Size exclusion chromatography of branched polymers: Star and comb polymers

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SUMMARY: Monte Carlo simulations were conducted to estimate the elution curve of size exclusion chromatography (SEC). The present simulation can be applied to various types of branched polymers, as long as the kinetic mechanism of nonlinear polymer formation is given. We considered two types of detector systems, (1) a detector that measures the polymer concentration in the elution volume to determine the calibrated molecular weights, such as by using the differential refractive index detector (RI), and (2) a detector that determines the weight-average molecular weight of polymers within the elution volume directly, such as a light scattering photometer (LS). For polydisperse star polymers, both detector systems tend to give a reasonable estimate of the true molecular weight distribution (MWD). On the other hand, for comb-branched polymers, the RI detector underestimates the molecular weight of branched polymers significantly. The LS detector system improves the measured MWD, but still is not exact. The present simulation technique promises to establish various types of complicated reaction mechanisms for nonlinear polymer formation by using the SEC data quantitatively. In addition, the present technique could be used to reinvestigate a large amount of SEC data obtained up to the present to estimate the true MWD.

Introduction

Size exclusion chromatography (SEC) provides a useful method for determining the molecular weight distribution (MWD) relative to standard calibration polymers quite easily, and has been used widely in research and development as well as quality control of product polymers. For linear polymers, the method to determine the MWD based on the elution curve of SEC has already been established well. On the other hand, for branched polymers, the measured SEC data are in many cases analyzed just qualitatively.

In a SEC measurement, polymer molecules are considered to be fractionated by the hydrodynamic volume. The size of branched polymer molecules is smaller than that of linear polymer molecules having the same molecular weight[1]. Therefore, the true MWD cannot be obtained through the usual procedure in which a set of linear polymer standards is used to establish the relationship between the elution volume and molecular weight. On the other hand, simultaneous measurements of light scattering intensity and concentration enable the weight-average molecular weight of the elution volume to be determined directly without the calibration. However, for a branched polymer mixture, polymer molecules whose hydrodynamic volume is the same but having different molecular weights coexist within the same elution volume because of the difference in their branched structure. Therefore, strictly speaking, the absolute MWD cannot be obtained even when one uses the on-line light scattering photometer. If the elution curve of a given nonlinear polymer system can be simulated on the basis of the formation mechanism, the use of SEC would expand remarkably.

Jackson[2] reported the simulation results of the direct tracings in a SEC analysis for the polymer molecules formed by random condensation of A_2-type monomer with a small amount of A_3. Analytical solutions of the MWD[3,4] and radii of gyration[1] were used to estimate the SEC tracings. However, these analytical solutions have been derived only for limited cases, and therefore, a more general approach is required to investigate real polymer systems.

Recently, a new Monte Carlo simulation approach based on the random sampling technique was proposed[5]. This method can be applied to various complex polymerization reactions that involve branching, crosslinking, and degradation during polymerization irrespective of the reactor types used, as long as the size and structure dependent reaction kinetics are of minor importance. In this method, one can observe the structure of each polymer molecule directly on the computer screen, and therefore, very detailed information can be obtained. This method was used to obtain the mean square radius of gyration for each polymer molecule that exists in the reaction mixture[6–9]. The estimated mean square radius of gyration could be used to determine the elution volume in a SEC analysis.

In this article, we apply the random sampling technique to estimate the SEC elution curves for two types of branched polymers, star and comb polymers.

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Method

Estimation of the mean square radius of gyration

Fig. 1 shows an example of the comb branched polymer structure, which was obtained in the random sampling technique for the simulation of free-radical copolymerization with macromonomer[10]. The horizontal line (bold) shows the backbone chain, and the vertical lines show the branch chains. By assuming the Θ condition, the 3D structure of this polymer can be estimated by drawing each primary chain as the trajectory of the random walk in the 3D space. Fig. 2 shows an example of the 3D structure whose 2D structure is shown in Fig. 1. By generating the 3D structure as shown in Fig. 2, it is straightforward to calculate the radius of gyration s for the given polymer conformation, and the sphere having the radius s is also shown in Fig. 2. The mean square radius of gyration of a particular branched polymer molecule $\langle s^2 \rangle_{br}$ can be estimated by taking the average of the radii of gyration for many types of conformation, i.e., by producing the 3D structure, as shown in Fig. 2, many times. We estimated the $\langle s^2 \rangle_{br}$-value for each polymer molecule by generating the 3D structure 100 times in the present investigation.

