Random Degradation of Branched Polymers. 1. Star Polymers

Hidetaka Tobita

Department of Materials Science and Engineering, Fukui University, 3-9-1 Bunkyo, Fukui, Japan 910

Received July 10, 1995; Revised Manuscript Received November 28, 1995[⊗]

ABSTRACT: A random sampling technique in which polymer molecules are sampled from an infinite number of polymer molecules in the reaction mixture is used to predict the molecular weight distribution (MWD) change during random scission reactions of star-shaped polymers. For simpler initial MWDs, the analytical solutions for the full MWD change, as well as the average molecular weights, can be derived in a straightforward manner. For any initial MWD, the concept of the random sampling technique provides a unique Monte Carlo simulation algorithm that enables one to estimate the change in the statistical properties during random degradation quite effectively. Compared with the random degradation of linear polymer molecules, the decrease in the weight-average molecular weight is slower; however, such differences are made smaller as the initial MWD becomes broader. In the course of random degradation, linear and branched polymer fractions are formed. As the degradation reaction proceeds, the polydispersity index of the linear and branched fractions approaches 2 and $(f + 1)/f$, respectively, irrespective of the initial polymer distribution, where f is the number of arms in a star polymer.

Introduction

Modification of the molecular weight distribution (MWD) via degradation reactions provides an attractive field of research, combining at the same time both fundamental and applied topics of great interest. Theoretical descriptions of the random chain scission and cross-linking of linear polymers have been studied for many years by the application of the analytical technique[1−14] for limited initial MWDs and by Monte Carlo simulations.[13−21] For degradation reactions of linear polymers, even nonrandom degradation has already been studied.[21−24]

In the present report, random degradation reactions of branched polymer molecules are considered. Publications concerning the theoretical description of degradation reactions for branched polymer molecules are scarce. Meddings and Potter[25] mentioned that degradation of branched polymers could be examined by the application of a Monte Carlo method in their short note. Quite recently, Giudici and Hamielec[26] proposed approximate deterministic equations for random chain scission of branched chains together with Monte Carlo simulation results for an initial uniform distribution of star and comb polymers with idealized structures. In comparison with the abundance of literature that deals with the theoretical description of simultaneous cross-linking and degradation[4−10,15−18] (or degradation of cross-linked polymers without cycles), why has the degradation of branched polymers been ignored so far? In the case of random cross-linking and degradation, the processes of cross-linking and degradation are interchangeable,[18,27] if the ring-free model[1−3] is assumed for cross-linking reactions and the two processes are considered independent of each other. Therefore, random degradation of homogeneously cross-linked polymers (without cycles) can be investigated by considering the random cross-linking of linear polymers that are formed after random chain scission reactions. On the other hand, the processes of branching and degradation are not interchangeable, as will be clarified in part 2 of the present series;[28] therefore, one has to examine the degradation of nonlinear polymers that results in various types of chain morphology.[26,29]

The Monte Carlo method is a versatile technique that can handle complicated phenomena in a straightforward manner, provided that each kinetic process, or the associated transition probabilities, can be defined explicitly. Conventional Monte Carlo simulations employ a finite reaction system to represent an infinite system approximately.[15−19,21] In such a method, a very small part is isolated from the reaction mixture, and the kinetic behavior of all molecules involved in this small volume is simulated. A notable advantage of using a finite reaction system is that one can employ very realistic models for the simulation, such as those that account for the effects of chain conformation and molecule mobility, in a straightforward manner.[30] However, mainly due to computational limitations, the "virtual reality" processed in a supercomputer is still far from simulating the real world, and the simulations are restricted to an extremely small reaction volume. To examine the accuracy of the simulated results, one needs to examine the effect of system size by systematically increasing the number of molecules involved. Especially when one needs to calculate the molecular weight distribution (MWD), the system size must be much larger than the largest polymer molecule in the finite reaction system.[31] (Note that the molecular weights of nonlinear polymers are usually much larger than those of linear polymer systems.)

A certain type of finiteness is required in Monte Carlo computer simulations due to the limited memory size of the computer. Monte Carlo simulations that employ a random sampling technique have been proposed recently to carry out simulations for free-radical and living cross-linking copolymerizations,[32−34] random cross-linking and degradation of polymer chains,[13,14,18] and free-radical polymerizations with long-chain branching due to chain transfers to polymer as well as polymerization with the terminal double bonds.[31,35−38] In this method, the system size considered is infinitely large and the number of polymer molecules sampled from the reaction mixture is finite. This method enables one to account for the kinetics of nonrandom history-dependent structure formation quite rigorously and can be applied irrespective of the reactor types used. The accuracy of the simulated results can simply be improved by increasing the number of polymer molecules sampled

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

0024-9297/96/2229-3000$12.00/0

from the infinite system, and the required amount of calculation is so small that personal computers may be used for the simulations. Another advantage of this method is that weight-based properties (such as the weight-average molecular weights and the weight fraction distribution), which are usually more important in discussing the physical characteristics of polymeric systems than number properties, can be obtained directly. (Note that, in the Monte Carlo simulations that employ finite systems, the simulations are carried out on the basis of the numbers of polymer molecules, and then the number distribution obtained is transformed into weight-based properties. If weight properties are the main interest, simulations on a number basis lack accuracy in Monte Carlo simulations, where errors are always involved as long as the sample size is finite.)

The fundamental idea of the random sampling technique is quite simple, i.e., we select a finite number of polymer molecules randomly from the "sea" of polymer molecules. Consider a linear polymer system for simplicity. The number fraction distribution is obtained if one samples polymer molecules by selecting chain ends randomly, and the expected chain length is the number-average chain length. On the other hand, when a unit bound into a polymer molecule is selected randomly, the polymer molecule that involves this particular unit follows the weight fraction distribution, and the expectation is the weight-average chain length. When a large number of molecules are collected by using Monte Carlo methods, the statistical properties of the polymer mixture can be determined. Furthermore, when the concept of the random sampling technique is used in a "thought experiment", analytical solutions can be obtained for simpler cases.[39]

In this and the following paper,[28] we consider the random degradation of branched polymer molecules by the application of a random sampling technique. Analytical solutions are developed for special cases. One of the simplest morphologies of a branched polymer molecule would be a star-shaped polymer. In the present paper, we deal with star polymers, and differences from the degradation of linear polymers are clarified. In part 2 of this series, we consider polymer molecules with multiple branches.

