Cascade Theory of Substitution Effects in Nonequilibrium Polycondensation Systems

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ABSTRACT: The substitution effect of neighboring groups on the statistical quantities in nonequilibrium condensation polymerization is analyzed by the vectorial cascade theory. In equilibrium condensation polymerization, the substitution is affected by the conversional distribution of building (monomer) units. In nonequilibrium condensation polymerization, however, it needs to be expressed by the distribution function of the local connection of *links*. The average degree of polymerization and the critical point of gelation are obtained by generalizing the conventional cascade theory. The molecular mass distribution is evaluated by direct recurring calculations with a cutoff in the original probability generation function or in the Groebner base. Compared with conventional treatment by Lagrange's expansion, the evaluation method developed here requires less computer memory. This allows us to complete the calculations within a reasonable time. As a typical example, formulation of the probability generating function for the first-shell substitution effect in trifunctional unit systems and the calculation of their molecular mass distribution are given.

Introduction

In his study of the condensation polymerization of functional monomers, Stockmayer found the molecular mass distribution by a statistical method based on a branching tree model.[1−3] Fukui and Yamabe extended this model to a multifunctional interunit junction system.[4,5] Although complete distribution functions were given, these theories are restricted to systems that consist of two kinds of functional groups. To remove such restrictions, Gordon and co-workers generalized Good's cascade theory.[6−9] The use of simpler mathematical probability generating functions (pgf) made the derivation of various statistical averages straightforward and routine.[10−12] This theory was applied to the evaluation of rubber elasticity and to the analysis of the scattering intensity from polymer gels.[13−15] Mikeš and Dušek[16] showed that the results of Monte Carlo study on the network formation by stepwise homopolymerization of trifunctional monomers differ from those obtained by the classical version of cascade theory concerning the size distribution of polymer molecules.[17] Simultaneously, they showed that, when functional groups are equal to each other and also when the reactivity of the functional groups is conversion-independent, the results by MC agree with those by the classical version of cascade theory. Galina and Szustalewicz[18] reached the same conclusions by the analytical method based on a kinetic equation. Gordon and Scantlebury studied the unequal reactivity caused by the neighboring groups, especially the first shell substitution effect (fsse), in equilibrium condensation reactions.[19] However, the treatment of such neighboring group effects have so far been developed neither for nonequilibrium *nonlinear* reactions nor for the calculation of molecular mass distribution.

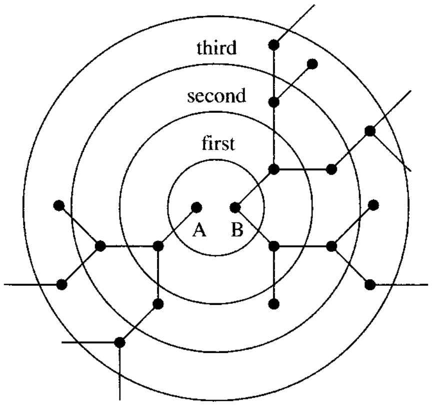

Figure 1. Successive shells for the condensation reaction of units A and B.

The reactivity of substituted monomers depends on the neighboring groups which are classified by successive shells as shown in Figure 1. This is similar to Gordon and Scantlebury's Figure 1.[19] The probability generating function of the equilibrium system can be expressed by the distribution of the substituted structure of units. For example, fsse for equilibrium polycondensation in f-functional (repeat) unit systems is expressed in terms of the pgf as

$$F_0(\theta) = N_0 \sum_{i=0}^{f} {}_fC_i \gamma^i (1-\gamma)^{f-i} \phi(i) \theta^i \tag{1}$$

where N_0 is a normalizing factor, γ the conversion parameter, and $\phi(i)$ the ratio of the number of units with i links relative to the total number of units in the fsse system. This ratio $\phi(i)$ can be written in terms of the standard free energy $\Psi(i)$ of reaction as

$$\phi(i) = \exp\{-\sum_{m=1}^{i-1} \Psi(m)/RT\} \quad (2 \le i \le f) \tag{2}$$

In terms of $\Psi(i)$, the standard free energy ΔG^0 of the reaction required to form a link between two units, each carrying i_1 and i_2 reacted links as shown in

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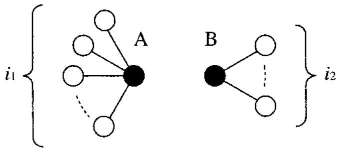


Figure 2. Local situation for the formation of a link between A and B.

Table 1. Possible Types of Reacted Units[a]

units	mole amount
	P_0
	P_1
	P_2
	P_3

[a] Circle denotes a unit, and straight line indicates reacted functionality or connected link.

Figure 2, is given by

$$\Delta G^0 = \Delta G^{0*} + \Psi(i_1) + \Psi(i_2) \tag{3}$$

Here, ΔG^{0*} denotes the free energy forming the same link in the absence of fsse, i.e., in random reaction. Equation 3 assumes that the fsse of A and B in equilibrium polycondensation reactions is independent. However, this assumption cannot be adopted for nonequilibrium *nonlinear* polycondensation reactions.[19] Therefore, a formula like eq 1 does not hold because the two conversions in mutually connected units are not independent of each other.