To examine if the 100 times of simulation for $\langle s^2 \rangle$ provides an estimate with sufficient accuracy, we conducted Monte Carlo simulations for a linear polymer mixture. For a linear polymer system, the radius of gyration in a Θ solvent is given by:

$$\langle s^2 \rangle_l = NL^2/6 \tag{1}$$

where N is the number of segments, and L is the length of a segment. Assuming that one segment consists of u monomeric units, the chain length that can be obtained from the estimated $\langle s^2 \rangle_l$-value is given by:

$$P^* = 6u\langle s^2 \rangle_l / L^2 \tag{2}$$

We used the following most probable distribution as a test distribution:

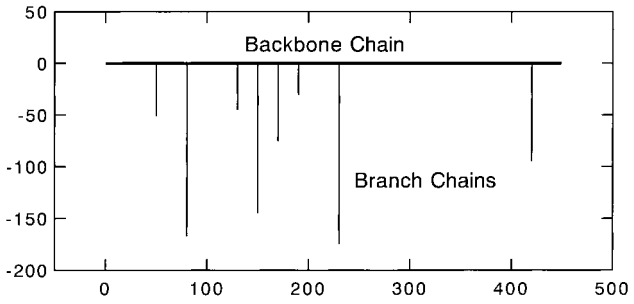

Fig. 1. Example of a comb-branched polymer molecule, formed in a free-radical copolymerization with macromonomer[10]. The axes show the length in the number of monomeric units

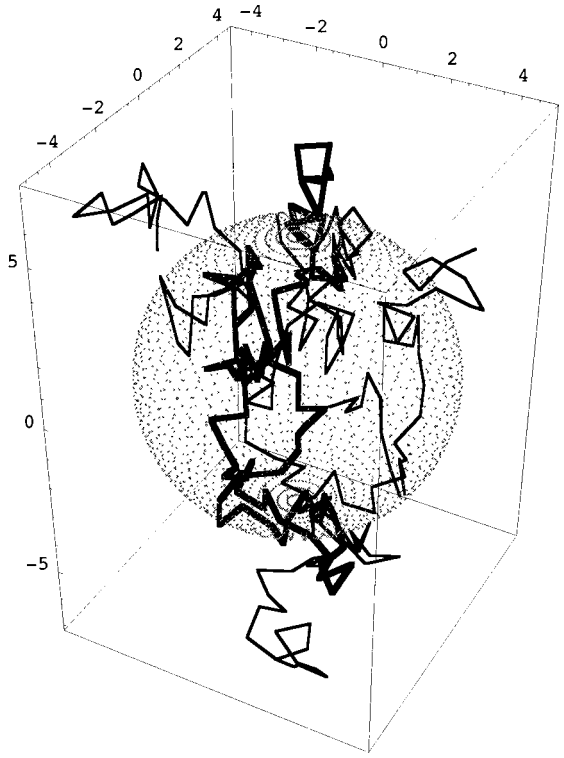

Fig. 2. Example of the 3D structure of the comb-branched polymer shown in Fig. 1 in a Θ solvent. The axes show the length in the number of segments. In this simulation, one segment consists of 5 monomeric units. The sphere shown by dots has the center at the center of mass and has the radius equal to the radius of gyration of this comb polymer

$$W(P) = \frac{P}{(\overline{P}_n)^2} \exp\left(-\frac{P}{\overline{P}_n}\right) \tag{3}$$

where P is the degree of polymerization (DP), and $\overline{P}_n$ is the number-average DP. The $\overline{P}_n$-value is assumed to be 100 in the present simulation.

As for the choice of the u-value, any u-value could be used as long as it makes the number of segments N large enough. For real chains, this arbitrariness can be removed[11], for example, by using the characteristic ratio (C_∞) and the fully extended length (r_{max}) of the real chain, as follows:

$$NL^2 = C_\infty n l^2 \tag{4}$$

$$NL = r_{max} \tag{5}$$

where n and l are the number of bonds and the bond length of the chain molecule, respectively. For polyethylene chains[11], $n/N \cong 10$ real bonds per equivalent segment, i.e., $u \cong 5$. We use $u = 5$ throughout the present article.