Simulation Method

To highlight the concept of the random sampling technique, we will elucidate the Monte Carlo simulation method before deriving analytical solutions. We consider the whole molecular constitution when the probability of chain scission for each bond is ϕ. Suppose we randomly select one unit from all of the units that exist in the reaction mixture. The chain length (degree of polymerization) of the primary polymer molecule that involves this particular unit before chain scission can be determined from the weight fraction distribution of the primary polymer molecules ($w_P(r)$), because the selection is made on a weight basis. The chain length of the selected primary polymer molecule (r) can be determined by using a equidistributed random number, y ($0 < y < 1$):

$$y = \int_0^r w_P(r)\, dr \tag{1}$$

For several types of distribution functions, simpler algorithms may be employed to generate random numbers that conform to special distributions.[18,39,40]

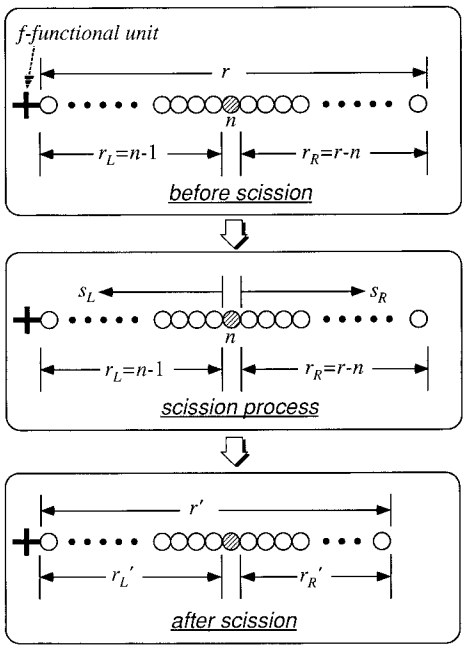

Figure 1. Schematic representation of the random scission process. The shaded unit, which is called the base unit in the text, is selected randomly, after which the sequence lengths of the units connected to this base unit are considered.

Suppose we have selected the nth unit in the primary polymer molecule, as shown in Figure 1. We call this unit the *base unit*. We have $r_R = (r - n)$ units on the right-hand side of the base unit, and $r_L = (n - 1)$ units on the left-hand side. Consider the random scission process for this primary polymer molecule. By looking from the base unit toward the right-hand side, the probability that chain scission occurs at the $(s_R + 1)$th bonding, thus leaving s_R units on the right-hand side, is given by the following most probable distribution:

$$N_s(s_R) = \phi(1 - \phi)^{s_R} \tag{2a}$$

$$\cong \phi \exp\{-\phi s_R\} \qquad (\phi \ll 1) \tag{2b}$$

Therefore, the chain length s_R can be determined from a random number y between 0 and 1 as follows:

$$s_R = ceiling\left[\frac{\ln y}{\ln(1 - \phi)} - 1\right] \tag{3a}$$

$$\cong ceiling\left[\frac{1}{\phi}\ln(1/y) - 1\right] \qquad (\phi \ll 1) \tag{3b}$$

where *ceiling*[a] indicates the closest integer not smaller than a. The chain length s_L can be determined similarly.

At this stage, a kind of competition of events is considered, namely, if $r_R > s_R$ chain scission really occurs, then the chain length after scission becomes $r'_R = s_R$. On the other hand, if $r_R < s_R$, then chain scission is not a *real* event, and $r'_R = r_R$. The chain length after scission on the left-hand side can be determined similarly, and the total chain length after scission is given by $r = r'_R + r'_L + 1$. If $r_L > s_L$, one obtains a linear polymer, while if $r_L < s_L$, the selected polymer molecule is a branched polymer.

When a branched polymer molecule is selected ($r_L < s_L$), the primary chains connected from the multifunctional unit (with f functional groups) follow the number fraction distribution of the primary polymer molecules

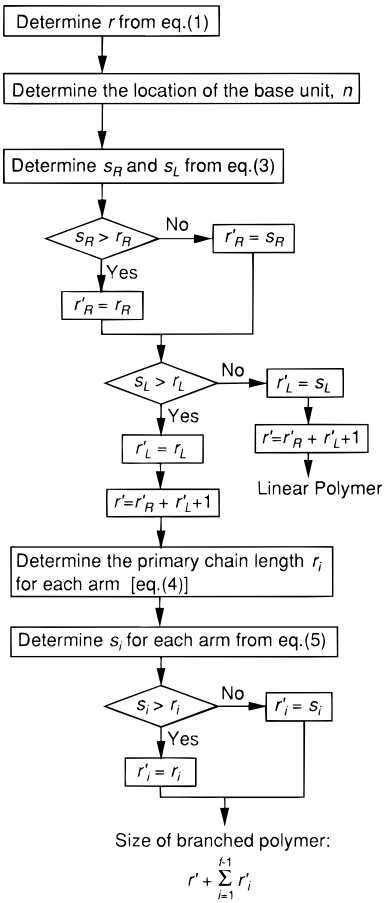

Figure 2. Monte Carlo simulation algorithm.

($n_p(r)$), because only chain ends can be connected. The chain length of the ith arm ($1 \le i \le f - 1$) before chain scission, r_i, can be determined from

$$y = \int_0^{r_i} n_p(r)\, dr \tag{4}$$

An "imaginary" chain length after scission for the ith arm, s_i, can again be determined from the following equation:

$$s_i = ceiling\left[\frac{\ln y}{\ln(1-\phi)} - 1\right] \tag{5a}$$

$$\cong ceiling\left[\frac{1}{\phi}\ln(1/y) - 1\right] \quad (\phi \ll 1) \tag{5b}$$

The "real" chain length for the ith arm after scission can be determined by employing the competition process discussed earlier. When the chain lengths for all arms are determined, the size and structure of a star polymer molecule are fixed. By simulating a large number of polymer molecules in this way, the statistical properties can be determined effectively. The whole simulation algorithm is shown in Figure 2.

Arms with the Most Probable Distribution

Let us first consider the degradation of star polymers whose chain length distribution of the arms (before scission) conforms to the most probable distribution, i.e., the number ($n_p(r)$) and weight ($w_p(r)$) fraction distributions of the primary polymer molecules are given by

$$n_p(r) = p^{r-1}(1-p) \tag{6}$$

$$w_p(r) = rp^{r-1}(1-p)^2 \tag{7}$$

where p is the probability that a unit is connected to the next unit.