For such a correlated reaction, Good derived the expression of molecular mass distributions by using Lagrange's expansion.[7] However, in the case of multiple unit systems, a very long computation time is necessary for practical calculation on the basis of his expression. One of the main causes of time consumption is the requirement for huge memory. An improved procedure which requires less memory is therefore required.

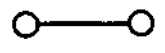
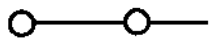
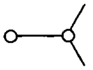
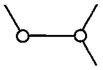
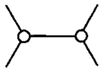
The purpose of this paper is to give the pgf of cascade theory for evaluating the neighboring group effect in nonequilibrium condensation polymerization and to establish an efficient calculation procedure for molecular mass distribution. We find that our method is sufficiently general and is therefore applicable to other more complex multiunit systems.

Formulation of Substitution Effects in Nonequilibrium Systems

In the case of nonequilibrium polycondensation systems, the pgf is derived from the distribution of the substituted structures of two units such as A and B in Figure 2 which react and form a link. For simplicity, let us consider the polycondensation of trifunctional units. The pgf of fsse in such a nonequilibrium polycondensation system is described as follows.

Link-Based Formulation. First, we show all possible types of reacted units in Table 1. Here, P_i denotes the molar population of the units whose i functional groups have already been reacted. Possible types of links are listed in Table 2. The symbol C_i means the molar amount of the links of type i in the first shell substituted structure.

Table 2. Possible Types of Linkage

units	mole amount
	C_1
	C_2
	C_3
	C_4
	C_5
	C_6

Hence, we have

$$P_1 = 2C_1 + C_2 + C_3 \tag{4}$$

$$P_2 = (C_2 + 2C_4 + C_5)/2 \tag{5}$$

$$P_3 = (C_3 + C_5 + 2C_6)/3 \tag{6}$$

The distribution of $\{C_i\}$ can be obtained by the following kinetic equations:

$$\frac{\mathrm{d}P_0}{\mathrm{d}t} = -P_0Q_0 \tag{7}$$

$$\frac{\mathrm{d}C_1}{\mathrm{d}t} = K(0,0)P_0P_0 - 2C_1Q_1 \tag{8}$$

$$\frac{\mathrm{d}C_2}{\mathrm{d}t} = K(1,0)\ P_0(2C_1 + C_2 + C_3) + 2C_1Q_1 - C_2(Q_1 + Q_2) \tag{9}$$

$$\frac{\mathrm{d}C_3}{\mathrm{d}t} = K(2,0)\ P_0(C_2 + 2C_4 + C_5)/2 + C_2Q_2 - C_3Q_1 \tag{10}$$

$$\frac{\mathrm{d}C_4}{\mathrm{d}t} = K(1,1)(2C_1 + C_2 + C_3)^2 + C_2Q_1 - 2C_4Q_2 \tag{11}$$

$$\frac{\mathrm{d}C_5}{\mathrm{d}t} = K(2,1)(2C_1 + C_2 + C_3)(C_2 + 2C_4 + C_5)/2 + C_3Q_1 + 2C_4Q_2 - C_5Q_2 \tag{12}$$

$$\frac{\mathrm{d}C_6}{\mathrm{d}t} = K(2,2)(C_2 + 2C_4 + C_5)^2/4 + C_5Q_2 \tag{13}$$

where

$$Q_0 = K(0,0)P_0 + K(1,0)(2C_1 + C_2 + C_3) + K(2,0)(C_2 + 2C_4 + C_5)/2 \tag{14}$$

$$Q_1 = K(1,0)P_0 + K(1,1)(2C_1 + C_2 + C_3) + K(2,\ 1)(C_2 + 2C_4 + C_5)/2 \tag{15}$$

$$Q_2 = K(2,0)P_0 + K(2,1)(2C_1 + C_2 + C_3) + K(2,2)(C_2 + 2C_4 + C_5)/2 \tag{16}$$

