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New Cascade Theory of Branched Polymers and Its Application to Size Exclusion Chromatography

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ABSTRACT: A generalized cascade theory is developed and applied to study the size distribution of branched polymers. The configuration of a polymer is expressed by a rooted tree. The rooted tree is described by the "*S*-expression" of Lisp language. Thus, the distribution of polymers in a system can be expressed by the polynomial $W = \sum \alpha_k T_k$, where T_k denotes the *k*-th *S*-expression corresponding to a *k*-th type of polymer and α_k is the probability that a randomly chosen unit in a system belongs to the polymer of *k*-th type. Terms of the polynomial are classified into equivalent classes according to the types of characterization of polymers, and the polynomial in these classes can be calculated from recursive coupled equations on the basis of the Markov branching process. Solving these equations enables us to calculate the parameters for configurations of polymers as well as to obtain the results of the conventional cascade theory. As a special case of this generalized theory, a recursive equation for size distribution is formulated. Using this formulation, the distributions of the mean-square radius of gyration and the shrink factor of branched polymers are calculated on the basis of the Gaussian chain statistics. The substitution effects of neighboring groups are reasonably found to give significant effects on these distributions.

1. Introduction

Size exclusion chromatography (SEC) provides information not only on the average size of polymers but also on the size distribution itself.[1,2] The use of an advanced detector, combined with column packages of high performance, makes SEC the standard method for the separation and analysis of polymers. For examples, when SEC is equipped with a low-angle laser light scattering (LALLS) detection instrument together with a concentration proportional detector, it enables us to evaluate the molecular mass distribution without the calibration curve, and if SEC is equipped with a multiangle laser light scattering (MALLS) detection machine, it can simultaneously determine the absolute molecular mass distribution as well as molecular size. However, compared with linear polymer systems, the analytical theory for SEC of branched polymers is not yet well established. Because of the branched structure, there are broad molecular mass distributions with a great many isomers.

Dobson and Gordon[3] derived the average of mean-square radius of gyration $\langle S^2 \rangle$ of polymers in a polycondensation system by using the cascade theory. Kajiwara et al.[4] calculated the scattering function by introducing the path-weighted function into the cascade theory which represents the length distribution of connected paths between units on a branched polymer. Kajiwara[5] extended the generating function of the cascade theory from the univariate function to the bivariate function, and he systematically derived the average degree of polymerization, the *Z*-average of hydrodynamic radius, the second virial coefficient for osmotic pressure, and the light scattering function of random *f*-functional polycondensation. However, these values and functions, being obtained from the conventional cascade theory, are the averages of all polymers existing in a system; their distribution is not obtainable.

Jackson[6] simulated SEC tracings for the random condensation of an A_2-type monomer with a small amount of A_3. However, as the molecular mass distribution is calculated using the Flory−Stockmayer model, this method can be applied only when the molecular mass distribution is simple. Kidera and Kohjiya[7] evaluated the $\langle S^2 \rangle$ distribution of a polymer cluster in the pregel state as a function of the conversion based on the Flory−Stockmayer model and the Gaussian chain statistics. All the species of the clusters were calculated using exhaustive enumerating iteration equations. However, Kidera and Kohjiya's first systematic approach assumes that all the reactivities of functionalities are of equal reactivity, like in Jackson's method. Hence, neither the first shell substitution effect (fsse) nor the nonequilibrium reaction can be treated. When this method was used in the analysis of some experimental results, a long tail in the large $\langle S^2 \rangle$ region was observed.[8−10] This indicates the tendency of clusters to connect linearly with each other. Moreover, the conventional analytical theory has been applicable neither to systems where various kinds of end-reactive precursor polymers and multifunctional cross-linkers are involved nor to the case where the connective reaction of linkers is possible. Therefore, a powerful analytical method that can deal with changeable reactivity of functionality is required.

Tobita et al.[11] simulated the SEC exclusion curve of a branched polymer using the Monte Carlo (MC) approach based on the "random sampling technique". The MC approach required numerous calculations; for example, to determine $\langle S^2 \rangle$ distribution, they generated 40 000 polymer molecules and calculated 100 three-dimensional structures for each polymer. In more complicated cases, the generation of isomers and the calculation of the three-dimensional structure become an enormous task; therefore, it is time-consuming to apply the MC approach for the analysis of a complex polymer cluster in the pregel state or the state in which many isomers exist.[12]

The purpose of this study is to develop an analytical theory by which the analysis of the radius of gyration of branched polymers can be routinely calculated within a relatively short

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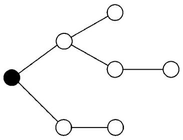
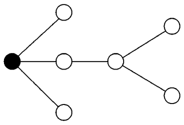
Table 1. Trees and Corresponding Terms[a]

tree	term
	$T_k = (\theta(\theta(\theta\theta(\theta))\theta(\theta)))$
	$T_l = (\theta(\theta\theta(\theta(\theta\theta))\theta))$

[a] Circle denotes a unit, straight line indicates connecting link, and filled circle is a unit chosen randomly in each system that is regarded as the root of each tree.

time. This study has extended the conventional cascade theory in order to deal with the configuration of the polymers. Subsequently, to routinely calculate the distribution of the mean-square radius of gyration $\langle S^2 \rangle$ and the hydrodynamic radius $\langle R_S \rangle$ (Stokes radius), two kinds of formulations and their respective operational rules are considered. A theory is illustrated below, using a simple case. We find that our formulation is sufficiently general to apply to many complex systems. Another purpose of this study is to show a versatility of the generalized cascade theory. Our theory and calculation enable us to obtain many types of parameters related to polymer configurations that cannot be derived from the conventional one.

2. Formulation and Calculation Procedure of $\langle S^2 \rangle$

2.1. Generalized Cascade Theory. Let a monomer such as an end-linker or a precursor that composes a polymer be a "unit", and let a connection between the units be a "link". Different units do not share an atom. Polymers can be described by graphs in which vertices represent the repeat units and edges represent the links between units. Although our theory can be applied to cases that contain cycles[1] resulting from *tree decomposition*, let us consider cases in which polymer graphs do not contain cycles in order to explain our theory as simple as possible in this paper.

When the configuration of polymer is expressed by a rooted tree, and the term exhibiting one-to-one correspondence to these rooted tree is defined, the distribution of polymers in a system can be expressed by the following polynomial:

$$W = \sum \alpha_k T_k \tag{2.1}$$

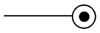
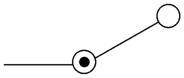
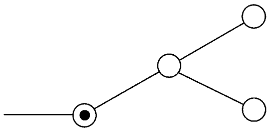
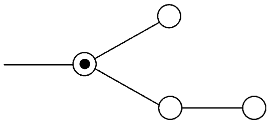
where T_k denotes the k-th term corresponding to a polymer of the k-th type and α_k denotes the probability that a unit chosen randomly in a system belongs to the polymer of the k-th type.