As clearly shown in eq 2, random scission is the process that produces the most probable distribution for the chains. That is why the MWD formed in the random degradation of linear chains approaches the most probable distribution as the scission probability ϕ increases, irrespective of the initial MWD. Therefore, the random degradation of star polymers whose arms conform to the most probable distribution yields corresponding information for the limiting MWD as a random scission reaction proceeds, starting from any initial MWD for the arms.

Linear polymers and branched polymers are formed via random scission processes. Because the linear and branched polymers follow different distributions, we need to consider them separately.

Weight Fraction of the Branched Polymers. The probability that a randomly selected unit belongs to the branched fraction is the weight fraction of the branched polymers, Φ_b. We select a unit from the polymer mixture and consider the probability that this particular unit is involved in a polymer molecule containing an f functional unit.

Let us examine Figure 1 again. The probability that a randomly selected unit is involved in the primary polymer molecule with chain length r (before scission) is given by the weight fraction distribution of the primary polymer molecule, $w_p(r)$, as discussed in the Simulation Method section. Suppose our randomly selected unit is the nth unit, as shown in Figure 1. The probability of making such a selection is $w_p(r)/r$. The probability that the chain scission does not occur until the chain is connected to reach an f functional unit, or $s_L > n - 1$, $P_b(n)$ is given by

$$P_b(n) = \sum_{s=n}^{\infty} N_s(s) = (1-\phi)^n \tag{8}$$

Therefore, Φ_b is given by

$$\Phi_b = \sum_{r=1}^{\infty} \frac{w_p(r)}{r} \sum_{n=1}^{r} P_b(n) = \frac{1-\phi}{\phi \bar{P}_{np}}\left\{1 - \frac{1-\phi}{\bar{P}_{np} - (\bar{P}_{np} - 1)(1-\phi)}\right\} \tag{9}$$

where $\bar{P}_{np}$ is the number-average chain length of the primary polymer molecules, which is given by $\bar{P}_{np} = 1/(1 - p)$.

Linear Polymer Fraction. The connection probability between units for the present case is simply give by $(p - \phi)$, except for the bonding connected to the f functional unit, which is given by $(1 - \phi)$. By neglecting the weight fraction of linear polymers formed by cutting the bond connected to the f functional unit, the weight fraction distribution of the linear fraction is simply given by the following most probable distribution:

$$W'_l(r) = r(p-\phi)^{r-1}(1-p+\phi)^2 \tag{10}$$

The fractional distribution of linear polymer molecules

in the whole MWD is simply given by multiplying the preceding expression by the weight fraction of linear polymers, $(1 - \Phi_b)$:

$$W_l(r) = (1 - \Phi_b)W'_l(r) \tag{11}$$

The number-average ($\bar{P}_{n,l}$) and weight-average ($\bar{P}_{w,l}$) chain lengths of linear polymers are given by

$$\bar{P}_{n,l} = \frac{1}{1 - p + \phi} \tag{12}$$

$$\bar{P}_{w,l} = \frac{1 + p - \phi}{1 - p + \phi} \tag{13}$$

$$\frac{\bar{P}_{w,l}}{\bar{P}_{n,l}} = 1 + p - \phi \cong 2 \quad [\text{when } (1 - p) \ll 1 \text{ and } \phi \ll 1] \tag{14}$$

Branched Polymer Fraction. The chain length of each arm follows the most probable distribution even after the scission processes, namely,

$$n_{arm}(r) = (p - \phi)^{r-1}(1 - p + \phi) \tag{15}$$

$$w_{arm}(r) = r(p - \phi)^{r-1}(1 - p + \phi)^2 \tag{16}$$

The distribution is the same as the MWD for the linear fraction, which is given by eq 10. Therefore, the number-average ($\bar{P}_{n,arm}$) and weight-average ($\bar{P}_{w,arm}$) chain lengths of the arms are also given by eqs 12 and 13, respectively.

First, we consider the number-average ($\bar{P}_{n,b}$) and weight-average ($\bar{P}_{w,b}$) chain lengths (degree of polymerization) for the branched fraction. By application of the concept of the random sampling technique, the average chain lengths can be obtained arithmetically.[18,39] The number-average chain length is the expected size of a polymer molecule when sampling is made on a number basis. Since every branched polymer molecule contains only one f functional unit, one can sample on a number basis by selecting an f functional unit randomly. The expectation that each arm is connected to an f functional unit is $\bar{P}_{n,arm}$, and the expected number of arms connected to an f functional unit is $(1 - \phi)f$; therefore,

$$\bar{P}_{n,b} = (1 - \phi)f\bar{P}_{n,arm} = \frac{(1 - \phi)f}{1 - p + \phi} \tag{17}$$

On the other hand, when one unit bound into a branched polymer molecule is selected randomly, the expected chain length is the weight-average chain length ($\bar{P}_{w,b}$). By referring to Figure 3, when one unit is selected randomly, the chain length of the selected arm follows the weight fraction distribution of the arms, and the expected chain length is $\bar{P}_{w,arm}$. The expected number of additional arms connected to the f functional unit is $(1 - \phi)(f - 1)$, and the expected chain length of these connected chains is the number-average chain length of the arms, $\bar{P}_{n,arm}$, because only the chain end can be selected randomly. Therefore, the weight-average chain length of the branched fraction is given by

$$\bar{P}_{w,b} = \bar{P}_{w,arm} + (1 - \phi)(f - 1)\bar{P}_{n,arm} = \frac{p + (1 - \phi)f}{1 - p + \phi} \tag{18}$$

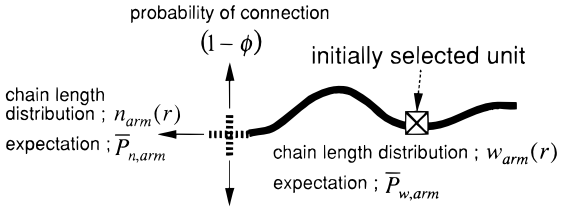

Figure 3. Schematic representation of the calculation of the weight fraction distribution of the branched fraction that involves a 4-functional unit. The chain length of the initially selected primary polymer molecule follows the weight fraction distribution of the primary polymer molecules ($w_p(r)$), while the other three chains, if connected, conform to the number fraction distribution ($n_p(r)$).

The polydispersity index (PDI) is given by

$$\frac{\bar{P}_{w,b}}{\bar{P}_{n,b}} = \frac{p + (1 - \phi)f}{(1 - \phi)f} \tag{19a}$$

$$\cong \frac{f + 1}{f} \quad [\text{when } (1 - p) \ll 1 \text{ and } \phi \ll 1] \tag{19b}$$

Equation 19 was developed a long time ago[41] for multichain condensation polymers on the basis of the consideration of the full MWD function. However, by using the concept of the random sampling technique, the same equation can be derived arithmetically, as shown earlier.