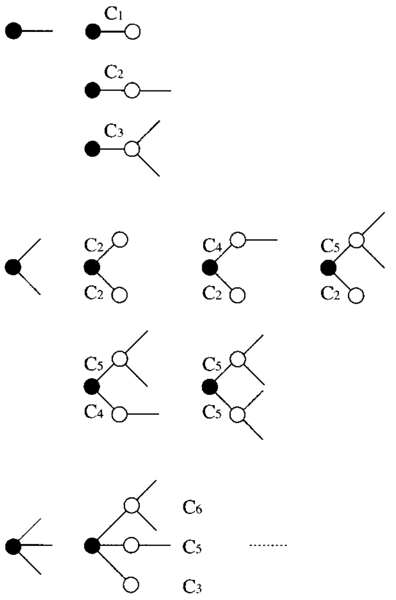
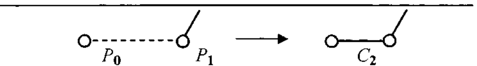
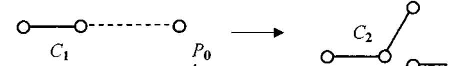
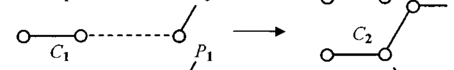
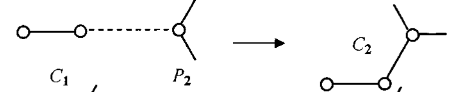
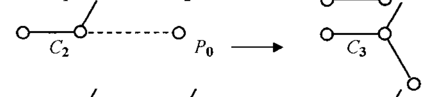
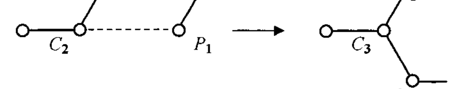
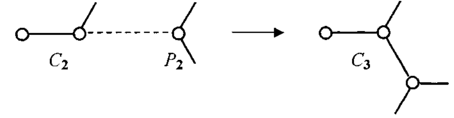
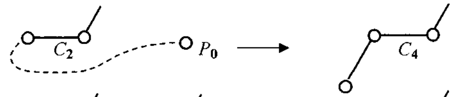
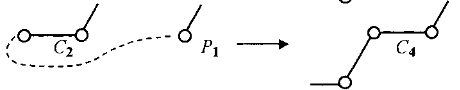
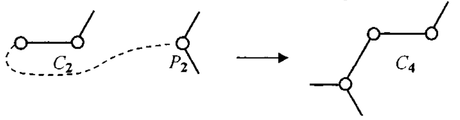


Figure 3. Restriction conditions for types of link belonging to various types of reacted units (●) and the links connecting neighboring units (○).

Table 3. Possible Types of Reaction

No.	types of reaction
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	

and $K(i, j)$ is the rate coefficient for the condensational reaction of a unit of the type i with another unit of the type j. Such kinetic equations can be intuitively derived from a list of all possible reactions. For example, Table 3 shows a list of 10 reactions needed to make eq 9 concerning the second type C_2 links. The first four reactions in Table 3 create second type links, while the remaining six eliminate them.

In nonequilibrium condensation, the two conversions of mutually connected units are correlated to each other. This correlation can be estimated by the distribution of the types of links. As Figure 3 shows, a unit that reacts with only one other unit belongs to the first, second, or third type of link. Similarly, a unit of which two functional groups are reacted belongs to the second, fourth, or fifth type of link, and a unit of which all three functional groups are reacted belongs to the third, fifth, or sixth type of link. Under the assumption of fsse, the type of link does not depend on the type of other links that belong to the same unit. Therefore, the pgfs W of fsse in nonequilibrium polycondensation is given by

$$W = \sum_{i=1}^{4} b_i W_i \tag{17}$$

$$W_1 = \theta \tag{18}$$

$$W_2 = \theta(2C_1U_1 + C_2U_2 + C_3U_3)/(2C_1 + C_2 + C_3) \tag{19}$$

$$W_3 = \theta(C_2U_1 + 2C_4U_2 + C_5U_3)^2/(C_2 + 2C_4 + C_5)^2 \tag{20}$$

$$W_4 = \theta(C_3U_1 + C_5U_2 + 2C_6U_3)^3/(C_3 + C_5 + 2C_6)^3 \tag{21}$$

$$U_1 = \theta \tag{22}$$

$$U_2 = \theta(C_2U_1 + 2C_4U_2 + C_5U_3)/(C_2 + 2C_4 + C_5) \tag{23}$$

$$U_3 = \theta(C_3U_1 + C_5U_2 + 2C_6U_3)^2/(C_3 + C_5 + 2C_6)^2 \tag{24}$$

where b_i means the mole fraction of the unit in which $i - 1$ functions have been reacted and θ denotes the dummy variable. W_i represents the function of U_i and corresponds to the unit of the zeroth generation in which $i - 1$ functions have been reacted. U_i indicates the auxiliary series of θ and corresponds to the unit of the first (or any subsequent) generation in which $i - 1$ functions have been reacted to generate $i - 1$ offspring.

Unit-Based Formulation. By differentiating eqs 4–6, we obtain

$$\frac{dP_1}{dt} = 2\frac{dC_1}{dt} + \frac{dC_2}{dt} + \frac{dC_3}{dt} \tag{25}$$

$$\frac{dP_2}{dt} = \frac{1}{2}\frac{dC_2}{dt} + \frac{dC_4}{dt} + \frac{1}{2}\frac{dC_5}{dt} \tag{26}$$

$$\frac{dP_3}{dt} = \frac{1}{3}\frac{dC_3}{dt} + \frac{1}{3}\frac{dC_5}{dt} + \frac{2}{3}\frac{dC_6}{dt} \tag{27}$$