Table 1 shows two examples of polymers possessing units randomly chosen in a system and the terms corresponding to them. Polymers of the k-th and the l-th type are expressed by rooted trees in a system, and the terms T_k and T_l are corresponding to these polymers as the S-expression of Lisp, respectively. Terms enclosed in brackets are commutative as follows:

$$T_l = (\theta(\theta\theta(\theta(\theta\theta))\theta)) = (\theta(\theta\theta\theta(\theta(\theta\theta)))) \tag{2.2}$$

When a unit that is at the root of a tree is regarded as the zeroth generation and the other units are regarded as descendants, these "forest polynomials" (2.1) can be calculated from recursive simultaneous equations as shown below on the basis of the Markov branching process:

Table 2. Subtrees and Corresponding Terms[a]

branch	term
	$B_j = (\theta)$
	$B_k = (\theta(\theta))$
	$B_l = (\theta(\theta(\theta\theta)))$
	$B_m = (\theta(\theta\theta(\theta)))$

[a] Circle with dot denotes the regarded as the ancestor of the subtree.

$$W = (\theta F_0(U)) \tag{2.3}$$

$$U = (\theta F_1(U)) \tag{2.4}$$

where F_0 and F_1 are polynomials of the recursive polynomials U that express the distribution of descendants possessing ancestors and descendants, respectively. The recursive polynomials U expresses the distribution of subtrees that belong to a tree:

$$U = \sum_k \beta_k B_k \tag{2.5}$$

where B_k denotes the k-th term corresponding to the k-th type subtree and β_k denotes the probability that those units regarded as descendants belong to classes of subtrees of the k-th type. Table 2 examplifies subtrees, which are the components of T_k and T_ℓ shown in Table 1. That is

$$T_k = (\theta(B_k B_m)) \tag{2.6}$$

$$T_\ell = (\theta(B_j B_j B_\ell)) \tag{2.7}$$

Formulations for trifunctional reversible polycondensation are shown as follows:

$$W = (\theta(a_0 + a_1 U_1 + a_2 U_1 U_1 + a_3 U_1 U_1 U_1)) \tag{2.8}$$

$$U_g = (\theta(b_0 + b_1 U_{g+1} + b_2 U_{g+1} U_{g+1})) \tag{2.9}$$

As shown in Table 3, a_i denotes the probability for a unit chosen randomly in a system to react with other i units, and b_i denotes the fraction of a unit of the g-th generation having i descendants of the $(g + 1)$-th generation. The calculation procedure of eqs 2.8 and 2.9 is the same as that in normal algebra except in the case of removal of brackets:

$$\begin{aligned}(\theta a_2 U_1 U_1) = {} & a_2(\theta(\theta(b_0 + b_1 U_2 + b_2 U_2 U_2))(\theta(b_0 + b_1 U_2 + b_2 U_2 U_2))) \\ & = a_2 b_0^2(\theta(\theta\theta)) + a_2 b_1^2(\theta(\theta(U_2)\theta(U_2))) + \\ & a_2 b_2^2(\theta(U_2 U_2)\theta(U_2 U_2)) + 2a_2 b_0 b_1(\theta(\theta\theta(U_2))) + 2a_2 b_0 b_2 \theta \\ & (\theta\theta(U_2 U_2)) + 2a_2 b_1 b_2(\theta(U_2)\theta(U_2 U_2))\end{aligned} \tag{2.10}$$

Table 3. Trees and Subtrees in Eqs 8 and 9

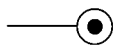
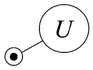
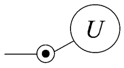
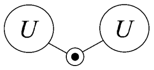
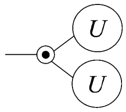
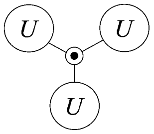
probability	tree	probability	subtree
a_0		b_0	
a_1		b_1	
a_2		b_2	
a_3			

Table 4. Corresponding Terms Transformed for Each Classification

case	T_k	T_l
1	θ^7	θ^7
2	$\theta_0\theta_1{}^2\theta_2{}^3\theta_2{}^3\theta_3$	$\theta_0\theta_1{}^3\theta_2\theta_3{}^2$
3	$\theta_1{}^3\theta_2{}^3\theta_3{}^1$	$\theta_1{}^4\theta_2\theta_3{}^2$
4	$\theta_{02}\theta_{12}\theta_{13}\theta_{21}{}^2\theta_{22}\theta_{31}$	$\theta_{03}\theta_{21}{}^2\theta_{22}\theta_{33}\theta_{41}{}^2$

where

$$\theta a_2U_1U_1 = a_2\sum_k\sum_l\beta_{1k}\beta_{1l}\theta(B_{1k}B_{1l}) \qquad (2.11)$$

$$2a_2b_1b_2(\theta(U_2)\theta(U_2U_2)) = 2a_2b_1b_2\sum_k\sum_l\sum_m\beta_{2k}\beta_{2l}\beta_{2m}(\theta(B_{2k})\ \theta(B_{2l}B_{2m})) \qquad (2.12)$$

As the forest polynomials are more generalized formulations, they are inclusive of the conventional cascade theory. In other words, the terms are classified into equivalent classes according to the types of characterizations of polymers, and the forest polynomials in these classes are derived along with their corresponding recursive simultaneous equations. Solving these equations enables us to obtain the results of both the conventional cascade theory and the parameters of configuration of polymers, which are evaluated by the generalized one. The objective of this study is to obtain the latter. The four cases listed in Table 4 are provided as examples.

Case 1: For the distribution of the degree of polymerization, brackets of the term T_k in eq 2.1 are removed, and the formulation of conventional cascade theory is obtained since differences in configurations of polymers are not classified.

$$W = \sum\alpha_k\theta^k \qquad (2.13)$$

$$W = \theta(a_0 + a_1U + a_2U^2 + a_3U^3) \qquad (2.14)$$

$$U = \theta(b_0 + b_1U + b_2U^2) \qquad (2.15)$$

where α_k denotes the sum of the coefficients of the terms T_k that exhibit the same degree of polymerization. Equation 2.13 agrees with the probability generating function (pgf) in which the distribution of the degree of polymerization was formulated by Gordon.[3]

Case 2: If polymers are classified by generations, the two terms in Table 1, for example, will be transformed as shown in Table 4. The corresponding forest polynomial is given by

$$W = \sum_k c_k(\prod_s\theta_s{}^{k(s)}) \qquad (2.16)$$

where $k(s)$ denotes the number of descendants of the s-th generation of polymers in the k-th class. This value is equivalent to the formulation that uses the path-weighted function proposed by Kajiwara.[5]

$$\theta_s \sim \theta^{\phi_s} \qquad (2.17)$$

that is

$$\prod_s\theta_s{}^{k(s)} \equiv \theta^{\Sigma_sk(s)\phi_s} \qquad (2.18)$$

From the recursive equations corresponding to eq 2.16, a scattering function can be derived by the same procedure as that of Kajiwara's.[5]

Case 3: If the units composing a polymer are classified by their number of reacted functionalities, i.e., conversions, a formulation that considers nonequilibrium fsse can be obtained.[14]

Case 4: As shown in Table 4, if the units are classified by generation and conversion, then the recursive equations are derived as follows:

$$W = a_0(\theta_{00}) + a_1(\theta_{01}(U_1)) + a_2(\theta_{02}(U_1U_1)) + a_3(\theta_{03}(U_1U_1U_1)) \qquad (2.19)$$

$$U_g = b_0(\theta_{g1}) + b_1(\theta_{g2}(U_{g+1})) + b_2(\theta_{g3}(U_{g+1}U_{g+1})) \qquad (2.20)$$

