method and the Recursive Equation

τ[a]	α(OH)[b]	$\bar{M}_w$[c]	$\bar{M}_w$[d]	(*col* 4–*col* 5)/*col* 5 × 100%
0	0.000	136	136	0.00
0.4	0.031	151	151	0.00
0.8	0.060	168	168	0.00
1.2	0.088	189	187	1.07
1.6	0.113	212	210	0.95
2	0.138	240	239	0.42
2.4	0.161	275	272	1.10
2.8	0.183	317	313	1.28
3.2	0.204	370	366	1.09
3.6	0.224	439	436	0.69
4	0.242	533	524	1.72
4.4	0.260	668	657	1.67
4.8	0.277	877	859	2.10
5.2	0.294	1250	1237	1.05
5.6	0.309	2070	2010	2.99
6	0.324	5520	5265	4.84
6.2	0.332	28000	36957	−24.24

[a] τ is an arbitrary scaled time (eq 8). [b] α(OH): conversion of –OH groups. [c] $\bar{M}_w$ calculated by the kinetic method of this work. [d] $\bar{M}_w$ calculated by the recursive equation as follows:[7]

$$\bar{M}_w = \frac{1+\alpha}{1-\alpha(f-1)}\left(M_{A_f} - \frac{fM_c}{2}\right) + \frac{(1-\alpha)fM_c/2}{1-\alpha(f-1)}\left[1 - \alpha\frac{(M_{A_f} - M_c)}{M_{A_f} - fM_c/2}\right]$$

where α is the conversion, f is the functionality of monomer, M_{A_f} and M_c are the molecular weights of the monomer and condensation byproduct, respectively.

Table III. Comparison of Critical Conversion, α_c, for Different Methods

K_0	K_1	K_2	α_c[a]	α_c[b]	α_c[c]	this work α_c
1.00	1.00	100.00	0.280–0.281	0.2802	0.2836	0.2788
1.00	1.00	10.00	0.346–0.347	0.3451	0.3467	0.3451
1.00	1.00	1.00	0.498–0.501	0.5000	0.5000	0.4999
1.00	1.00	0.10	0.617–0.620	0.6171	0.6171	0.6171
1.00	1.00	0.01	0.657–0.660	0.6569	0.6569	0.6569
1.00	0.10	100.00	0.441–0.444	0.4433	0.4979	0.4433
1.00	0.10	10.00	0.453–0.455	0.4538	0.5006	0.4538
1.00	0.10	1.00	0.489–0.491	0.4902	0.5217	0.4902
1.00	0.10	0.10	0.560–0.563	0.5619	0.5772	0.5619
1.00	0.10	0.01	0.630–0.634	0.6302	0.6331	0.6305

[a] The discretized conversion statistical model.[17] [b] The kinetic model of Galina and Szustalewicz.[16] [c] The minimal statistical model.[6,16]

found that the critical conversions of –OH are equal to 0.33, not affected by considering the condensation byproducts or not, and both the $\bar{M}_w$ and $\bar{M}_n$ profiles of the system with byproducts are little lower than the system without byproducts as shown in Figure 10. These results are consistent with those by Macosko and Miller using a recursive equation[7] (Table II), except for the conversions near gel point where the value of $\bar{M}_w$ tends to infinity.

III. Polymerization with a First-Shell Substitution Effect. We consider a system of stepwise homopolymerization of a trifunctional monomer reacting with a first-shell substitution effect (FSSE).[6,14] With this effect, the reactivity of an unreacted group depends on the number of reacted groups in the same monomer. Let A_i denotes the unit with i reacted functionalities, i = 0, 1, 2, 3. The rate constant, k_{ij}, of the reaction between A_i and A_j may be assumed to be

$$k_{ij} = k^0(3-i)\,K_i(3-j)\,K_j \tag{21}$$

where k^0 is the rate constant of a reference group, and K_i, or K_j, is the relative rate constant of the group of type i, or j, with the reference group.

As shown in Table III, the critical conversions are dependent on the values of K_j, and the results agree well with those by the other approaches.[6,16,17]

4. Conclusion

A generalized kinetic method for calculating the molecular weight has been developed for nonlinear polymerization before gelation in this work. Our kinetic method can directly provide the relationship between the average molecular weight and the reaction time and can be readily extended to the systems of multicomponents with a multistage process. According to our computer modeling calculations for the systems of three components with a two-stage process, the profiles of weight-average molecular weight and the critical conversion depend on the second-stage time and the ratio of reactivity of the two stages. Furthermore, the homopolymerization with condensation products and the homopolymerization with a first-shell substitution effects were calculated, and the results agree with those by statistical methods.