Upon substitution of eqs 8−13 into these equations, we find

$$\frac{\mathrm{d}P_0}{\mathrm{d}t} = -P_0(2K(0,0)P_0 + K(1,0)P_1 + K(2,0)P_2) \quad (28)$$

$$\frac{\mathrm{d}P_1}{\mathrm{d}t} = P_0(2K(0,0)P_0 + K(1,0)P_1 + K(2,0)P_2) - P_1(K(1,0)P_0 + 2K(1,1)P_1 + K(2,1)P_2) \quad (29)$$

$$\frac{\mathrm{d}P_2}{\mathrm{d}t} = P_1(K(1,0)P_0 + 2K(1,1)P_1 + K(2,1)P_2) - P_2(K(1,0)P_0 + K(2,1)P_1 + 2K(2,2)P_2) \quad (30)$$

$$\frac{\mathrm{d}P_3}{\mathrm{d}t} = P_2(K(2,0)P_0 + K(2,1)P_1 + 2K(2,2)P_2) \quad (31)$$

These are kinetic equations based on the units. The pgfs in equilibrium reaction is obtained from them by setting all the time derivatives to zero. The corresponding pgfs in equilibrium polycondensation are

$$W = \theta(b_1 + b_2U + b_3U^2 + b_4U^3) \quad (32)$$

$$U = \theta(b_2 + 2b_3\,U + 3b_4U^2)/(b_2 + 2b_3 + 3b_4) \quad (33)$$

This pair of equations {(32), (33)} is equivalent to eqs 17−24 when the correlation between the two connected units can be neglected. Thus, eqs 17−24 based on links are a generalization of eqs 32 and 33 based on units.

Calculation of Average Molecular Mass

The average molecular mass, or average degree of polymerization multiplied by the monomer mass, and the critical point of gelation are obtained in the same way as for the equilibrium cascade theory.

The weight-average molecular mass in nonequilibrium condensation polymerization is obtained from expressions 34−41 which are derived by differentiating eqs 17−24:

$$\mathrm{DP_w(nonequilibrium)} = \left(\frac{\partial W}{\partial \theta}\right)_{\theta=1} = \sum_{i=1}^{4} b_i\left(\frac{\partial W_i}{\partial \theta}\right)_{\theta=1} \quad (34)$$

where

$$\left(\frac{\partial W_1}{\partial \theta}\right)_{\theta=1} = 1 \quad (35)$$

$$\left(\frac{\partial W_2}{\partial \theta}\right)_{\theta=1} = 1 + \left(2C_1\left(\frac{\partial U_1}{\partial \theta}\right)_{\theta=1} + C_2\left(\frac{\partial U_2}{\partial \theta}\right)_{\theta=1} + C_3\left(\frac{\partial U_3}{\partial U}\right)_{\theta=1}\right)/(2C_1 + C_2 + C_3) \quad (36)$$

$$\left(\frac{\partial W_3}{\partial \theta}\right)_{\theta=1} = 1 + 2\left(C_2\left(\frac{\partial U_1}{\partial \theta}\right)_{\theta=1} + 2C_4\left(\frac{\partial U_2}{\partial \theta}\right)_{\theta=1} + C_5\left(\frac{\partial U_3}{\partial U}\right)_{\theta=1}\right)/(C_2 + 2C_4 + C_5) \quad (37)$$

$$\left(\frac{\partial W_4}{\partial \theta}\right)_{\theta=1} = 1 + 3\left(C_3\left(\frac{\partial U_1}{\partial \theta}\right)_{\theta=1} + C_5\left(\frac{\partial U_2}{\partial \theta}\right)_{\theta=1} + 2C_6\left(\frac{\partial U_3}{\partial U}\right)_{\theta=1}\right)/(C_3 + C_5 + 2C_6) \quad (38)$$

$$\left(\frac{\partial U_1}{\partial \theta}\right)_{\theta=1} = 1 \quad (39)$$

$$\left(\frac{\partial U_2}{\partial \theta}\right)_{\theta=1} = \frac{2(2C_5C_3 + C_5{}^2 + C_3C_4 + C_5C_2 + C_3C_2 - 2C_6C_2 + C_5C_4 - 2C_6C_4)}{-C_5{}^2 + C_3C_2 + C_5C_3 + C_5C_2 - 2C_6C_2 - 2C_6C_5} \quad (40)$$

$$\left(\frac{\partial U_3}{\partial \theta}\right)_{\theta=1} = \frac{3C_5C_3 + 5C_5C_2 + 4C_5C_4 + 2C_6C_5 + 3C_5{}^2 + 3C_3C_2 + 2C_6C_2}{-C_5{}^2 + C_3C_2 + C_5C_2 - 2C_6C_2 - 2C_6C_5} \quad (41)$$

Let us first check that these equations reduce to conventional ones in the limitation of equilibrium substitutional effects. When the correlation between the two conversions of mutually connected units can be neglected, these links can be derived from the distribution of conversion as

$$C_1 = b_2{}^2C \quad (42)$$

$$C_2 = 4b_2b_4C \quad (43)$$

$$C_3 = 6b_2b_4C \quad (44)$$

$$C_4 = 4b_3{}^2C \quad (45)$$

$$C_5 = 12b_3b_4C \quad (46)$$

$$C_6 = 9b_4{}^2C \quad (47)$$

where C is defined by

$$C = \frac{b_2 + 2b_3 + 3b_4}{2(b_2{}^2 + 4b_2b_3 + 6b_2b_4 + 4b_3{}^2 + 12b_3b_4 + 9b_4{}^2)} \quad (48)$$