Here, θ_{ij} denotes a dummy variable indicating a unit in which the j functionalities of i-th generation are reacted, and the calculations are shown as

$$a_1(\theta_{01}(U_1)) = a_1b_0(\theta_{01}\theta_{11}) + a_1b_1(\theta_{01}\theta_{12}(U_2)) + a_1b_2(\theta_{01}\theta_{13}(U_2U_2)) \qquad (2.21)$$

$$a_2(\theta_{02}(U_1U_1)) = a_1b_0{}^2(\theta_{02}(\theta_{11}\theta_{11})) + a_1b_1{}^2(\theta_{02}(\theta_{12}(U_2)\theta_{12}(U_2))) + a_1b_2{}^2\theta_{02}(\theta_{13}(U_2U_2)\theta_{13}(U_2U_2)) + 2a_2b_0b_1(\theta_{02}(\theta_{11}\theta_{12}(U_2))) + 2a_2b_0b_3(\theta_{02}(\theta_{11}\theta_{13}(U_2U_2))) + 2a_2b_1b_3(\theta_{02}(\theta_{12}(U_2)\theta_{13}(U_2U_2))) \qquad (2.22)$$

The formulation for the distribution of the length of polymer chain can be derived by the classification of the case.[15]

2.2. Estimation of the Mean-Square Radius of Gyration $\langle S^2\rangle$. The mean-square radius of gyration $\langle S^2\rangle$ of a polymer defined by formula 2.23 can be described as the sum of two terms in formula 2.24 by a simple transformation of formula 2.23:

$$\langle S^2\rangle = \frac{1}{N_a}\sum_i^{N_a}(\mathbf{r}_c - \mathbf{r}_i)^2 \qquad (2.23)$$

$$\langle S^2\rangle = \frac{1}{N_a}\sum_x^k P_k\langle S_k{}^2\rangle + \frac{1}{2N_a{}^2}\sum_k^x\sum_k^x P_kP_\ell(\mathbf{r}_k - \mathbf{r}_\ell)^2 \qquad (2.24)$$

where vectors $\mathbf{r}_c$ and $\mathbf{r}_i$ denote the center of gravity of a polymer and of the i-th atom, respectively, N_a is the total number of atoms contained in a polymer, x denotes the total number of units composing a polymer, P_k denotes the number of atoms contained by the k-th unit in a polymer, and $\langle S_k{}^2\rangle$ denotes the mean-square radius of gyration of the k-th unit. Moreover, $\mathbf{r}_k$ and $\mathbf{r}_\ell$ denote vectors of the center of gravity of the k-th and ℓ-th units, respectively, while "$(\mathbf{r}_k - \mathbf{r}_\ell)$" denotes the distance in space between the k-th and ℓ-th units. When a graph, in which a vertex represents a unit of a polymer and an edge represents a link, exhibits a tree structure that does not contain a ring structure, a path with these two units at both end points is determined uniquely. Therefore, the number of links contained in this path $n_{k\ell}$ is determined uniquely. That is, the value of the distance $(\mathbf{r}_k - \mathbf{r}_\ell)$ is drived by formula 2.25 on the basis of the Gaussian chain statistics

$$(\mathbf{r}_k - \mathbf{r}_\ell)^2 = \sigma^2 n_{k\ell} \qquad (2.25)$$

where σ denotes an effective unit link length.

Since the first term on the right side of formula 2.24 can be calculated if the type and number of units contained in a polymer are known, then the conventional cascade theory can be applied to estimate the $\langle S^2\rangle$. There are two methods for employing the new formulation and operation rule that facilitates the calculation of the second term. First, the formulation using Kramer's theorem[16] suitable for the analysis of experimental data is shown. Next, the formulation in which Kajiwara's path-weighted function was effectively extended to a theoretical study is shown.

2.3. Formulation Based on Generalized Kramer's Theorem. Formula 2.26 is derived from formula 2.25 by Kramer's theorem, which was generalized by Dobson and Gordon:[3]

$$\Big(\sum_k\sum_l(\mathbf{r}_k - \mathbf{r}_l)^2\Big)/2x^2 = \frac{1}{x^2}\sum_i^{x-1} m_i(x - m_i)\sigma_i^2 \qquad (2.26)$$

where m_i denotes the number of units in one of the moieties that are divided into two by the ith link in a polymer. Although the value of m_i varies according to the choice of moiety, the result of the summation does not depend on the moiety. In this study the chosen moiety is always at a distance from a root.

In the formulation using the generalized Kramer's theorem, an equivalent class $[T_k]$ of T_k is defined as follows:

$$[T_k] = [x_k, y_k, z_k] \qquad (2.27)$$

where

$$y_k = \sum_i^{x_k-1} m_{ik} \qquad (2.28)$$

$$z_k = \sum_i^{x_k-1} m_{ik}^{\,2} \qquad (2.29)$$

Parameter x_k denotes the number of units in a polymer belonging to the equivalent class, and m_{ik} is the number of units in one of the moieties that are divided by the i-th link of the k-th isomer. Similarly, the equivalent class of subtree is defined as follows:

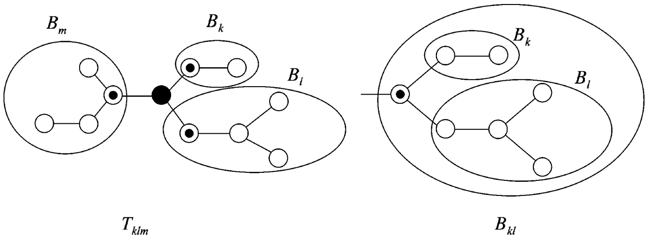
$$[B_k] = [x_k, y_k, z_k] \qquad (2.30)$$

where

$$y_k = \sum_i^{x_k} m_{ik} \qquad (2.31)$$

$$z_k = \sum_i^{x_k} m_{ik}^{\,2} \qquad (2.32)$$

In subtree B_k, one of the links (edge) does not have a unit (vertex) at one end. The moiety corresponding to this link is B_k itself. Forest polynomials W of the equivalent class and the polynomials U are



$$[B_k] = [x_k, y_k, z_k]$$
$$[B_l] = [x_l, y_l, z_l]$$
$$[B_m] = [x_m, y_m, z_m]$$
$$[T_{klm}] = [x_k + x_l + x_m + 1,\ y_k + y_l + y_m,\ z_k + z_l + z_m]$$
$$[B_{kl}] = [x_k + x_l + 1,\ y_k + y_l + (x_k + x_l + 1),\ z_k + z_l + (x_k + x_l + 1)^2]$$

Figure 1. Diagram of the operation rule shown in formula 40. Unit ● that is randomly selected in a system has unit ⊙ as its descendant. Furthermore, unit ⊙ has units ○ as its descendants. If the branches to which units B_k and B_ℓ are expressed as (x_k, y_k, z_k) and (x_ℓ, y_ℓ, z_ℓ), respectively, and the probabilities of appearance are expressed as β_k and β_ℓ, respectively, the branch $(x_{k\ell}, y_{k\ell}, z_{k\ell})$ to which unit ⊙ belongs can be obtained from the calculations $x_{k\ell} = x_k + x_\ell + 1$, $y_{k\ell} = y_k + y_\ell + x_{k\ell}$, and $z_{k\ell} = z_k + z_\ell + x_{k\ell}^2$, and the probability of appearance $\beta_{k\ell}$ can be obtained from the calculation of $b_2\beta_k\beta_\ell$.