We generated 4×10^4 random numbers that follow Eq. (3). A quick method to generate random numbers that follow the most probable distribution can be found else-

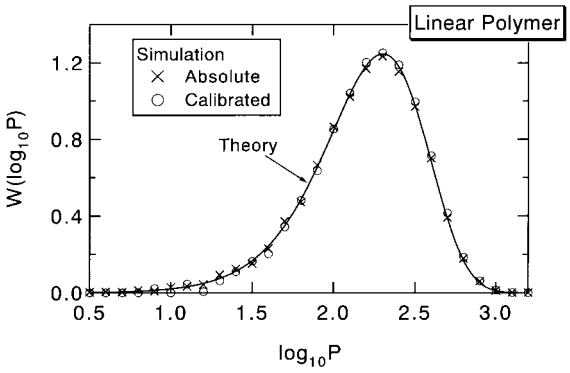

Fig. 3. Simulated weight fraction distribution of the linear polymers following the most probable distribution. The total of 4×10^4 polymer molecules were simulated

where[12]. For each chain, we conducted the random walk in 3D space and calculated s^2-values 100 times to determine the $\langle s^2 \rangle_l$-value. Then, Eq. (2) is used to obtain the "calibrated" DP. Because a small amount of error in the estimated $\langle s^2 \rangle_l$-value is inevitable, the "calibrated" DP is not exactly equal to the true DP.

Fig. 3 shows the simulated weight-based DP distribution. The independent variable is the logarithm of DP as usually employed in a SEC analysis. The solid curve shows the theoretical distribution given by Eq. (3). The absolute DP distribution obtained by generating 4×10^4 random numbers that follow Eq. (3) is given by the x-symbol. The weight-average DP of the simulated polymer samples was $\overline{P}_w$ = 200.7, while the theoretical value is $\overline{P}_{w,theory}$ = 200. The total of 4×10^4 polymer molecules can give an excellent estimate for the DP distribution.

The circular symbols in Fig. 3 show the "calibrated" DP distribution. The weight-average DP of the calibrated distribution was $\overline{P}_w$ = 205.4. A 2.7% of error was observed. However, as shown in Fig. 3, the whole distribution profile agrees reasonably well with the theoretical distribution, and a 2.7% of error would be acceptable when one considers the experimental errors in SEC measurements. In addition, because the variance of s^2-distribution is smaller for branched polymers, the error is expected to be smaller for branched polymers, as shown later. Note that when we simulate a polymer mixture that involves both linear and branched polymers, we will use the absolute DP for the linear polymers instead of the calibrated DP, because from the theoretical point of view the absolute and calibrated DPs must be the same for the linear polymers. Therefore, we calculate the mean square radius of gyration by simulating 100 types of spatial conformation only for each branched polymer molecule.

Calibrated DP of branched polymer

We assume that the universal calibration is valid and polymer molecules are fractionated by the hydrodynamic volume of the solvated molecule. Suppose that the SEC is calibrated by using a set of linear polymer standards whose monomeric units are the same as those in branched polymers. The calibrated DP, P^* is given by:

$$P^* = \frac{[\eta]_{br}}{[\eta]^*} P \tag{6}$$

where $[\eta]_{br}$ and $[\eta]^*$ are the intrinsic viscosity of the branched polymer and that for a linear polymer molecule whose elution volume is the same, respectively, and P is the true DP of the branched polymer molecule.

The factor g, which shows the reduction in size of branched polymers is defined by[1]:

$$g = \langle s^2 \rangle_{br} / \langle s^2 \rangle_l \tag{7}$$

where $\langle s^2 \rangle_{br}$ and $\langle s^2 \rangle_l$ are the mean square radius of gyration of branched and linear polymer molecules having the same DP, respectively.

For a Θsolvent, $\langle s^2 \rangle_l$ is given by Eq. (1). Although the eluent used in a SEC experiment is usually a thermodynamically good solvent, the g-factor is known to be relatively insensitive to the goodness of the solvent used[13], and therefore, the present random walk approach would provide a reasonable approximation for the g-factor.

The g-factor is usually equated to the ratio of the intrinsic viscosity by using the exponent b as follows:

$$g^b = [\eta]_{br} / [\eta]_l \tag{8}$$

The b-value is usually between 0.5 and 1.5, depending on the type of branched polymer[14, 15].