By substitution of eqs 42−48 into eq 34, the average degree of polymerization written by the conversions b_i of the units reduces to

$$\mathrm{DP_w(equilibrium)} = \frac{b_2{}^2 + 6b_2b_4 + b_2 + 4b_2b_3 + 12b_3b_4 + 9b_4{}^2 + 4b_3{}^2 - 3b_4}{b_2 - 3b_4} \quad (49)$$

This agrees with the results of conventional equilibrium substitution. In the special case of equal reactivity, mole fraction b_i can be obtained in terms of the conversion α of the functional groups by using the relationship

$$F_0(\theta) = (1 - \alpha + \alpha\theta)^3 \qquad (50)$$

as

$$b_1 = 1 - 3\alpha + 3\alpha^2 - \alpha^3 \qquad (51)$$

$$b_2 = 3\alpha - 6\alpha^2 + \alpha^3 \qquad (52)$$

$$b_3 = 3\alpha^2 - 3\alpha^3 \qquad (53)$$

$$b_4 = \alpha^3 \qquad (54)$$

The average degree of polymerization for equal reactivity then reduces to

$$\mathrm{DP_w(equilibrium)} = \frac{1+\alpha}{1-2\alpha} \qquad (55)$$

Let us next find the critical gel point. The critical gel point is defined by the point at which the weight-average molecular mass extends to infinity. From eq 34 it is generally given by the condition

$$-C_5{}^2 + C_3C_2 + C_5C_3 + C_5C_2 - 2C_6C_2 - 2C_6C_5 = 0 \qquad (56)$$

in the case of nonequilibrium, and from eq 49

$$b_2 - 3b_4 = 0 \qquad (57)$$

in the case of equilibrium, and

$$\alpha_c = \frac{1}{2} \qquad (58)$$

in the case of equilibrium with equal reactivity.

Finally, we find the molecular mass distribution. The molecular mass distribution from monomer to x-mer is evaluated by recurring calculation of the coupled polynomial eqs 22−24. Therefore, we can find a solution as follows. First, we substitute θ as U_i^1 for U_i and obtain U_i^0. We then discard all terms that have higher powers than θ^x. These terms correspond to larger mers than x-mer generated from U_i^0. Next we define U_i^0 as new U_i^1 and substitute U_i^1 for U_i. We repeat this process more than x times or until the U_i becomes equal to the previous U_i. Then, the distribution function is obtained by substitution of U_i for eqs 18−21.

Results of Numerical Calculations

In this chapter, we compare the results of numerical calculations by using our formulas for nonequilibrium condensation polymerization with those for equilibrium polycondensation. To obtain the coefficients of nonequilibrium pgfs (17)−(24), the amount of the remaining monomer P_0 and of each type of link C_i are calculated by using the kinetic equations (7)−(16). Then, results are substituted into the pgf of fsse in the trifunctional unit system, and the molecular mass distribution is evaluated by recurring calculation. The distributions b_i of the conversion units obtained from C_i by eqs 4−6 are substituted for the unit based equilibrium pgfs (32) and (33). Then the molecular mass distributions are similarly estimated by recurring calculation. These molecular mass distributions must agree with the results obtained by using Lagrange's expansion method.

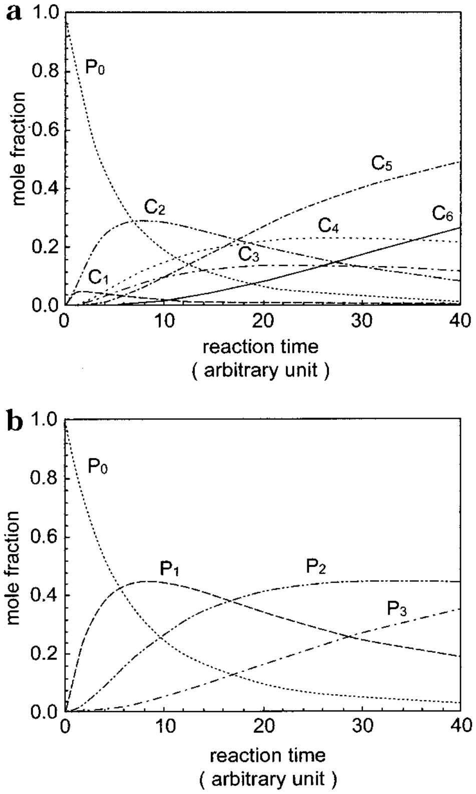


Figure 4. Kinetic calculation for the number of units and links. (a) The kinetic equations (7)−(16) are solved under the assumption that the rate coefficients are given by the ratio $K(0,0)$:$K(0,1)$:$K(0,2)$:$K(1,1)$:$K(1,2)$:$K(2,2)$ = 9:12:6:4:4:1. This corresponds to equal reactivity (random reaction). Relative populations P_i are plotted against the reaction time. The reaction time in abscissa means the number of calculation steps in the Runge−Kutta method. The initial mole fraction of monomer P_0 is 1.0, and the initial mole fraction for the other links is zero. (b) The kinetic equations (28)−(31) are solved using the same rate coefficients as for (a).