Next, we consider the full distribution function. The weight fraction distribution of the branched polymer molecules ($W'_b(r)$) consists of the fractional weight-based chain length distribution containing 1, 2, ..., f arms:

$$W'_b(r) = \sum_{i=1}^{f} W_i(r) \tag{20}$$

First, consider the fractional weight-based distribution containing i arms, $W_i(r)$. By referring to Figure 3, the initially selected arm follows the weight fraction distribution given by eq 16. If all other $(f - 1)$ bonds connected to the f functional unit are cut, one obtains a polymer molecule with only one arm that contains an f functional unit. (For simplicity, we consider all polymer molecules that contain an f functional unit as branched.) The weight fraction distribution containing only one arm is given by

$$W_1(r) = \binom{f - 1}{0} \phi^{f-1} w_{arm}(r) \tag{21}$$

If $(f - 2)$ bonds connected to the f functional unit have been cut, then a two-arm polymer is obtained. Suppose our randomly selected unit belongs to a primary polymer whose chain length is v_1 ($v_1 < r$). A polymer molecule with two arms whose total chain length is r can be obtained if the chain length of the connected chain, which is also selected randomly, is $v_2 = r - v_1$. The primary polymer molecule connected from the f functional unit must be selected on a number basis ($n_{arm}(r)$), because only the chain end can be connected; therefore, $W_2(r)$ is given by

$$W_2(r) = \binom{f - 1}{1} (1 - \phi)\phi^{f-2} \sum_{v_1 + v_2 = r} w_{arm}(v_1) n_{arm}(v_2) \tag{22}$$

In general, $W_i(r)$ is given by

$$W_i(r) = \binom{f-1}{i-1}(1-\phi)^{i-1}\phi^{f-i} \times \sum_{\sum_{j=1}^{f} v_j = r} w_{arm}(v_1) n_{arm}(v_2) n_{arm}(v_3) \cdots n_{arm}(v_i) \quad (23)$$

where the summation term with a sum as its limit means that the summation is taken for all possible combinations of positive integers v_j under the restriction $\sum_{j=1}^{f} v_j = r$.

The solution for eq 23 is given by[39]

$$W_i(r) = \binom{f-1}{i-1}(1-\phi)^{i-1}\phi^{f-i}(p-\phi)^{r-i}(1-p+\phi)^{i+1}\binom{r}{i} \quad (24)$$

Therefore,

$$W'_b(r) = \sum_{i=1}^{f}\binom{f-1}{i-1}(1-\phi)^{i-1}\phi^{f-i}(p-\phi)^{r-i}(1-p+\phi)^{i+1}\binom{r}{i} \quad (25)$$

When $\phi \ll 1$, the weight fraction of branched polymer molecules with less than f arms is negligibly small. For such cases, eq 25 reduces to

$$W'_b(r) \cong (p-\phi)^{r-f}(1-p+\phi)^{f+1}\binom{r}{f} \quad (26)$$

The fractional distribution of branched polymer molecules in the whole MWD is simply given by multiplying by the weight fraction of branched polymers, i.e., $W_b(r) = \Phi_b W'_b(r)$.

It is worth noting here that eq 26 reduces to the Schulz−Zimm distribution[42,43] when $\bar{P}_{n,b} \gg f$:

$$W'_b(r) = \frac{f^f}{\bar{P}_{n,b}\Gamma(f)}\left(\frac{r}{\bar{P}_{n,b}}\right)^f \exp(-fr/\bar{P}_{n,b}) \quad (27)$$

The weight fraction distribution of the branched fraction follows the Schulz−Zimm distribution throughout the degradation reaction (as long as $\phi \ll 1$ and $f \ll \bar{P}_{n,b}$).

Calculated Results. We examine the case with $f = 4$ and $p = 0.996$, i.e., the number-average chain length of the primary polymer molecules $\bar{P}_{np} = 250$, and the number- and weight-average chain lengths of the initial star polymers, $\bar{P}_n{}^0 = 1000$ and $\bar{P}_w{}^0 = 1250$, respectively. Figure 4 shows the average chain length change during the random degradation reaction. The x-axis shows the average number of scission points per initial polymer molecule, i.e., $\alpha = \phi\bar{P}_n{}^0$. Comparison is made with the random degradation of linear polymer molecules whose initial MWD is the same as that for the star polymer molecules, i.e., the linear polymer molecules that possess the Schulz−Zimm distribution:[42,43]

$$W(r) = \frac{\sigma^\sigma}{\bar{P}_n{}^0\Gamma(\sigma)}\left(\frac{r}{\bar{P}_n{}^0}\right)^\sigma \exp(-\sigma r/\bar{P}_n{}^0) \quad (28)$$

where σ is a parameter indicating the narrowness of the distribution breadth, namely,

$$\sigma = \frac{\bar{P}_n{}^0}{\bar{P}_w{}^0 - \bar{P}_n{}^0} \quad (29)$$

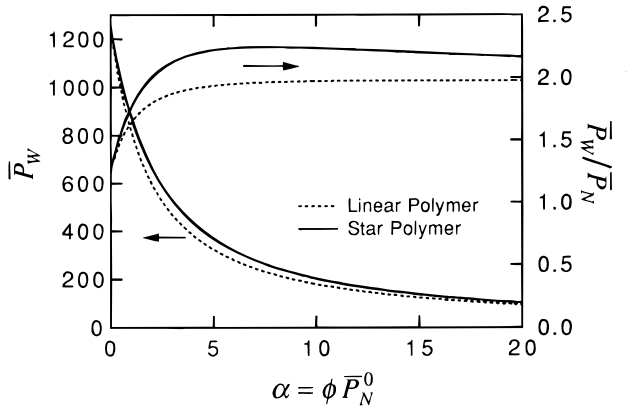

Figure 4. Average chain length development during random scission reactions. The solid curves represent the star polymers with four arms that conform to the most probable distribution, in which $p = 0.996$. The dashed curves show the changes for the linear polymer molecules whose initial MWD is the same as that of the star polymers.

In the present example, $\bar{P}_n{}^0 = 1000$ and $\sigma = f = 4$.