By using the Mark-Houwink-Sakurada equation for the intrinsic viscosity, $[\eta]_l$ and $[\eta]^*$ are given by:

$$[\eta]_l = KP^a \tag{9}$$

$$[\eta]^* = K(P^*)^a \tag{10}$$

The exponent, a is usually between 0.5 and 0.8.

By substituting Eqs. (1), and (7)–(10) into Eq. (6), one obtains:

$$P^* = g^{\alpha} P = \left(\frac{6u \langle s^2 \rangle_{br}}{L^2} \right)^{\alpha} P^{1-\alpha} \tag{11}$$

where $\alpha = b/(a + 1)$.

By estimating $\langle s^2 \rangle_{br}$ through the Monte Carlo simulation, one can obtain the calibrated DP P^*, which leads to obtain the calibrated DP distribution. This type of distribution would be obtained by using a detector that measures the polymer concentration in the elution volume, such as the differential refractive index detector (RI). On the other hand, by calculating the "true" weight-average molecular weight of each fraction, one can obtain the distribution when one uses a detector system that measures

the weight-average molecular weight of polymer molecules within the elution volume, such as the light scattering photometer (LS). We consider these two types of detector systems.

Results and discussion

Preliminary investigation for regular star polymers

Before considering polydisperse systems that are of practical interest in SEC measurements, we consider a regular star polymer system to highlight a general trend, in particular, the effects of parameters *a* and *b* on the calibrated DP.

For star polymers having *f* arms with the same DP, *g* is given by[16]:

$$g = \frac{3}{f} - \frac{2}{f^2} \qquad (12)$$

By substituting Eq. (12) into Eq. (11), one obtains the calibrated DP of a star polymer.

For star polymers, the *b*-value is usually claimed[15] to be 0.5. Fig. 4 shows the effect of the *a*-value, which shows the goodness of the eluent used, on the calibrated DP. The introduction of arms makes the calibrated DP smaller, however, the goodness of the solvent used has only a minor effect on the calibrated DP.

In the case of star polymers, the *b*-value would be 0.5, however, in order to investigate a general effect of *b*, we calculated the calibrated DP by changing the *b*-value from 0.5 to 1.5. Fig. 5 shows the effect of *b*. The difference from the "true" DP becomes larger as the *b*-value increases. Therefore, it is expected that the difference between the true and calibrated DP is larger for the branched polymers whose *b*-value is large, such as the case for comb-branched polymers ($b \approx 1.5$) rather than the star polymers ($b = 0.5$).

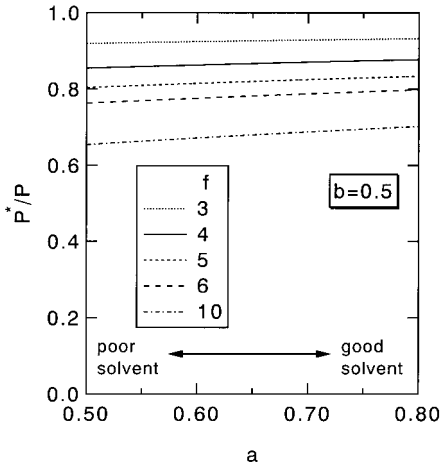

Fig. 4. Effect of the solvent used in a SEC measurement for regular star polymers having *f* arms

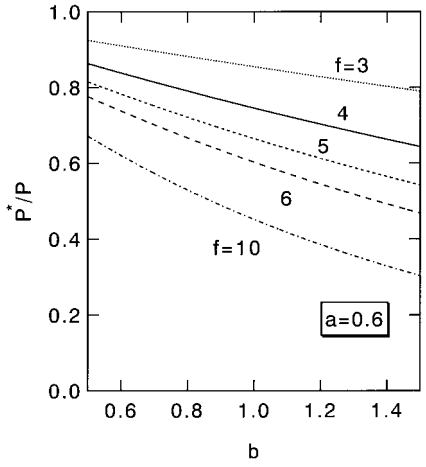

Fig. 5. Effect of the exponent *b* in a SEC measurement for regular star polymers having *f* arms