$$W = \sum \alpha_k[x_k, y_k, z_k]$$
$$U = \sum \beta_k[x_k, y_k, z_k] \qquad (2.33)$$

The recursive equation of W and U are the same as eqs 2.8 and 2.9; their calculation procedure is defined as shown in Figure 1. For example

$$a_0\theta = a_0[1, 0, 0] \qquad (2.34)$$

$$a_1\theta U = a_1\sum_{k\beta_k}\beta_k[x_k + 1, y_k, z_k] \qquad (2.35)$$

$$a_2\theta UU = a_2\sum_k\sum_l \beta_k\beta_\ell[x_k + x_\ell + 1, y_k + y_\ell, z_k + z_\ell] \qquad (2.36)$$

$$a_3\theta UUU = a_3\sum_k\sum_\ell\sum_m \beta_k\beta_\ell\beta_m[x_k, x_\ell, x_m + 1, y_k + y_\ell + y_m, z_k + z_\ell + z_m] \qquad (2.37)$$

$$b_0\theta = b_0[1, 1, 1] \qquad (2.38)$$

$$b_1\theta U = b_1\sum_k\beta_k[x_k + 1, y_k + (x_k + 1), z_k + (x_k + 1)^2] \qquad (2.39)$$

and

$$b_2\theta UU = b_2\sum_k\sum_l \beta_k\beta_\ell\theta^{x_{kl}}[y_{k\ell}, z_{k\ell}] \qquad (2.40)$$

where

$$x_{k\ell} = x_k + x_\ell + 1$$

$$y_{k\ell} = y_k + y_\ell + x_{k\ell}$$
$$z_{k\ell} = z_k + z_\ell + x_{k\ell}^{\,2}$$

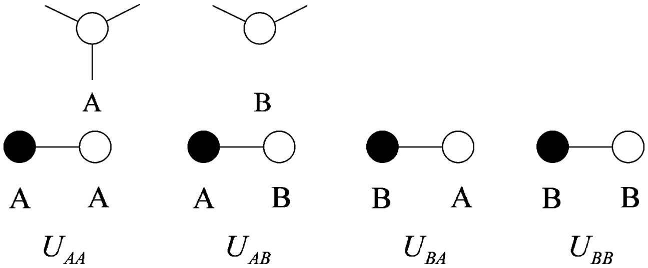


Figure 2. Two types unit A, B and their links.

$\langle S^2\rangle$ of the k-th polymer is calculated by formula 2.24.

$$\langle S_k^{\,2}\rangle = \frac{P}{x_k}\sum_i^{x_k}\langle Su^2\rangle + \frac{\sigma^2P^2}{x_k^{\,2}}(x_ky_k - z_k) \qquad (2.41)$$

where $\langle Su^2\rangle$ denotes the mean-square gyration of a unit.

Our formulation can be extended to the case where a polymer consists of several types of units. The reaction between a trifunctional cross-linker and a bifunctional telechelic polymer is shown in Figure 2, as an example. The pgf of this binary system corresponding to eq 2.33 is

$$W = \sum_k \alpha_k[X_k, Y_k, Z_k] \qquad (2.42)$$

$$X_k = (x_{\mathrm{A}}, x_{\mathrm{B}}, x_{\mathrm{AA}}, x_{\mathrm{AB}}, x_{\mathrm{BB}})_k \qquad (2.43)$$

$$Y_k = (y_{\mathrm{AA}}, y_{\mathrm{AB}}, y_{\mathrm{BB}})_k \qquad (2.44)$$

$$Z_k = (z_{\mathrm{AA}}, z_{\mathrm{AB}}, z_{\mathrm{BB}})_k \qquad (2.45)$$

$$\theta = (\theta_{\mathrm{A}},\theta_{\mathrm{B}},\theta_{\mathrm{AA}},\theta_{\mathrm{AB}}\theta_{\mathrm{BB}})_k \qquad (2.46)$$

$$\theta^X = (\theta_{\mathrm{A}}^{\,x_{\mathrm{A}}},\theta_{\mathrm{B}}^{\,x_{\mathrm{B}}},\theta_{\mathrm{AA}}^{\,x_{\mathrm{AB}}},\theta_{\mathrm{AB}}^{\,x_{\mathrm{AB}}},\theta_{\mathrm{BB}}^{\,x_{\mathrm{BB}}}) \qquad (2.47)$$

where x_{A} and x_{B} denote the number of units of type A and B, respectively, which exist in a polymer, x_{AB} denotes the number of links between units of type A and B in the k-th polymer, and y_{AB} and z_{AB} are defined as follows:

$$y_{\mathrm{AB}} = \sum_i^{x_{\mathrm{AB}}}(m_{ik\mathrm{AB}}) \qquad (2.48)$$

$$z_{\mathrm{AB}} = \sum_i^{x_{\mathrm{AB}}}(m_{ik\mathrm{AB}})^2 \qquad (2.49)$$

where $m_{ik\mathrm{AB}}$ denotes the number of units belonging to one side of the moieties which are divided into two by the i-th A−B link of the k-th polymer.

Assuming that all the reactivities of the functionalities are equal, that is, the fsse can be disregarded, the recursive equation can be formulated as follows:

$$W = a_{\mathrm{A}}W_{\mathrm{A}} + a_{\mathrm{B}}W_{\mathrm{B}} \qquad (2.50)$$

$$W_{\mathrm{A}} = \theta_{\mathrm{A}}(a_1 + a_2U_{\mathrm{AA}} + a_3U_{\mathrm{AB}})^3 \qquad (2.51)$$

$$W_{\mathrm{B}} = \theta_{\mathrm{B}}(a_4 + a_5U_{\mathrm{BA}} + a_6U_{\mathrm{BB}})^2 \qquad (2.52)$$

$$U_{\mathrm{AA}} = \theta_{\mathrm{A}}\theta_{\mathrm{AA}}(b_1 + b_2U_{\mathrm{AA}} + b_3U_{\mathrm{AB}})^2 \qquad (2.53)$$

$$U_{\mathrm{AB}} = \theta_{\mathrm{B}}\theta_{\mathrm{AB}}(b_4 + b_5U_{\mathrm{BA}} + b_6U_{\mathrm{BB}}) \qquad (2.54)$$

$$U_{\mathrm{BA}} = \theta_{\mathrm{A}}\theta_{\mathrm{AB}}(b_7 + b_8U_{\mathrm{AA}} + b_9U_{\mathrm{AB}})^2 \qquad (2.55)$$

$$U_{\mathrm{BB}} = \theta_{\mathrm{B}}\theta_{\mathrm{BB}}(b_{10} + b_{11}U_{\mathrm{BA}} + b_{12}U_{\mathrm{BB}}) \qquad (2.56)$$

where

$$U_{\mathrm{AA}} = \sum_k \beta_{k\mathrm{AA}}[\mathbf{X}_k, \mathbf{Y}_k, \mathbf{Z}_k]$$

$$U_{\mathrm{AB}} = \sum_k \beta_{k\mathrm{AB}}[\mathbf{X}_k, \mathbf{Y}_k, \mathbf{Z}_k]$$

$$U_{\mathrm{BA}} = \sum_k \beta_{k\mathrm{BA}}[\mathbf{X}_k, \mathbf{Y}_k, \mathbf{Z}_k]$$

$$U_{\mathrm{BB}} = \sum_k \beta_{k\mathrm{BB}}[\mathbf{X}_k, \mathbf{Y}_k, \mathbf{Z}_k]$$