Appendix

In eq 1, the unit A_{ij} may be the same as A_{rs} (i, r = 1, 2, ..., m; j, s = 1, ..., 4), although (i, j) is not equal to (r, s); then the element p_{ij} of the matrix **P** may not be independent. Thus we consider this system consisting of n independent reacting and resultant units, B_i (i = 1, 2, ..., n), and m reaction steps and then define a vector **E** to characterize the structure isomer, $\langle \mathbf{E} \rangle$, rather than matrix **P**:

$$\begin{aligned}\mathbf{E} &= (e_1, e_2, e_3, ..., e_n, e_{n+1}, ..., e_{n+m} + e_{n+m+1}) \\ &= (e_1, e_2, e_3, ..., e_n, e_{c_1}, ..., e_{c_m}, e_w)\end{aligned} \tag{A1}$$

where e_i (i = 1, 2, ..., n) is the number of units B_i; $e_{c_j} = e_{n+j}$ (j = 1, 2, ..., m) is the number of times the ith reaction occurs to form the molecule $\langle \mathbf{E} \rangle$; and $e_w = e_{n+m+1}$ is the molecular weight of $\langle \mathbf{E} \rangle$ if no condensation byproducts form.

Then a new generating function is defined as

$$H[\tau, w_i\ (i = 1, 2, ..., n+m+1)] = \sum_{\text{all } \mathbf{E}} \left(\prod_{i=1}^{n+m+1} w_i^{e_i} \right) [\mathbf{E}] \tag{A2}$$

where $\sum_{\text{all } \mathbf{E}}$ denotes the summation for all possible values of vector **E**, w_i (i = 1, 2, ..., $n+m+1$) are dummy variables, and [**E**] is the dimensionless number fraction of $\langle \mathbf{E} \rangle$, which is defined as

$$[\mathbf{E}] = N(\mathbf{E})/N_0 \tag{A3}$$

here $N(\mathbf{E})$ is the number of $\langle \mathbf{E} \rangle$, and N_0 is an arbitrary reference number.

For example, in a reacting system, the reactions between units are assumed to be:

$$B_1 + B_2 \xrightarrow{k_1} B_3 + B_4 + C_1 \tag{A4}$$

$$B_1 + B_3 \xrightarrow{k_2} B_5 + B_6 + C_2 \tag{A5}$$

where B_1, B_2, ..., B_6 are reacting or resultant units, and C_1 and C_2 are condensation byproducts.

The relations between A_{ij}, in eq 1, and B_r (r = 1, 2, ..., 6) are

$$B_1 = A_{11} = A_{21};\ B_2 = A_{12};\ B_3 = A_{13} = A_{22};\ B_4 = A_{14};\ B_5 = A_{23};\ B_6 = A_{24} \tag{A6}$$

Then elements e_r (r = 1, 2, ..., 6) of the vector **E** can be connected with p_{ij} of the matrix **P**:

$$e_1 = p_{11} = p_{21};\quad e_2 = p_{12};\quad e_3 = p_{13} = p_{22};\quad e_4 = p_{14};$$
$$e_5 = p_{23};\quad e_6 = p_{24};\quad e_7 = p_{15};\quad e_8 = p_{25};\quad e_9 = p_{\mathrm{w}} \quad \text{(A7)}$$

where e_1, e_2, ..., e_6 is the number of B_1, B_2, ..., B_6, respectively.

In this system, the variables x_{11}, x_{21}, x_{13}, and x_{22} of the generating function G (eq 10) are not independent; thus, G is transformed into H (eq A2), in which $w_1, w_2, ..., w_9$ are independent.

For the general case, we define a set of variables x^*_{ij}: $x^*_{ij} = w_r$, if the unit B_r represents the unit A_{ij}. In the above example,

$$w_1 = x^*_{11} = x^*_{21};\quad w_2 = x^*_{12};\quad w_3 = x^*_{13} = x^*_{22};\quad w_4 = x^*_{14};$$
$$w_5 = x^*_{23};\quad w_6 = x^*_{24} \quad \text{(A8)}$$

Being analogous to eqs 10 and 11, for the general case, the time derivative of the generating function H can be obtained:

$$\frac{\partial H}{\partial \tau} = \sum_{i=1}^{m} \hat{k}[\mathrm{H}_{x^*_{i1}} H_{x^*_{i2}} x^*_{i3} x^*_{i4} x^*_{i5} - x^*_{i1} H x^*_{i1} H_{i2} - x^*_{i2} H x^*_{i2} H_{i1}] \quad \text{(A9)}$$

where $k'_i = k_i/2$ for $A_{i1} = A_{i2}$ (homopolymerization); $k'_i = k_i$ for $A_{i1} \neq A_{i2}$; $\hat{k}_i = (k'_i/k_0)(V/V_0)$; $Hx^*_{ij} = \partial H/\partial x^*_{ij}$; and $H_{ij} = Hx^*_{ij}|$ with all dummy variables x^*_{ij} equal to 1, i.e., w_q ($q = 1, ..., n + m + 1$) = 1.