The number-average chain length can be derived from the stoichiometric argument whether the initial polymers are star-shaped or linear:

$$\bar{P}_n = \frac{\bar{P}_n{}^0}{1 + (\bar{P}_n{}^0 - 1)\phi} \quad (30)$$

On the other hand, random degradation of linear polymers with the Schulz−Zimm distribution results in the following weight-average chain lengths:[8,10]

$$\bar{P}_w = \frac{1}{\bar{P}_n{}^0\phi^2}\left\{\bar{P}_n{}^0[1-(1-\phi)^2] - 2(1-\phi) + 2(1-\phi)\left(\frac{\sigma}{\sigma - \bar{P}_n{}^0\ln(1-\phi)}\right)^\sigma\right\} \quad (31a)$$

$$\cong \frac{2}{\bar{P}_n{}^0\phi^2}\left\{\bar{P}_n{}^0\phi - 1 + \left(1 + \frac{\bar{P}_n{}^0\phi}{\sigma}\right)^{-\sigma}\right\} \quad (\phi \ll 1) \quad (31b)$$

Figure 4 clearly shows that the weight-average chain length of the star polymer system decreases more slowly than that for the linear polymer system. The PDI ($\bar{P}_w/\bar{P}_n$) becomes larger than 2 and then approaches 2 as the scission reaction proceeds, while it approaches 2 monotonously for the initial linear polymers.

Figure 5 shows the weight fraction of branched polymers (Φ_b) as well as the weight-average chain length of each fraction. The symbols are the Monte Carlo simulation results, while the solid curves are the analytical solutions. The simulations were made to obtain 2×10^4 polymer molecules at each scission level. The accuracy of the simulated results is satisfactory. The weigth-average chain length of the total polymer, $\bar{P}_w$, decreases from that for the branched fraction, $\bar{P}_{w,b}$, to that for the linear fraction, $\bar{P}_{w,l}$, because the weight fraction of linear polymers ($1 - \Phi_b$) increases as degradation proceeds.

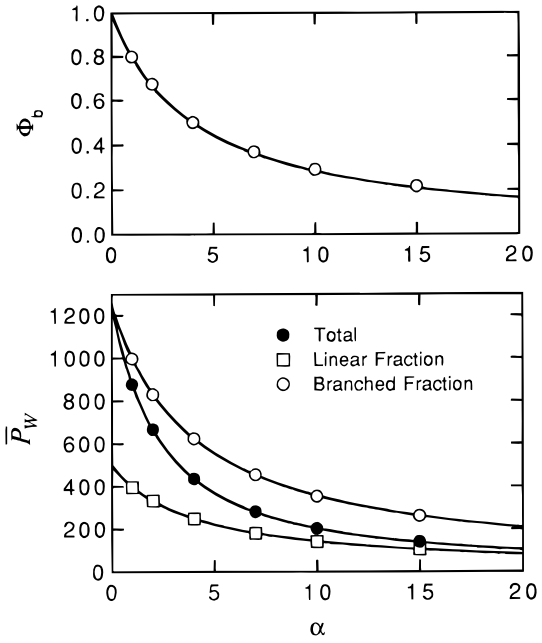

Figure 5. Weight fraction of branched polymers (Φ_b) and weight-average chain length for each fraction as a function of the average number of scission points per initial polymer molecule, α. The calculation conditions are the same as for the star polymers in Figure 4. The solid curves are the analytical solutions calculated from eqs 9, 13, and 18, while the symbols are the Monte Carlo simulation results.

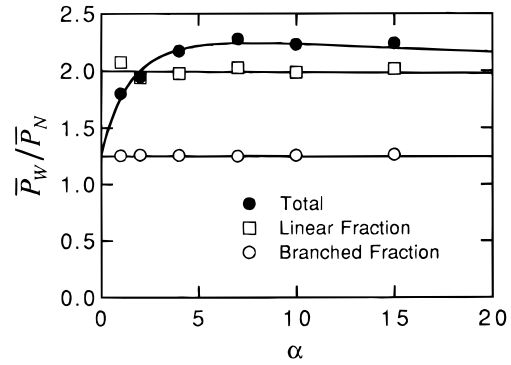

Figure 6. Polydispersity index ($\bar{P}_w/\bar{P}_n$) for each fraction. The solid curves are the analytical solutions, while the symbols are the Monte Carlo simulation results.

Figure 6 shows the PDI of each fraction. Although the behavior of the overall PDI appears to be complicated, the PDI of each fraction does not change during the scission reactions. The PDI of the linear fraction is 2, and that for the branched fraction is 1.25 (=$(f + 1)/f$). The PDI of the total polymer changes due to the change in the relative contribution of each fraction. Since the present Monte Carlo simulations are made on a weight basis, the accuracy of the number-average chain length ($\bar{P}_n$) is somewhat worse than that for $\bar{P}_w$. That is why a small fluctuation is observed in the simulated results for the PDI.

Figure 7 shows the weight fraction distribution for the total polymer as well as for the linear and branched fractions. The Monte Carlo simulation results agree satisfactorily with the theoretical distribution functions. The linear and branched polymers follow completely different distributions, as shown in the figure. Because the physical properties of linear and branched polymers differ significantly, fractionation on the basis of chain morphology as shown here would be quite important.

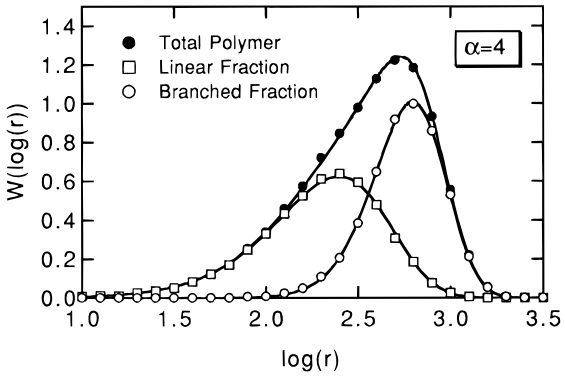

Figure 7. Weight fraction distribution of each fraction when the extent of scission reaction α = 4. The solid curves are the analytical solutions, while the symbols are the Monte Carlo simulation results.

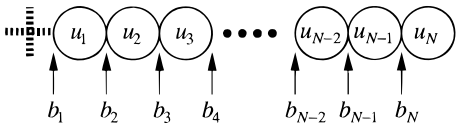

Figure 8. Schematic representation of the derivation of the MWD in the linear polymer fraction for an initial uniform distribution.