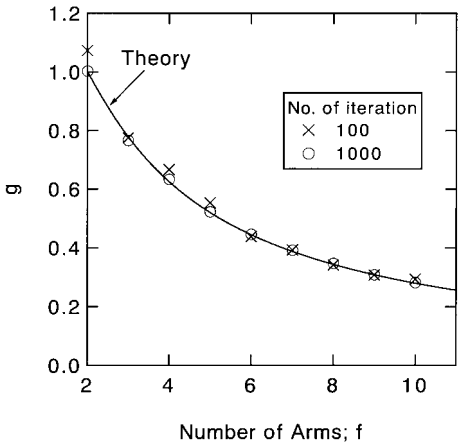

Fig. 6. Simulated results of the *g*-factor in comparison with the analytical solution for regular star polymers having *f* arms

To examine the precision of the Monte Carlo simulation for estimating the *g*-factor, we simulated the *g*-factor for regular star polymer systems. Fig. 6 shows the comparison with the theoretical value (solid curve). The x-symbols show the estimate obtained by simulating the 3D polymer structure 100 times, while the circular symbol shows that for 1000 times. Obviously, the results from 1000 times of simulation give a better fit than those with 100 times of simulation. However, except for the linear polymer ($f = 2$) whose variance is larger than that of the branched polymers, the errors in the 100 times of simulation are not too large. We use the 100-time method to reduce the amount of calculation required.

Star polymers

The random sampling technique to determine the size and structure of star polymers based on the reaction mechanism can be found in ref.[12] By simulating the mean square radius of gyration for each sampled polymer molecule, the elution curve of SEC can be simulated.

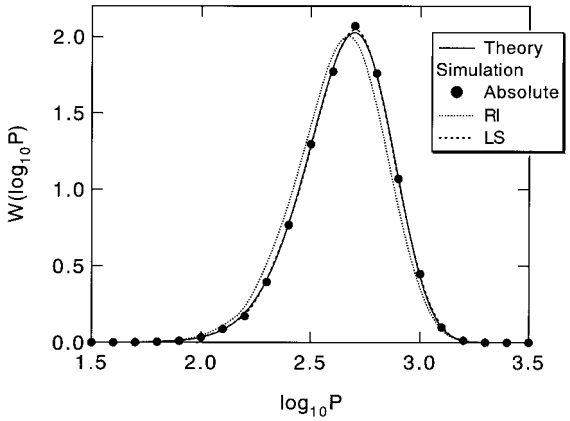

Fig. 7. Simulated weight fraction distribution of the star polymer molecules having 4 arms

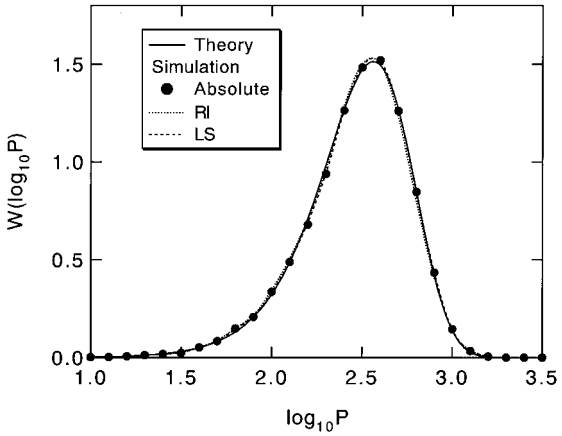

Fig. 8. Simulated weight fraction distribution of the star polymer molecules that are formed by connecting the chain ends of linear polymers by tetrafunctional units with probability $p = 0.5$

Our first example is the star polymer having 4 arms. The arm chains are assumed to follow the most probable distribution represented by Eq. (3) with the number-average DP of arms, $\overline{P}_{n,arm} = 100$. The DP distribution obtained from the random sampling technique, by generating 2×10^4 polymer molecules, is shown by the circular symbols in Fig. 7, which agrees well with the theoretical distribution[12, 17, 18]. The weight-average DP of the theoretical distribution is $\overline{P}_{w,theory} = 500$, while the simulated absolute value was $\overline{P}^{abs}_{w,sim} = 501.1$.

By assuming $u = 5$, the $\langle s^2 \rangle_{br}$-value of each polymer molecule was determined to follow the dotted curve indicated by the legend RI in Fig. 7. The exponent of the Mark-Houwink-Sakurada equation is $a = 0.6$ for the present calculation. The obtained weight-average DP is $\overline{P}^{RI}_{w,sim} = 468.8$, which is 6.2% smaller than the true value.