First of all, let us examine the case of random reaction in which the reactivity of the functional groups does not change irrespective of the conversion unit. The result of kinetic calculation is shown in Figure 4. Figure 4a shows C_i as a function of time (the number of calculation steps in the Runge−Kutta method). Figure 4b shows the change of the amount P_i. The first and second type of link initially increase, but they soon decrease. The fourth, fifth, and sixth type of link are generated later. These tendencies are the same as for the change in P_i of reacted units. Values for three different times during the calculated reaction period for residual monomer and for each type of link are chosen, and the corresponding three molecular mass distributions are evaluated by recurring calculation for the link-based eqs 17−24 and for the unit-based eqs 32 and 33, respectively. As shown in Figure 5, no discrepancy is found between the two methods for all three data when reactivity is equal.

The discrepancies are found when reactivities are not equal. For example, in the case where the rate of the "monomer with monomer" reaction is 10 times faster than that of other reactions, the distribution functions estimated by the two different methods are plotted against the degree x of polymerization in Figure 6a−c for each reaction. Both link-based calculation and unit-based calculation give a peak of molecular mass distri-

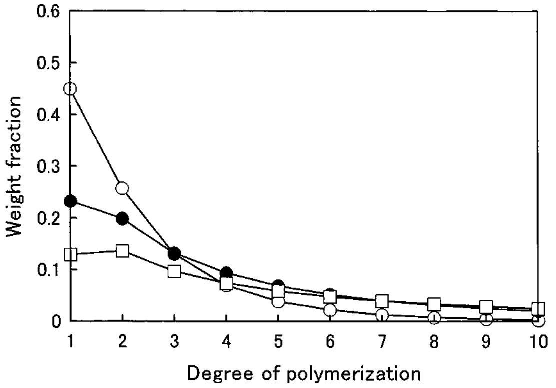


Figure 5. Molecular mass distribution in the case of equal reactivity. Conventional unit-based pgf and link-based pgf for nonequilibrium polycondensation are calculated respectively at three different reaction times taken from the kinetic calculation shown in Figure 4a,b. For example, the residual amounts of monomer P_0 in these data are 0.45, 0.23, and 0.13. (○, ●, and □, respectively) The two lines of the distributions calculated from link-based pgf of nonequilibrium polycondensation and from unit-based pgf are superimposed, because the two distributions are equal.

bution at $x = 2$. However, the link-based distribution is slightly sharper than the other. Figure 7a−c shows the same but for the case where the reaction rate of "monomer with monomer" and of "monomer with one reacted unit from a functional group" is 10 times faster than the other ones. The peak in the degree of polymerization for link-based distribution is larger than that for unit-based calculation.

The link-based calculation can be applied to the analysis of other specific reactions. Figure 8a−c shows the case where the rate of the second type reaction in Table 3 is 10 times faster than that of the other types of reaction. The difference between the two pgfs is clearly shown. The molecular mass distribution estimated by the link-based pgfs (17)−(24) has a peak at three, while the pgf formulated by unit conversions does not show this feature.