Arms with a Uniform Distribution

Because random degradation is the process that leads to the most probable distribution for the chains, as clearly shown by eq 2, star polymers with any chain length distribution of the arms will approach the distribution given in the previous section as the probability of chain scission, ϕ, increases. However, it is interesting to know how fast the approach will be, depending on the breadth of the MWD for the arms. In this section, we consider an extremely narrow distribution for the arms, i.e, a uniform distribution, where the number and weight fraction distributions of the primary polymer molecules are given by

$$n_p(r) = w_p(r) = \delta(r - N) \tag{32}$$

where δ is Kronecker's δ, i.e., $\delta(x) = 0$ where $x \neq 0$ and 1 for $x = 0$. N is the chain length of each arm.

Weight Fraction of the Branched Polymers. By following the argument for deriving eq 9, the weight fraction of branched polymer molecules, Φ_b, is given by

$$\Phi_b = \sum_{r=1}^{\infty} \frac{w_p(r)}{r} \sum_{n=1}^{r} (1 - \phi)^n$$
$$= \frac{1}{N} \sum_{n=1}^{N} (1 - \phi)^n = \left(\frac{1 - \phi}{N\phi}\right)\{1 - (1 - \phi)^N\} \tag{33}$$

Linear Polymer Fraction. First, let us consider the weight fraction of a linear polymer with chain length unity, $W_l(1)$. Suppose our randomly selected unit is the Nth unit, u_N shown in Figure 8, then the polymers with chain length unity would be obtained by cutting the bonding, b_N, whose probability is given by ϕ. On the other hand, if we select any unit from u_1 to u_{N-1}, then the polymer with chain length unity is obtained by cutting both neighboring bonds, whose probability is given by ϕ^2. Therefore,

$$W_l(1) = \frac{1}{N}\{\phi + (N - 1)\phi^2\} \tag{34}$$

Next consider $W_l(2)$. There are four types of events that will produce linear chains with chain length 2: (1) If our randomly selected unit is the Nth unit, u_N, polymers with chain length 2 would be obtained by cutting the bonding, b_{N-1}, whose probability is given by $\phi(1-\phi)$. (2) If our randomly selected unit is the $(N-1)$th unit, u_{N-1}, polymers with chain length 2 would be obtained by cutting the bonding, b_{N-1}, or by cutting both b_{N-2} and b_N, whose probability is given by $\phi(1-\phi)+\phi^2(1-\phi)$. (3) If we select u_1, the connections b_1 and b_3 must be cut, whose probability is given by $\phi^2(1-\phi)$. (4) If any unit u_2 to u_{N-2} is the selected unit (u_j), polymers with chain length 2 are obtained by cutting bonds b_j and b_{j+2} or b_{j-1} and b_{j+1}, whose probability is given by $2\phi^2(1-\phi)$. As a consequence, $W_l(2)$ is given by

$$W_l(2) = \frac{1}{N}\{\phi(1-\phi) + [\phi(1-\phi) + \phi^2(1-\phi)] + \phi^2(1-\phi) + 2(N-3)\phi^2(1-\phi)\}$$
$$= \frac{1}{N}\{2\phi(1-\phi) + [2(N-3)+2]\phi^2(1-\phi)\} \quad (35)$$

Similarly, $W_l(3)$ is given by

$$W_l(3) = \frac{1}{N}\{3\phi(1-\phi)^2 + [3(N-5)+2+4]\phi^2(1-\phi)^2\} \quad (36)$$

In general, the weight fraction of linear chains with chain length r, $W_l(r)$, is given by

$$W_l(r) = \frac{1}{N}\{r\phi(1-\phi)^{r-1} + [r(N-2r+1) + 2\sum_{j=1}^{r-1} j]\phi^2(1-\phi)^{r-1}\} \quad (37)$$

which reduces to

$$W_l(r) = \begin{cases} \frac{\phi r}{N}\{1+(N-r)\phi\}(1-\phi)^{r-1} & (1 \le r \le N) \\ 0 & (r > N) \end{cases} \quad (38)$$

From the distribution function, the number-average ($\bar{P}_{n,l}$) and weight-average ($\bar{P}_{w,l}$) chain lengths of linear polymers are given by

$$\bar{P}_{n,l} = \frac{\phi(N+1) - 1 + (1-\phi)^{N+1}}{\phi^2 N} \quad (39)$$

$$\bar{P}_{w,l} = \frac{\phi N\{2-\phi+2(1-\phi)^{N+1}\} - (1-\phi)(4-\phi)\{1-(1-\phi)^N\}}{\phi\{\phi(N+1) - 1 + (1-\phi)^{N+1}\}} \quad (40)$$

Branched Polymer Fraction. The number fraction distribution of each arm after random scission follows the following distribution function:

$$n_{arm}(r) = \begin{cases} (1-\phi)^r\phi & (0 \le r < N) \\ (1-\phi)^N & (r = N) \\ 0 & (r > N) \end{cases} \quad (41)$$

The number-average ($\bar{P}_{n,arm}$) and weight-average ($\bar{P}_{w,arm}$) chain lengths of the arm chains can be obtained from the distribution function, $n_{arm}(r)$.

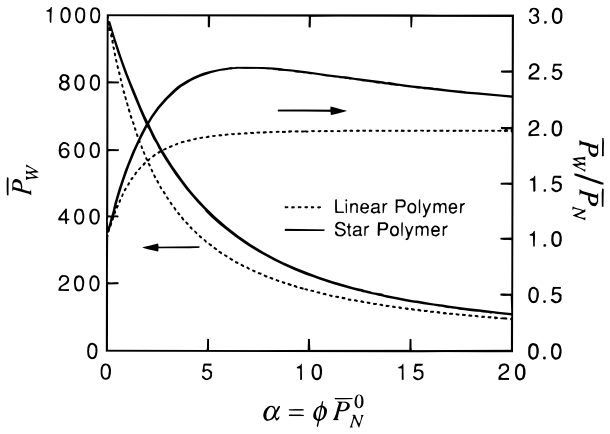

Figure 9. Average chain length development during random scission reactions. The solid curves are for the star polymers with four arms that conform to a uniform distribution in which $N = 250$. The dashed curves show the changes for the linear polymer molecules whose chain length is 1000.