The operation rule is the same as that in the above-mentioned case in which only one type of unit exists. Two calculations of terms shown in Figure 3 are illustrated as follows:

$$b_9\theta_{\mathrm{A}}\theta_{\mathrm{AB}}U_{\mathrm{AB}} = b_9\sum_{kl}\beta_{kl}[X_{kl}, Y_{kl}, Z_{kl}] \qquad (2.57)$$

$$X_{kl} = (x_{\mathrm{A}} + 1, x_{\mathrm{B}}, x_{\mathrm{AA}}, x_{\mathrm{AB}} + 1, x_{\mathrm{BB}})_{kl}$$

$$Y_{kl} = (y_{\mathrm{AA}}, y_{\mathrm{AA}} + x_{\mathrm{A}} + x_{\mathrm{B}} + 1, y_{\mathrm{BB}})_{kl}$$

$$Z_{kl} = (z_{\mathrm{AA}}, z_{\mathrm{AB}} + (x_{\mathrm{A}} + x_{\mathrm{B}} + 1)^2, z_{\mathrm{BB}})_{kl}$$

and

$$2b_8b_9\theta_{\mathrm{A}}\theta_{\mathrm{AB}}U_{\mathrm{AA}}U_{\mathrm{AB}} = 2b_8b_9\sum_k\sum_m \beta_{k\mathrm{AA}}\beta_{k\mathrm{AB}}[\mathbf{X}_{km}, \mathbf{Y}_{km}, \mathbf{Z}_{km}] \qquad (2.58)$$

$$\mathbf{X}^{\mathbf{T}}_{\mathbf{kl}} = \begin{pmatrix} x_{\mathrm{A}k} + x_{\mathrm{A}m} + 1 \\ x_{\mathrm{B}k} + x_{\mathrm{B}m} \\ x_{\mathrm{AB}k} + x_{\mathrm{AB}m} + 1 \\ x_{\mathrm{BB}k} + x_{\mathrm{BB}m} \end{pmatrix}$$

$$\mathbf{Y}^{\mathbf{T}}_{\mathbf{kl}} = \begin{pmatrix} y_{\mathrm{AA}k} + y_{\mathrm{AA}m} \\ y_{\mathrm{AB}k} + y_{\mathrm{AB}m} + (x_{\mathrm{AB}k} + x_{\mathrm{AB}m} + 1) \\ y_{\mathrm{BB}k} + y_{\mathrm{BB}m} \end{pmatrix}$$

$$\mathbf{Z}^{\mathbf{T}}_{\mathbf{kl}} = \begin{pmatrix} z_{\mathrm{AA}k} + z_{\mathrm{AA}m} \\ z_{\mathrm{AB}k} + z_{\mathrm{AB}m} + (x_{\mathrm{AB}k} + x_{\mathrm{AB}m} + 1)^2 \\ z_{\mathrm{BB}k} + z_{\mathrm{BB}m} \end{pmatrix}$$

When units of type A and B have P_{A} and P_{B} atoms, respectively, $\langle S_k^2\rangle$ of the k-th isomer is

$$\langle S_k^{\,2}\rangle = (x_{\mathrm{A}}P_{\mathrm{A}}\langle S_{\mathrm{A}}^{\,2}\rangle + x_{\mathrm{B}}P_{\mathrm{B}}\langle S_{\mathrm{B}}^{\,2}\rangle)/N_{\mathrm{a}} + \{\sigma_{\mathrm{AA}}^{\,2}(N_{\mathrm{a}}y_{\mathrm{AA}} - z_{\mathrm{AA}}) + \sigma_{\mathrm{AB}}^{\,2}(N_{\mathrm{a}}y_{\mathrm{AA}} - z_{\mathrm{AB}}) + \sigma_{\mathrm{BB}}^{\,2}(N_{\mathrm{a}}y_{\mathrm{BB}} - z_{\mathrm{BB}})\}/N_{\mathrm{a}}^{\,2} \qquad (2.59)$$

$$N_{\mathrm{a}} = x_{\mathrm{A}} + x_{\mathrm{B}} = x_{\mathrm{AA}} + x_{\mathrm{BB}} + x_{\mathrm{AB}} + 1 \qquad (2.60)$$

where σ_{AB} denotes the length of an A−B link. It is assumed that values of both $\langle S_{\mathrm{A}}^2\rangle$ and $\langle S_{\mathrm{B}}^2\rangle$ do not change irrespective of whether a unit is combined with another unit.

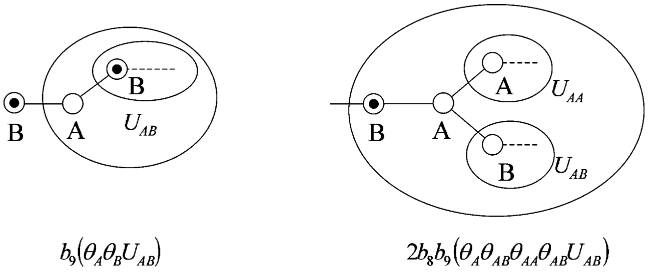


Figure 3. Diagram of the operation rules shown in eq 57.

2.4. Formulation by the Extension of the Path-Weighted Function. To statistically calculate the connection length of all the polymers in a system, Kajiwara introduced a pgf W using the path-weighted function as follows:

$$W(\{\theta\}) = \theta_1\theta_2^{\phi_0}(1 - \alpha + \alpha U_1(\{\theta\}))^f \tag{2.61}$$

$$U_n(\{\theta\}) = \theta_1\theta_2^{\phi_n}(1 - \alpha + \alpha U_{n+1}(\{\theta\}))^f \tag{2.62}$$

where the path-weighted function ϕ_n is an arbitrary function of the number of links n, α is the fraction of the functionalities that has reacted to form the links, and θ_1 and θ_2 are dummy variables. The substitution effect is neglected; the reactivities of all functionalities are assumed to be equal. The pgf W is defined as follows:

$$W(\theta_1,\theta_2) = \sum_k w_k x^{-1}\theta_1{}^x\sum_{\ell}^{x}\theta_2{}^{\sum_n N_{k\ell n}\phi_n} \tag{2.63}$$

$$\sum_{\ell}^{x} N_{k\ell n} = 2N_{kn} \tag{2.64}$$

where w_k denotes the weight fraction of a polymer in the k-th class, $N_{k\ell n}$ denotes the number of distinct paths of length n starting at the unit ℓ, and N_{kn} denotes the number of distinct paths of length n in the k-th polymer. Once N_{kn} of each polymer is obtained, then the radius of gyration and the hydrodynamic radius (the Stokes radius) can be calculated.