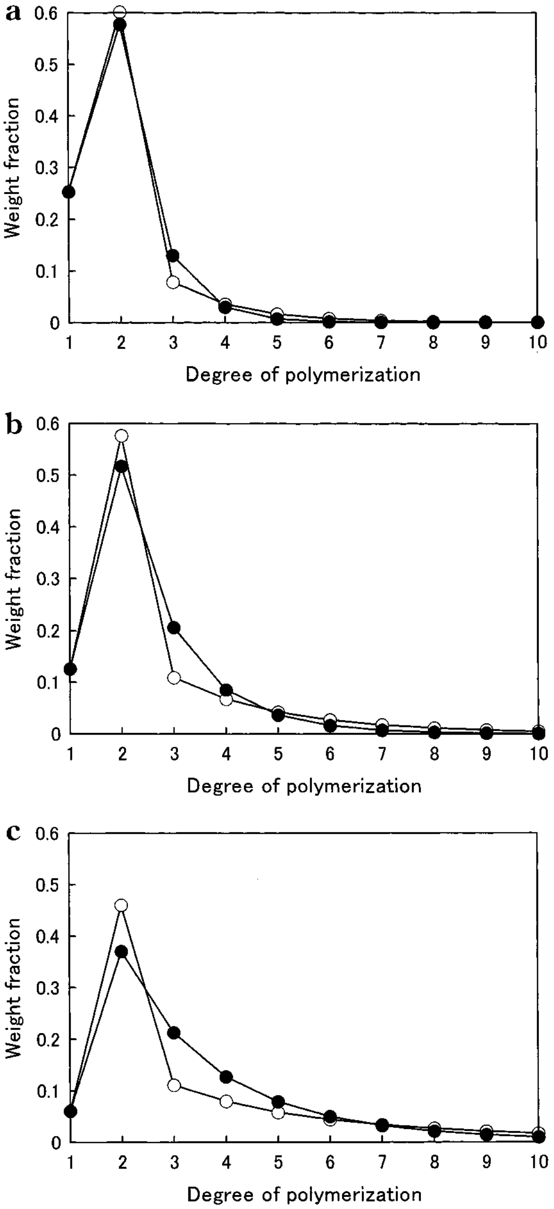


Figure 6. Molecular mass distribution in the case of nonequal reactivity. The rate coefficient for the reaction in the kinetic equation is given by the ratio $K(0,0)$:$K(0,1)$:$K(0,2)$:$K(1,1)$:$K(1,2)$:$K(2,2)$ = 90:12:6:4:4:1. This is where reaction of "monomer with monomer" is 10 times faster than other reactions. The degree of polymerization is estimated in a similar manner, as shown in Figure 5. The residual amounts P_0 of monomers in three selected data are 0.25, 0.13, and 0.06. (●) Distribution calculated from pgf of nonequilibrium polycondensation; (○) distribution calculated from unit-based pgf.

Discussion

The pgf of fsse in a trifunctional unit system was formulated, and the molecular mass distributions of typical cases were estimated by recurring calculation. The formula developed here can be applied to the nonequilibrium polycondensation of more complex systems. The pgf of multiunit systems can be derived in a manner similar to the present one. For example, the pgf of fsse in a phenol−formaldehyde system can be formulated by using 11 auxiliary variables U_i from consideration of the 21 types of links C_i. The formulation developed here is applicable to much higher-order Markovian treatment for such long-range correlation. For example, the pgf of *second* shell substitution effect in the trifunctional unit system is given by 34 auxiliary variables U_i from 269 types of substituted links. Miller and Macosko[20] defined a unit-based "superspecies" for fsse analysis by combining the kinetic method and the Markovian method classified as the "rank" model by Samolia and Miller.[21] When we formulate the homopolycondensation of tetrafunctional monomer, the approximate method requires 341 kinetic differential equations, 341 *W*s, and 1253 *U*s of cascade formulations. The link-based formulation presented here only needs eight DEs, five *W*s, and four *U*s. Galina and Szustalewicz[18] presented a kinetic model that makes use of a coagulation equation like the one Smoluchowski used. The evolution of the molecular size distribution during stepwise homopolymerization of trifunctional monomers reacting with substitution effect was described by the kinetic model. However, in terms of fsse, the model is only applicable when it is assumed that activation energies are additive (*linear*[19]) and when the kinetic rate's constants are factorizable as

$$K_{ij} = k(f - i)(f - j)K_i K_j \tag{59}$$

Local ring formation can also be taken into account under the same assumption, which will be reported in

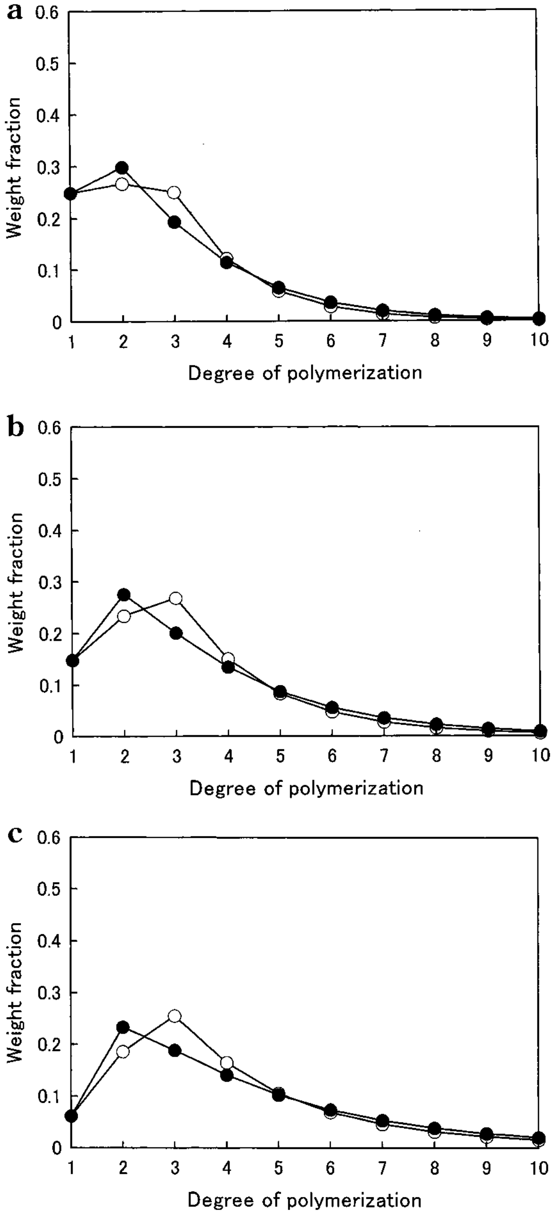


Figure 7. Molecular mass distribution in the case of nonequal reactivity. The rate coefficient is given by $K(0,0)$:$K(0,1)$:$K(0,2)$: $K(1,1)$:$K(1,2)$:$K(2,2) = 9{:}12{:}0.6{:}0.4{:}0.4{:}0.1$. This is where reaction of "monomer with monomer" and "monomer with one-reacted unit" is faster than other reactions. The residual amounts P_0 of monomers in three selected data are 0.25, 0.15, and 0.06.