Next, we calculated the weight-average DP of each fraction, and plotted the weight fractions as a function of such averages after normalization (to make the total area unity). This type of plot is shown by the dashed curve in Fig. 7 (legend LS), which agrees so well with the theoretical distribution that it is difficult to distinguish from the solid curve. Note that, in principle, the weight-average DP, $\overline{P}^{LS}_{w,sim} = \overline{P}^{abs}_{w,sim}$, even when the MWD profiles do not agree.

Next example is the reaction between the tetrafunctional units (A_4) and monofunctional polymeric chains (B-Polymer) with the exact stoichiometry ($[A]_0 = [B]_0$). We assumed that the monofunctional linear polymer molecules conform to the most probable distribution with the number-average DP 100. In practice, not all functional groups would react, and we assumed that the probability that a functional group is reacted is equal to $p = 0.5$. This type of star polymers could be synthesized by employing an ideal tetrafunctional chain transfer agent in free-radical polymerization[12, 18]. In this case, linear polymer molecules (polymers with 1 and 2 arms) coexist with branched polymers (polymers with 3 and 4 arms). The full weight fraction distribution as well as the fractional distribution possessing 1, 2, 3, and 4 arms can be found in figure 5 of ref.[12]

Fig. 8 shows the simulated results. The total of 2×10^4 polymer molecules were simulated. The weight-average DPs are as follows: $\overline{P}_{w,theory} = 350$, $\overline{P}^{abs}_{w,sim} = 351.2$, and $\overline{P}^{RI}_{w,sim} = 342.7$. As shown in Fig. 6 and 7, both detector systems may give a reasonable estimate of the true molecular weight distribution for polydisperse star polymer systems.

Comb polymers

The random sampling technique when applied to comb-branched polymer systems can be found in ref.[10] For comb-branched polymers, the *b*-value[15, 19] may be close to 1.5 or slightly smaller than 1.5. To investigate how the magnitude of *b*-value changes the elution curve, we used both $b = 1.0$ and 1.5.

Our first example is the case where both backbone and branch chains conform to the most probable distribution whose number-average DPs are 200 and 100, respectively. The branching density of the backbone chain is $\rho = 0.02$.

The solid curve in Fig. 9 shows the analytical solution[10, 20, 21] for the present comb-branched polymer system. The circular symbols in Fig. 9 show the absolute weight fraction distribution obtained from the random sampling technique. The total of 2×10^4 polymer molecules were simulated. The weight-average DPs are $\overline{P}_{w,theory} = 1332$, and $\overline{P}^{abs}_{w,sim} = 1334$. The dotted and dashed curves in Fig. 9 show the simulated weight fraction distribution for an RI system with $a = 0.6$. The elution curve in a SEC measurement may lie somewhere between these two curves. The weight-average DP of these two curves are $\overline{P}^{RI}_{w,sim}\big|_{b=1.0} = 886.7$ and $\overline{P}^{RI}_{w,sim}\big|_{b=1.5} = 729.3$. The RI sys-

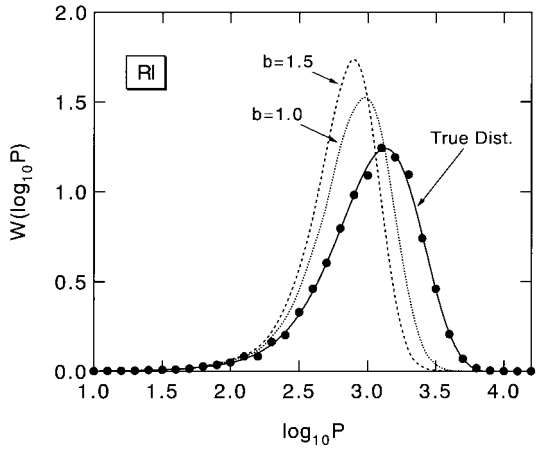

Fig. 9. Simulated weight fraction distribution of an RI detector system for the comb polymer molecules

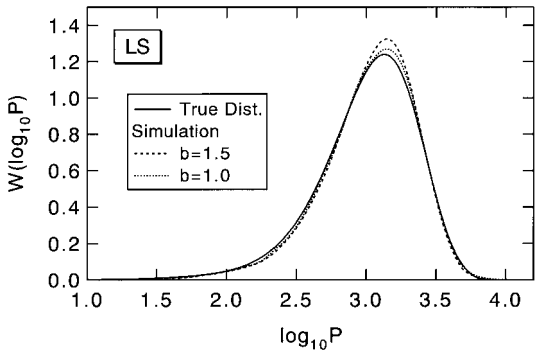

Fig. 10. Simulated weight fraction distribution of an LS detector system for the comb polymer molecules

tem clearly underestimates the DP of comb-branched polymers.