Although the purpose of their formulation is to calculate the average value of the entire system, each individual value cannot be calculated from this formulation. In this section, we introduce a new procedure to calculate the path length distribution in each polymer by extending Kajiwara's "path-weighted function" and by employing a new function and operation rule. The polynomial is formulated as follows:

$$W = \sum_k \alpha_k(x_k,\Phi_k,\Gamma_k) \tag{2.65}$$

$$U = \sum_k \beta_k(x_k,\Phi_k,\Gamma_k) \tag{2.66}$$

where

$$\Phi_k(\theta) = \sum_i \gamma_{ik}\theta^i \tag{2.67}$$

$$\Gamma_k(\theta) = \sum_i \delta_{jk}\theta^j \tag{2.68}$$

The denotation of α_k, β_k is the same as that in eqs 2.1 and 2.5. As in the previous section, "k" is a provisional symbol not only for an isomer having the same degree of polymerization but also for all the polymers with different degrees of polymerization in a system. Here, γ_{ik} denotes the number of units that are descendants of the i-th generation when a randomly chosen unit is regarded as the zeroth generation, and δ_{jk} denotes the path of length j in the k-th polymer. The relation between the degree of polymerization x and the function $\Phi_k(\theta)$ is given by

$$x = \Phi_k(1) + 1 \tag{2.69}$$

The newly defined operation rule that is not used in the previous section is employed to calculate the recursive eqs 2.8 and 2.9. It is also a spontaneous rule derived from the definition of the functions Φ_k and Γ_k and the assumption of the Markov branching process. For example

$$b_1\theta U = b_1\sum_k \beta_k(x_1,\Phi_{k1},\Gamma_{k1}) \tag{2.70}$$

$$b_2\theta U = b_2\sum_k\sum_{\ell}\beta_k\beta_{\ell}(x_{k\ell},\Phi_{k\ell},\Gamma_{k\ell}) \tag{2.71}$$

$$a_3\theta UUU = a_3\sum_k\sum_{\ell}\sum_m \beta_k\beta_{\ell}\beta_m(x_{k\ell m},\Phi_{k\ell m},\Gamma_{k\ell m}) \tag{2.72}$$

Here

$$x_1 = x_k + 1$$

$$x_{k\ell} = x_k + x_{\ell} + 1$$

$$x_{k\ell m} = x_k + x_{\ell} + x_m + 1$$

$$\Phi_{k1} = \theta + \theta\Phi_k$$

$$\Gamma_{k\ell 1} = \Gamma_k + \Phi_{k1}$$

$$\Phi_{k\ell} = \Phi_{k1} + \Gamma_{\ell 1}$$

$$\Gamma_{k\ell} = \Gamma_{k1} + \Gamma_{\ell 1} + \Phi_{k1}\Phi_{l1}$$

$$\Phi_{k\ell m} = \Phi_{k1} + \Phi_{\ell 1} + \Phi_{m1}$$

$$\Gamma_{k\ell m} = \Gamma_{k1} + \Gamma_{\ell 1} + \Gamma_{m1} + \Phi_{k1}\Phi_{\ell 1} + \Phi_{\ell 1}\Phi_{m1} + \Phi_{m1}\Phi_{k1}$$

The hydrodynamic radius $\langle S_{\mathrm{h}}\rangle$ and the radius of gyration $\langle S^2\rangle$ of a polymer can be calculated by using the functions Φ and Γ. The sum of the reciprocal of the path length that is required to calculate $\langle S_{\mathrm{h}}\rangle$ can be obtained from the integration of Φ and Γ as follows:

$$\sum_i \gamma_{ik}\frac{1}{i} = \left|\int\left(\frac{\Phi_k}{\theta}\right)\mathrm{d}\theta\right|_{\theta=1} \tag{2.73}$$

$$\sum_j \delta_{jk}\frac{1}{j} = \left|\int\left(\frac{\Gamma_k}{\theta}\right)\mathrm{d}\theta\right|_{\theta=1} \tag{2.74}$$

The summation of the path length that is required to calculate $\langle S^2\rangle$ can be obtained by differentiating the function Γ with respect to a dummy variable θ and then substituting θ with 1.

3. Results of Numerical Calculations

Equations 2.8 and 2.9 are applied to several trifunctional polycondensation systems, where the conversions and substitution effects are not equal.

3.1. Calculation Procedure. Although there are a large number of different types of isomers, the probability of their existense is negligible. Therefore, to obtain the results with sufficient accuracy within a short time, a calculation procedure to select an isomer efficiently with a high expected value is required. The expected values of the randomly selected units belonging to a branch or to a tree of the *k*-th type $\beta_k x_k$ and $\alpha_k x_k$ are obtained from eq 2.33. If the terms are selected in the order of these expected values, the approximate branch and forest polynomials consisting of a finite term can be obtained with sufficient accuracy. For example, by substituting $U_{(0)}$ into the recursive eq 2.9, a new polynomial $U_{(1)}$ is obtained.

$$U_0 = b_1[1, 0, 0]$$

$$U_{(1)} = (\theta(b_0 + b_1 U_{(0)} + b_2 U_{(0)} U_{(0)}))$$

$$\vdots$$

$$U_{(n+1)} = (\theta(b_0 + b_1 U_{(n)} + b_2 U_{(n)} U_{(n)})) \tag{3.1}$$

By selecting 4000 terms of polynomials the $U_{(n+1)}$ in the order of size, new approximate polynomials $U_{(n+1)}$ are obtained. Then, these polynomials are again substituted into eq 2.9. The approximate branch polynomials are obtained by repeating this procedure. The approximate forest polynomials can be obtained by substituting these branch polynomials into eq 2.8 and then selecting a finite number of terms in the order of the value of $\alpha_k x_k$. In this example, the terms in which the values of $\alpha_k x_k$ are greater than 1.0×10^{-6} are selected. The theoretical SEC trace $F(v)$ is simulated by the summation of the Gaussian function as follows:

$$F(v) = \sum_k \alpha_k \sqrt{\frac{{h_k}^2}{\pi}} \exp[-{h_k}^2(v - v_{0,k})^2] \tag{3.2}$$

where v denotes the exclusion volume, ${h_k}^2$ is a quantity related to the inverse of the half-width of the peak corresponding to the *k*-th isomer, and v_0 is the value of v at the maximum of the peak.

$$v_{0,k} = \frac{4\pi}{3}(\langle {S_k}^2 \rangle)^{3/2} \tag{3.3}$$

In this calculation, the value of h_k is fixed at 200, regardless of the types of isomers. The mean-square radius of gyration $\langle {S_k}^2 \rangle$ of the *k*-th isomer is calculated assuming that the diameter of a unit and the intercentral distance between units connected with each other are unity as follows:

$$\langle {S_k}^2 \rangle = \left(\frac{1}{2}\right)^2 x_k + (x_k y_k - z_k)/{x_k}^2 \tag{3.4}$$

The shrink factor g_s of the *k*-th isomer is calculated using the following formulas:

$$g_{s,k} = \langle {S_k}^2 \rangle / \langle S^2 \rangle_L \tag{3.5}$$

where $\langle S^2 \rangle_L$ denotes the mean-square radius of gyration $\langle S^2 \rangle$ of the linear *x*-mer.

$$\langle S^2 \rangle_L \equiv \left(\frac{1}{2}\right)^2 x_k + \left(\frac{1}{6}\right)\left(\frac{{x_k}^2 - 1}{x_k}\right) \tag{3.6}$$

The distribution of the degree of polymerization was calculated using the recursive pgf.

3.2. Results of Calculation. Tables 5 and 6 show the number of terms, the weight-average degree of polymerization DP_W of each approximate forest polynomial, and the coefficients $\{a\}$ in the calculated system. Systems (a), (b), and (c) do not experience the fsse, and their DP_Ws are 5, 10, and 100, respectively. Although the DP_Ws of both systems (d) and (e) are 10, they are examples of the fsses that have mutually opposite tendencies.