As discussed in deriving eqs 17 and 18, the number-average ($\bar{P}_{n,b}$) and weight-average ($\bar{P}_{w,b}$) chain lengths of branched polymer fraction are given by $\bar{P}_{n,b} = (1-\phi)f\bar{P}_{n,arm}$ and $\bar{P}_{w,b} = \bar{P}_{w,arm} + (1-\phi)(f-1)\bar{P}_{n,arm}$, respectively. Therefore,

$$\bar{P}_{n,b} = \frac{(1-\phi)f}{\phi}\{1-(1-\phi)^{N-1}(1-\phi+\phi^2 N)\} \quad (42)$$

$$\bar{P}_{w,b} = \frac{2-\phi-(1-\phi)^{N-1}\{(2-\phi)(1-\phi)+\phi N[\phi^2 N + 2(1-\phi)]\}}{\phi\{1-(1-\phi)^{N-1}(1-\phi+\phi^2 N)\}} + \left(\frac{(1-\phi)(f-1)}{\phi}\right)\{1-(1-\phi)^{N-1}(1-\phi+\phi^2 N)\} \quad (43)$$

Next, consider the MWD of the branched polymer fraction. Each branched polymer molecule contains one f functional unit. By selecting an f functional unit randomly, one obtains the number fraction distribution, and therefore,

$$N'_b(r) = \sum_{\sum_{j=1}^{f} v_j = r} n_{arm}(v_1) n_{arm}(v_2) n_{arm}(v_3) \cdots n_{arm}(v_f) \quad (44)$$

In the preceding equation, the summation term with a sum as its limit means that the summation is taken for all possible combinations of nonnegative integers v_j under the restriction, $\sum_{j=1}^{f} v_j = r$.

From eq 44, one can calculate the MWD of the branched polymer molecules numerically. Obviously, the fractional weight-based distribution of branched polymer molecules in the whole molecular species is simply given by

$$W_b(r) = \Phi_b r N'_b(r)/\bar{P}_{n,b} \quad (45)$$

Calculated Results. We examine the case with $f = 4$ and $N = 250$, i.e., $\bar{P}_n^0 = \bar{P}_w^0 = 1000$. Figure 9 shows the average chain length change during a random degradation reaction. Comparison is made with the random degradation of uniform linear polymer molecules with $\bar{P}_n^0 = 1000$. For linear polymers, the

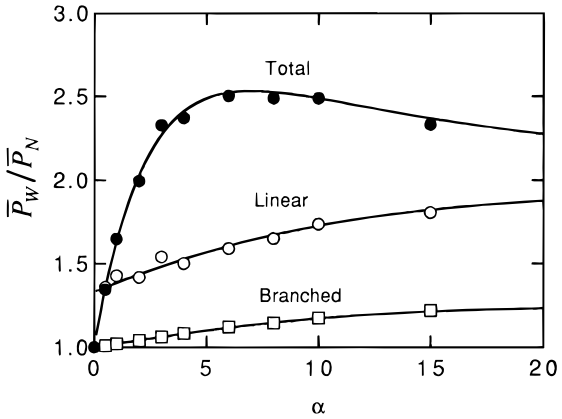

Figure 10. Polydispersity index ($\bar{P}_w/\bar{P}_n$) of each fraction in the random degradation of initial uniform star polymers. The solid curves are the analytical solutions, while the symbols are the Monte Carlo simulation results. A total of 2×10^4 polymer molecules is simulated.

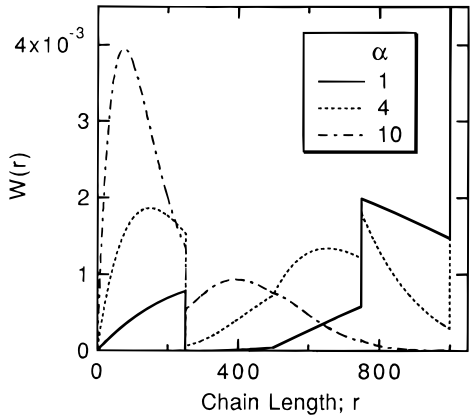

Figure 11. Weight fraction distribution development during the random degradation of initial uniform star polymers. All curves are the analytical solutions for the total MWD.

weight-average chain lengths can be calculated from[8,10]

$$\bar{P}_w = \frac{\{1-(1-\phi)^2\}\bar{P}_n^{\,0} - 2(1-\phi) + 2(1-\phi)^{\bar{P}_n^0+1}}{\bar{P}_N^0\phi^2} \quad (46a)$$

$$\cong \frac{2}{\bar{P}_n^{\,0}\phi^2}\{\bar{P}_n^{\,0}\phi - 1 + \exp(-\bar{P}_n^{\,0}\phi)\} \qquad (\phi \ll 1) \quad (46b)$$

As shown in Figure 9, the weight-average chain length of the star polymers decreases more slowly than that for linear polymers, and the difference from the degradation of linear polymers is more significant than that for arms with the most probable distribution that was shown in Figure 4. The PDI ($\bar{P}_w/\bar{P}_n$) of the star polymer system becomes significantly larger than 2 and then approaches 2 as the scission reaction proceeds, while it monotonously approaches 2 for initial linear polymers.

Figure 10 shows the PDIs of the linear and branched polymer fractions. Although the behavior of the overall PDI appears to be complicated, the PDI of each fraction approaches a fixed value monotonously, i.e., PDI = 2 for the linear fraction and 1.25 for the branched fraction.

Figure 11 shows the weight fraction distribution development during random degradation. When the average number of scission points per polymer molecule α (=$\phi\bar{P}_n^{\,0}$) is small, it is highly probable that some of the four arms do not experience chain scission, i.e., some arms may possess chain length 250. As a consequence, a discontinuous change in the MWD profile is observed at r = 500 and 750. Even when α is as high as 10, these points are still distinguishable, as shown by the arrows in Figure 12. The chain lengths of the linear polymers must be smaller than or equal to 250, and most polymers with chain length smaller than 250 are linear polymers up to α = 4. However, at α = 10, a significant amount of branched polymers whose chain length is smaller than 250 exists, and MWDs for both linear and branched fractions overlap each other significantly. It can also be seen from Figure 12 that the Monte Carlo simulation can be conducted with sufficient accuracy.

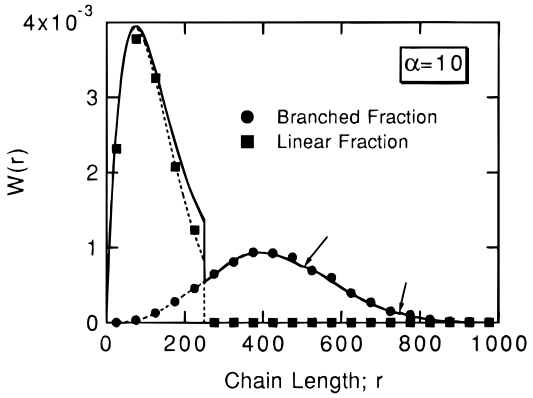

Figure 12. Weight fraction distribution of each fraction when the average number of scission points per initial polymer is α = 10. The solid curve shows the analytical solution for the total MWD, and the MWDs for each fraction are shown by the dashed curves. The symbols are the Monte Carlo simulation results. The discontinous points in the MWD of the branched fraction (at r = 500 and 750) are still observable even at this very high extent of scission reaction, as shown by the arrows.