Note that, if B_r represents A_{ij}, i.e., $w_r = x^*_{ij}$

$$\frac{\partial H}{\partial x^*_{ij}} = \frac{\partial H}{\partial w_r}$$

By setting all dummy variables x^*_{ij} in eq A9 equal to 1, the time derivative of H along w_q ($q = 1, 2, ..., n + m + 1$) = 1, can be written as

$$\frac{\partial H^*}{\partial \tau} = \sum_{i=1}^{m} \hat{k}_i(-H_{i1}H_{i2}) \quad \text{(A10)}$$

where $H^* = H|_{w_q=1}$.

The partial derivatives of H along w_q ($q = 1, 2, ..., n + m + 1$) = 1 can be obtained by differentiating eq A9 with respect to w_r or to both w_r and w_s:

$$\frac{\partial H^*_r}{\partial \tau} = \sum_{i=1}^{m} \hat{k}_i H_{i1} H_{i2} \left(\frac{\partial X^*}{\partial w_r} - \frac{\partial x^*_{i1}}{\partial w_r} - \frac{\partial x^*_{i2}}{\partial w_r} \right) \quad \text{(A11)}$$

$$\frac{\partial H^*_{r,s}}{\partial \tau} = \sum_{i=1}^{m} \hat{k}_i \Bigg[H_{i1,r} H_{i2,s} + H_{i1,s} H_{i2,r} + (H_{i1,r} H_{i2} + H_{i1} H_{i2,r}) \left(\frac{\partial X^*}{\partial w_s} \right) + (H_{i1,s} H_{i2} + H_{i1} H_{i2,s}) \left(\frac{\partial X^*}{\partial w_r} \right) + H_{i1} H_{i2} \left(\frac{\partial^2 X^*}{\partial w_r \partial w_s} \right) - \left(\frac{\partial x^*_{i1}}{\partial w_r} H_{i1,s} + \frac{\partial x^*_{i1}}{\partial w_s} H_{i1,r} \right) H_{i2} - \left(\frac{\partial x^*_{i2}}{\partial w_r} H_{i2,s} + \frac{\partial x^*_{i2}}{\partial w_s} H_{i2,r} \right) H_{i1} \Bigg] \quad \text{(A12)}$$

and the initial conditions are

$$H^*(\tau{=}0) = \sum_{\text{all } \mathbf{E}} [\mathbf{E}]_0 \quad \text{(A13)}$$

$$H^*_r(\tau{=}0) = \sum_{\text{all } \mathbf{E}} e_r [\mathbf{E}]_0 \quad \text{(A14)}$$

$$H^*_{r,s}(\tau{=}0) = \sum_{\text{all } \mathbf{E}} e_r e_s [\mathbf{E}]_0 \quad \text{for } r \neq s \quad \text{(A15)}$$

$$H^*_{r,s}(\tau{=}0) = \sum_{\text{all } \mathbf{E}} e_r (e_r - 1) [\mathbf{E}]_0 \quad \text{for } r = s \quad \text{(A16)}$$

where $H^*_r = \partial H/\partial w_r|_{w_q}{=}1$; $H_{ij,r} = H_{r,ij} = \partial^2 H/\partial x^*_{ij} \partial w_r|_{w_q=1}$; $H_{ij,s} = H_{s,ij} = \partial^2 H/\partial x^*_{ij}|_{w_q=1}$; $X^* = x^*_{i3} x^*_{i4} x^*_{i5}$; and $[\mathbf{E}]_0 = [\mathbf{E}]$ at $\tau = 0$, in which $q, r, s = 1, 2, ..., n + m + 1$. Note that, if B_r represents A_{ij}, i.e., $w_r = x^*_{ij}$, $H_{ij,s} = H_{r,s}$.