Table 5

system	conversion	DP_W	no. of terms
(a)	0.36(4/11)	5	17 104
(b)	0.4285714286(3/7)	10	22 314
(c)	0.4925373134	100	40 149

Table 6

system	coefficients[a]		DP_W	no. of terms
	a_2/a_3	a_4		
(b)	4/3	0.07872012	10	22 314
(d)	10/1	0.1500072466	10	17 768
(e)	4/10	0.1194861070	10	36 946

[a] $a_1 = 0.1865889212$.

Figure 4 shows the result of simulating the distribution of $\langle S^2 \rangle$ in each system listed in Tables 5 and 6. Figures 4a−c shows that several isomers are produced following an increase in conversion. Although each probability of existence is small, the summation of their forms results in a large peak. Figure 4b,d,e shows that the distributions of $\langle S^2 \rangle$ are characteristically different depending on the fsses although the systems have the same DP_W.

Figure 5 shows the results of the classification of isomers by the degree of polymerization and the shrink factor g_s. To make the isomers with a small probability of existence legible, the value of the summation of each probability of existence is magnified to the 1/4 power. Figure 5 provides the details of the distribution of the isomers. Following an increase in the degree of polymerization, the distribution of $\langle S^2 \rangle$ expands by the branching, and the center value of the distribution becomes smaller than the $\langle S^2 \rangle$ value of linear polymer.

Figures 6 and 7 show the distribution function plotted against the degree of polymerization. It is found that the distribution of $\langle S^2 \rangle$ is more affected by the conversion and fsse than the distribution of DP_W.

4. Discussion

The purpose of this study is to develop an analytical method for routinely evaluating the size of a branched polymer. The conventional cascade theory is further developed so that the distribution of the configuration could be calculated. The calculation procedure for the size distribution is derived as one corollary of the extended theory. The calculation procedure illustrated in this paper can be considered as an extension of that formulated by Kidera et al. also in accord with the cascade theory. The present procedure is routinely applicable to many systems without the assumption of the equal reactivity for the functional groups. This generalized cascade theory can also be applied to polymers containing a ring structure as a result of the tree decomposition. Subgraphs defined as “parts”, according to “tree decomposition” in the Graph theory, share a vertex when they are connected to each other.[13]

Although Figures 4 and 5 are based on the simplest model, these calculation results show usefulness of our new procedure for analysis of SEC trace. For example, Figure 4 suggests that each fsse gives the corresponding characteristic pattern of SEC traces. This means that fsse can be estimated from experimental SEC data within a reasonable computational time. If the degree of polymerization of polymers becomes large, the number of

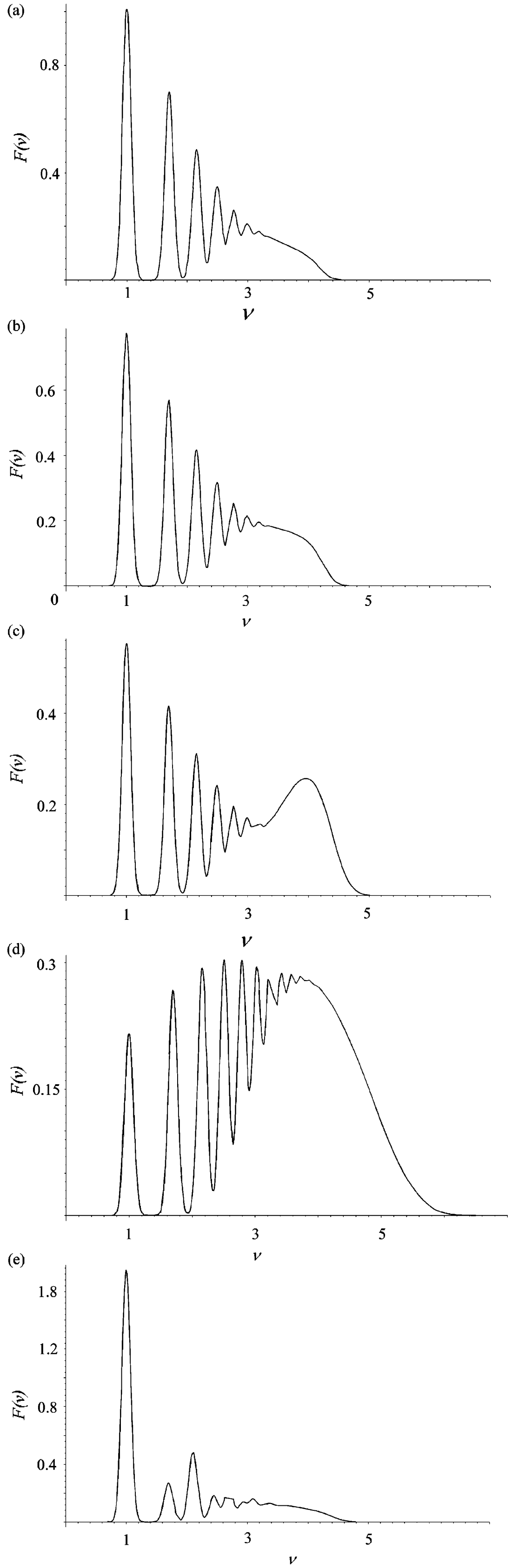


Figure 4. Computational results of an SEC trace. The chromatogram trace $F(\nu)$ was calculated as a function of the elusion volume n, given by formula 3.2. Weight-average degree of polymerization (DPw) of (a), (b), and (c) is 4, 10, and 100, respectively, for the case of equal reactivity of the functionality. The first shell substitution effect exists in systems (d) and (e). Although the values of DP_W for both the systems are 10, the order of the conversion of functionality is $a_2 > a_4 > a_3$, $a_3 > a_2 > a_4$, as shown in Table 6.