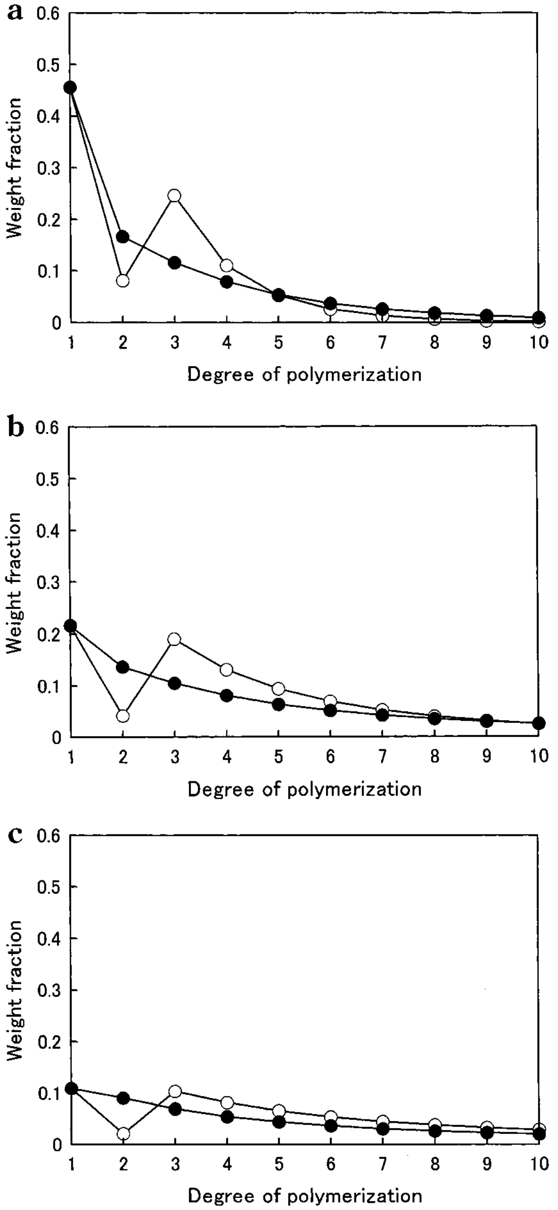


Figure 8. Influence of a specific reaction on molecular mass distribution in nonequilibrium polycondensation. The terms $2K(0,1)P_0(t)C_1(t)$ in eqs 7–9 are substituted for $10K(0,1)P_0(t)\cdot C_1(t)$. This is where the second type of reaction in Table 3 is 5 times faster than other reactions. The residual amounts P_0 of monomers in three selected data are 0.46, 0.22, and 0.11.

a forthcoming paper. Systems with multiple junctions can also be derived from the same procedure. For the estimation of molecular mass distribution, conventional Lagrange's expansion needs a much bigger memory of the order $(f - 1)^s$ as compared with the recurrent calculation. Here, s denotes the number of kinds of units and f is the number of functional groups in each unit. In the case of pgf of nonequilibrium polycondensation, s is the product of the number of kinds of unit and the number of functional groups in those units. Therefore, Lagrange's expansion is particularly impractical for multiunit systems. The memory that a computer needs decreases by about half by using a Groebner base of the pgf in lexicographic order. Moreover, when only a few auxiliary functions are calculated, a Groebner base is efficient because it is not necessary to calculate all the auxiliary functions. When the pgf is approximated by a Pade function such as the cross-linking of linear polymers, recurrent calculation is also applicable. Because the distribution in arbitrary generation can be estimated by using recurrent calculations, both the evaluation of elastically active network chains (EANC) and the analysis of scattering intensity from polymer chains are also possible.

Our cascade theory on the basis of the link-based kinetic equations can be compared with Monte Carlo (MC) simulation. Smoluchowski's equation for coagulation is suitable for describing nonequilibrium condensation polymerization.[22] However, MC simulation is required, because the infinite system of kinetic equations becomes analytically intractable.[23] MC simulation can provide detailed information on network formation and molecular mass distribution, and further development is expected in the future.[16,24,25] Yamagishi et al.[26,27] have investigated phenolic co-condensation reactions by MC simulation based on the on-lattice percolation model and the off-lattice model. Platkowski and Reichert[28] tested the potential and the limitations of MC in their model kinetic polymerization reactions. Especially, they examined the various distributions of the final products. However, a significant disadvantage of MC, especially when dealing with polycondensation reactions, is the length of computation time required due to the tremendous amount of propagational events during the lifetime of a growing polymer chain. Cheng and Chiu[29] found that the gel point and distribution function determined by MC differ according to the change in the size of the simulation system. The larger the number of molecules, the closer the estimated values come to the exact values obtained by the generating function method. Thus, efficient cascade theory as presented in this paper is necessary for examining the validity of MC.

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