This set of ordinary differential equations (A10)–(A12) with one dependent variable, τ, can be calculated by using the Runge–Kutta method with automatically adjusted length of time step to obtain $H^*(\tau)$, $H^*_r(\tau)$, and $H^*_{r,s}(\tau)$, and the gel time, τ_c, identified with the time corresponding to the divergence of $H^*_{r,s}$.[15,16]

Furthermore, the dimensionless number fraction and the conversion of unit B_r can be obtained by the following equations:

$$[B_r] = N(B_r)/N_0 = \sum_{\text{all } \mathbf{E}} e_r[\mathbf{E}] = H^*_r \ (r = 1, 2, ..., n) \quad \text{(A17)}$$

where $N(B_r)$ is the number of units B_r.

$$\text{conversion of } B_r = 1 - N(B_r)/N_0(B_r) = 1 - H^*_r(\tau)/H^*_r(0) \ (r = 1, 2, ..., n) \quad \text{(A18)}$$

where $N_0(B_r) = N(B_r)$ at $\tau = 0$.

According to eqs 12–17, the moments of the MWD can be calculated as follows:

$$M_0 = \frac{N_0}{N_{\mathrm{T}}} H^* \quad \text{(A19)}$$

$$M_1 = \frac{N_0}{N_{\mathrm{T}}} \left(H^*_{n+m+1} - \sum_{i=1}^{m} W_{\mathrm{C}_i} H^*_{n+i}\right) \quad \text{(A20)}$$

$$M_2 = \frac{N_0}{N_{\mathrm{T}}} \Bigg[H^*_{n+m+1,n+m+1} + H^*_{n+m+1} - 2\sum_{i=1}^{m} W_{\mathrm{C}_i} H^*_{n+m+1,n+i} + \sum_{\substack{i=1,...,m \\ j=1,...,m \\ (i \neq j)}} W_{\mathrm{C}_i} W_{\mathrm{C}_j} H^*_{n+i,n+j} + \sum_{i=1}^{m} W^2_{\mathrm{C}_i} (H^*_{n+i,n+i} + H^*_{n+i})\Bigg] \quad \text{(A21)}$$

where W_{C_i} is the weight of condensation byproduct C_i ($i = 1, 2, ..., m$), and N_{T} is the total number of molecules of the system.

The relation among the average molecular weight, $\bar{M}_{\mathrm{n}}$ and $\bar{M}_{\mathrm{w}}$, and reaction time can be solved by the following algorithm (for either the one-stage process, all reactants were mixed to react simultaneously, or the multistage process, some reactants were reacted first and then the other components were added into the former system at following stages in sequence):

(1) According to the eqs A13–A16, calculate the initial conditions, $H(0)^*$, $H^*_r(0)$, and $H^*_{r,s}(0)$, from the concentrations of the added reactants at the first stage, $\tau = 0$.

(2) Set $\tau \leftarrow \tau + \Delta\tau$, where $\Delta\tau$ is the specified step time length.

(3) Use the Runge–Kutta method to calculate the values of $H^*(\tau)$, $H^*_r(\tau)$, and $H^*_{r,s}(\tau)$ by the set of ODE (eqs A10–A12).

(4) If $\tau = \tau_i$ (the ith stage time, at which the new reactants will be added into the reacting system), set

$$H^*(\tau_i) \leftarrow H^*(\tau_i) + \sum_{\text{all } \mathbf{E}} [\mathbf{E}]_{\text{stage } i} \quad \text{(A22)}$$

$$H_r^*(\tau_i) \leftarrow H_r^*(\tau_i) + \sum_{\text{all } \mathbf{E}} e_r [\mathbf{E}]_{\text{stage } i} \tag{A23}$$

$$H_{r,s}^*(\tau_i) \leftarrow H_{r,s}^*(\tau_i) + \sum_{\text{all } \mathbf{E}} e_r e_s [\mathbf{E}]_{\text{stage } i} \qquad \text{for } r \neq s \tag{A24}$$

$$H_{r,r}^*(\tau_i) \leftarrow H_{r,r}^*(\tau_i) + \sum_{\text{all } \mathbf{E}} e_r (e_r - 1) [\mathbf{E}]_{\text{stage } i} \tag{A25}$$

where $[\mathbf{E}]_{\text{stage } i} = N(\mathbf{E})_{\text{stage } i}/N_0$, in which $N(\mathbf{E})_{\text{stage } i}$ is the number of molecules $\langle \mathbf{E} \rangle$ added into the former system at time τ_i.

(5) Calculate the $\bar{M}_n$, $\bar{M}_w$, and conversions by eqs A19–A21, 16, and 17.

(6) Repeat steps (2)–(5) until the scaled time, τ, is equal to either the specified end time or the gel time, τ_c.

References and Notes

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