On the other hand, when the LS system is used, the obtained MWD is improved significantly both for b = 1.0 and 1.5, but it does not agree perfectly with the theoretical distribution profile as shown in Fig. 10. The obtained MWD is slightly narrower than the true MWD.

Finally, to show the broad applicability of the present simulation method, we conducted a simulation for free-radical copolymerization with macromonomer. The detailed simulation algorithm can be found in ref.[10] The reaction condition is as follows. The reactivity ratios are $r_1 = r_2 = 0.5$, and the initial mole fraction of macromonomer is 0.01. The DP distribution of the macromonomer molecules is assumed to be given by the Schulz-Zimm distribution whose weight fraction distribution is represented by:

$$W_{macro}(P) = \frac{\sigma^{\sigma}}{\overline{P}_n \Gamma(\sigma)} \left(\frac{P}{\overline{P}_n}\right)^{\sigma} \exp\left(\frac{\sigma P}{\overline{P}_n}\right) \qquad (13)$$

where σ is a parameter indicating the narrowness of the distribution breadth, i.e., $\sigma = \overline{P}_n / (\overline{P}_w - \overline{P}_n)$. We used $\overline{P}_n$ = 100 and σ = 10. The condition with σ = 10 corresponds to the polydispersity index $\overline{P}_w / \overline{P}_n$ = 1.1. The macromonomer molecules synthesized through living polymerization often follow the Schulz-Zimm distribution.

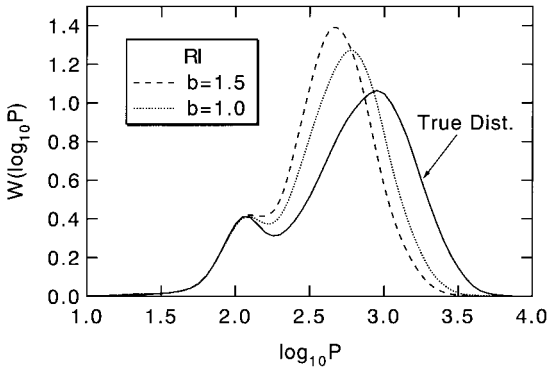

Fig. 11. Simulated weight fraction distribution of an RI detector system for the comb polymer molecules formed through free-radical copolymerization with macromonomer

We assumed that the dominant chain stoppage mechanism is chain transfer reactions to the chain transfer agent (CTA). The initial ratio of the concentrations of CTA to monomer is $[CTA]_0/[M]_0 = 4 \times 10^{-3}$, and the chain transfer constant is $C_{jCTA} = 2.5$. In this case the average DP of the backbone chain increases during polymerization. We simulated the reaction system at the total monomer conversion, x = 0.6.

In the reaction system, because the unreacted macromonomer molecules also exist, we took account of these linear polymer molecules in the MWD. The simulation was conducted for 2×10^4 polymer molecules (the unreacted macromonomers are not included in this number). For the present case, the analytical solution for the MWD has not been derived. On the other hand, a general solution for the weight-average molecular weight was obtained recently[21], and $\overline{P}_{w,theory}$ = 827.8.

Fig. 11 shows the simulated weight fraction distribution. The solid curve shows the true weight fraction distribution estimated by the random sampling technique, and $\overline{P}^{abs}_{w,sim}$ = 839.2. The peak at smaller DP corresponds to the unreacted macromonomer molecules. The dotted and dashed curves in Fig. 11 show the simulated weight fraction distribution for an RI detector system with a = 0.6. Clearly, the molecular weights of comb-branched polymers are underestimated. The weight-average DPs of these two curves are $\overline{P}^{RI}_{w,sim}\big|_{b=1.0}$ = 587.3 and $\overline{P}^{RI}_{w,sim}\big|_{b=1.5}$ = 495.2.

Fig. 12 shows the simulated weight fraction distribution for an LS detector system. The measured distribution profile is improved significantly, but still is not exact. The measured distribution tends to be narrower than the true distribution. For comb-branched polymers, the deviation from the true MWD tends to be larger compared with that for star polymers.