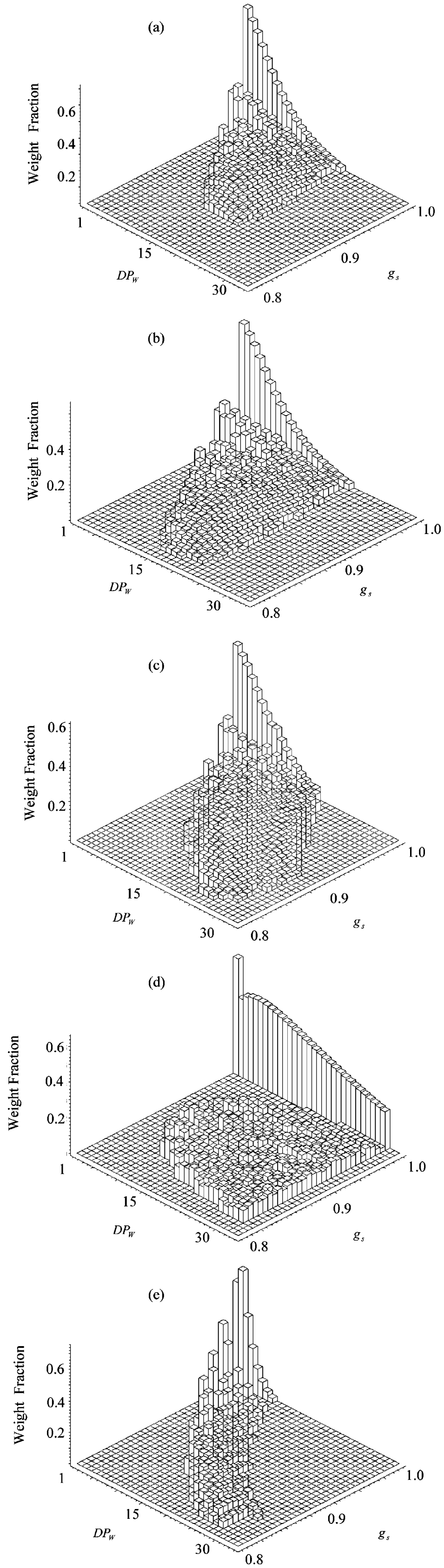


Figure 5. Distribution of isomers classified by the degree of polymerization DP_W and the shrink factor g_s are shown in (a)−(e). The calculation conditions are the same as those of Figure 4 as listed in Tables 5 and 6. The first shell substitution effect of system (d) is apt to generate linear polymers. In contrast, the substitution effect of system (e) is apt to generate branched polymers. Thus, the generalized cascade theory enables estimation of the distribution of polymer configuration and size.

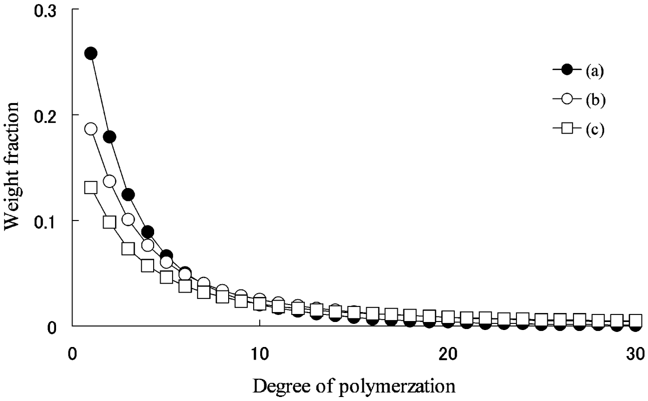


Figure 6. Molecular mass distribution in the case of the equal reactivity. The calculation conditions are the same as those of (a), (b), and (c) in Figures 4 and 5.

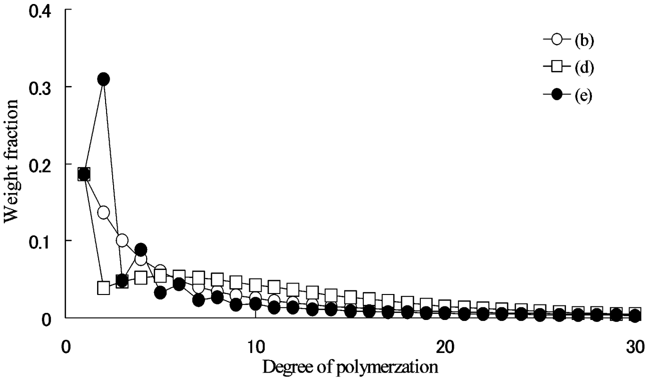


Figure 7. Molecular mass distribution for nonequal reactivity resulting from the effects of the first shell substitution. The calculation conditions are the similar to those of (b), (d), and (e) in Figures 4 and 5.

isomers greatly increases. If all these isomers are to be taken into consideration, the calculation procedure would be extremely lengthy and difficult. Experimentally, the peaks of SEC trace are distinguishable in a relatively lower molar mass region and are not much distinguishable in a higher molar mass region. This suggests that several isomers of a similar size overlap each other, as shown in Figure 4. Therefore, the analysis of higher molar mass region may be impossible. To estimate the conversion and fsse in the polymerization system from the SEC trace, it will be sufficient method to investigate the lower molar mass region with distinguishable peaks in detail.

The distributions of shrink factor are sensitive to fsse, as shown in Figure 5. In the case of system d, the shrink factors are widely dispersed, and most of the existence probabilities of these values are small. This means that the existence ratio of branching molecules is small in the system d. The shrink factor of system e, in contrast, has a narrow distribution, and each main shrink factor has large existence probabilities. This shows that the most of high molar mass molecules in system e are branching types.

The analysis of fsse by SEC based on our calculation procedure will enable wide application to a field of macromolecule reactions. The end-linking method is a powerful technique that can be used to design the structure of polymer networks. It opens up a new phase in the study of the relation between the equilibrium elastic modulus and the network topology.[17] Urayama et al. used the end-linking method effectively to study the contribution of the trapped entanglement to the equilibrium modulus.[18,19] They estimated the functional form of the phenomenological strain energy density for an end-linking network on the basis of the stress−strain relation of general biaxial deformation.[20,21] In their papers, end-linked polymer networks were prepared from end-reactive precursor polymer, and multifunctional cross-linker, the network chain, the number of cross-links, and the functionality of the cross-linker were well characterized. If the end-linking reaction proceeds in an ideal manner, the chain length of the precursor polymer is equal to that between the neighboring cross-links. However, some swelling experiments on end-linker networks suggest that this expectation is inadequate.[24] To study the correlation between structure and physical properties quantitatively and with sufficient accuracy, it is necessary to investigate the structure of the experimentally prepared end-linking polymer in detail. For this purpose, the investigation of the distribution of the polymer clusters in the pregel state by SEC and its analysis by the calculation of our method are expected to be useful.

Matsumoto et al. experimentally confirmed, using SEC-LALLS, that the molecular size of a primary polymer (a linear polymer obtained by cutting all the cross-linking structures) was larger in the copolymerization system than in the homopolymerization system of vinyl and divinyl monomers under similar conditions.[22] They considered that the diffusion of a propagating radical was bound by the cyclization reaction in a molecule,[23] and the termination reaction was limited.[24] From this noteworthy result, it can be deduced that our present technique is probably effective for further detailed analysis of their results by applying "parts".[13]

The accuracy of the method that developed in the study would be improved by applying more precise models. For instance, the conformation entropy of a polymer decreases when it enters into a pore from free space. Casassa and Tagami calculated the entropy reduction of the linear chain and a star-shaped polymer on the basis of the assumption of the Gaussian chain statistics and derived a distribution coefficient.[25] It was reported that the flexibility of the chain also affects the compatibility of universal calibration.[1,26] Since the flexibility of a chain is not an average of its parts, or the length between the parts, but that of the information obtained from a variance, the MC method can be used here. However, a special technique is required to analyze a portion of the actual molecular structure that affects the variance since the MC method requires a long calculation time. Hence, the MC method proposed by one of the present authors (T. Nakao) using the analysis of variance (ANOVA) may be more effective.[27] When polymer has N_r rings, the radius becomes small compared to linear polymer.[28]

$$\langle S^2\rangle = \frac{1}{1+n_r}\langle S^2\rangle_L \tag{4.1}$$

The radius change must be considered in the case of the probability of ring formation is not negligible. Burchard reported that an internal chain of the star polymer is expanding.[29] Spakowitz and Wang provided the exact analytical solutions for the Laplace-transformed partition function of a wormlike chain.[30] The results will be able to improve the estimations of semiflexible polymer. In addition to the light-scattering method, SEC can be used for the analysis of branched polymers by applying the present generalized cascade theory.

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