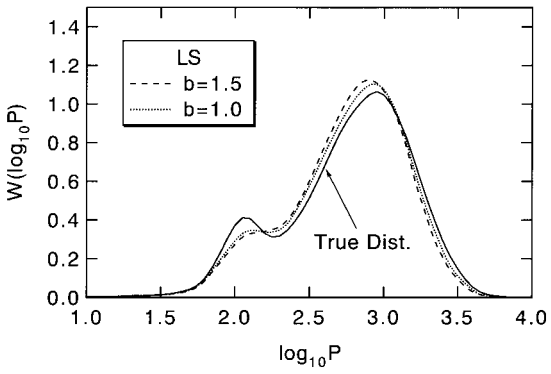

Fig. 12. Simulated weight fraction distribution of an LS detector system for the comb polymer molecules formed through free-radical copolymerization with macromonomer

Conclusions

By application of the random sampling technique, the size and structure of polymer molecules sampled randomly from the reaction mixture can be determined. We obtained the mean square radius of gyration for each polymer molecule by calculating 100 types of conformation, and estimated the elution curve of SEC. This technique can be applied to various types of nonlinear polymers whose formation mechanism is known. In the present article, we applied the method to star and comb polymers. It was found that for polydisperse star polymer systems, both RI and LS detector systems may give a reasonable estimate of the true molecular weight distribution. On the other hand, for comb-branched polymers, the RI detector system clearly underestimates the molecular weight of branched polymers significantly. The LS system improves the measured molecular weight distribution, but still is not exact.

The present simulation method enables one to predict the SEC-trace on the basis of known or assumed polymerization kinetics, and could be used to investigate the complicated kinetics of nonlinear polymer formation. In addition, a large amount of SEC data accumulated so far, especially those obtained from the RI detector systems, could be reinvestigated more quantitatively.

[1] B. H. Zimm, W. H. Stockmayer, *J. Chem. Phys.* **17**, 1301 (1949)
[2] C. Jackson, *J. Chromatogr. A* **662**, 1 (1994)
[3] W. H. Stockmayer, *J. Chem. Phys.* **11**, 45 (1943)
[4] P. J. Flory, "*Principles of Polymer Chemistry*", Cornell University Press, Ithaca, NY 1953, p. 393
[5] H. Tobita, *Macromol. Theory Simul.* **5**, 1167 (1996).
[6] H. Tobita, *Macromolecules* **27**, 5413 (1994)
[7] H. Tobita, K. Hatanaka, *J. Polym. Sci., Part B: Polym. Phys.* **33**, 841 (1995)
[8] H. Tobita, *J. Polym. Sci., Part B: Polym. Phys.* **33**, 1191 (1995)
[9] H. Tobita, K. Hatanaka, *J. Polym. Sci., Part B: Polym. Phys.* **34**, 671 (1996)
[10] H. Tobita, "*Comb-Branched Polymer Formation During Copolymerization with Macromonomer*", *Polym. React. Eng.*, in press
[11] P. J. Flory, "*Statistical Mechanics of Chain Molecules*", Wiley, New York 1969, p. 12
[12] H. Tobita, *Macromolecules* **29**, 693 (1996)
[13] J. F. Douglas, J. Roovers, K. F. Freed, *Macromolecules* **23**, 4168 (1990)
[14] P. A. Small, *Adv. Polym. Sci.* **18**, 1 (1975)
[15] S. Mori, "*Size Exclusion Chromatography*", Kyoritsu-Shuppan, Tokyo, Japan 1991
[16] W. C. Forsman, *Macromolecules* **1**, 343 (1968)
[17] J. R. Schaefgen, P. J. Flory, *J. Am. Chem. Soc.* **70**, 2709 (1948)
[18] C. M. Yuan, G. Silvestro, M. Farina, *Macromol. Theory Simul.* **3**, 193 (1994)
[19] I. Noda, T. Hirokawa, T. Kato, T. Fujimoto, N. Nagasawa, *Macromolecules* **3**, 795 (1970)
[20] S. Zhu, D. Li, W. Zhou, C. M. Crowe, *Polymer* **39**, 5203 (1998)
[21] H. Tobita, *Polymer* **40**, 3565 (1999)