Arms with a Broader Distribution

To further examine the effect of the breadth of the MWD of the arms, we examine a broad chain length distribution for the arms. In this section, only the Monte Carlo simulation results are shown. When Monte Carlo simulations are used, one can use any type of initial distribution, including an experimentally determined one. For simplicity, however, we use the Schulz−Zimm distribution for the MWD of the arms. We examine the case with f = 4, the number-average chain length of the primary polymer molecules (initial arms) $\bar{P}_{np}$ = 250, and $\sigma = \bar{P}_{np}/(\bar{P}_{wp} - \bar{P}_{np}) = 0.1$, i.e., $\bar{P}_{wp}$ = 2750, $\bar{P}_n^{\,0}$ = 1000, and $\bar{P}_w^{\,0}$ = 3500.

Simulation Results. Figure 13 shows the average chain length change during a random degradation reaction. Comparison is made with the random degradation of the linear polymer molecules that conform to the Schulz−Zimm distribution, with $\bar{P}_n^{\,0}$ = 1000 and $\bar{P}_w^{\,0}$ = 3500. Equations 30 and 31 are used for the calculation of linear polymers ($\bar{P}_n^{\,0}$ = 1000 and σ = 0.4). The difference from the degradation of linear polymers is very small. The PDI ($\bar{P}_w/\bar{P}_n$) approaches 2 monotonously as the scission reaction proceeds. By comparison with Figures 4 and 9, it is found that the differences between linear and star-shaped polymers become smaller as the initial MWD of the arms becomes broader. This phenomenon can be understood as follows. When a very broad distribution for the arms is used, an extremely large number of small chains may exist. In such a case, when we select a polymer molecule on a weight basis, it is likely to have a star polymer that consists of 1 long chain and (f − 1) short chains. For such types of star

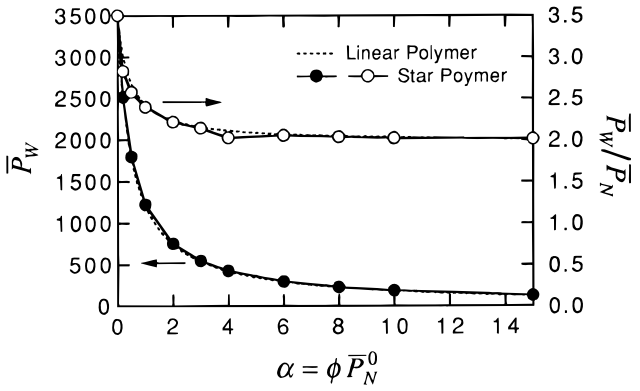

Figure 13. Average chain length development during random scission reactions. The solid lines with symbols are for the star polymers with four arms that conform to the Schulz–Zimm distribution in which $\bar{P}_{np} = 250$ and $\sigma = 0.1$. The dashed curves show the changes for the linear polymer molecules whose initial number- and weight-average chain lengths are the same as those for the star polymers.

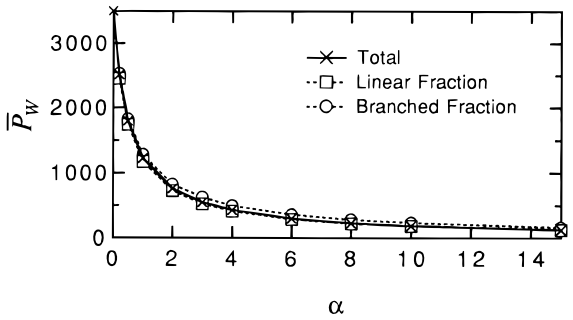

Figure 14. Simulated weight-average chain length development for each fraction as a function of the average number of scission points per initial polymer molecule, α. The calculation conditions are the same as for the star polymers in Figure 13.

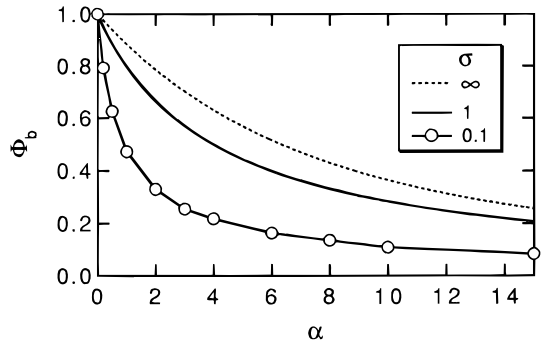

Figure 15. Effect of the MWD breadth of the arms on the weight fraction of branched polymers, Φ_b, under conditions with $f = 4$ and $\bar{P}_{np} = 250$. The Schulz–Zimm distribution is assumed for the MWD of the arms before scission. In the figure, σ is the parameter for the Schulz–Zimm distribution given by eq 28. The curves for $\sigma = \infty$ and 1 are the analytical solutions given by eqs 33 and 9, respectively.

polymers, the effect of the branches on the random scission reactions would be quite small.

Figure 14 shows the weight-average chain length development for linear and branched polymer fractions, as well as for the total polymer. The difference in the weight-average chain lengths between the linear and branched fractions is very small.

Figure 15 shows the effect of the MWD breadth of the arms on the weight fraction of branched polymers. We assumed the Schulz–Zimm distribution for the MWD of the arms before scission. Note that σ is the parameter for the Schulz–Zimm distribution, indicating the narrowness of the distribution breadth. The value of $\sigma = \infty$ corresponds to the uniform distribution, and the curve shown in Figure 15 was calculated from eq 33. On the other hand, $\sigma = 1$ is the case for the most probable distribution, and the curve was calculated from eq 9. As shown in the figure, the decrease in Φ_b is faster for the broader MWD of the initial arms.

Conclusions

A random sampling technique in which polymer molecules are sampled from an infinite number of polymer molecules in the reaction mixture is used to investigate MWD development during random degradation reactions of star polymers. The analytical solutions for the full MWD change, as well as the average molecular weights, are derived for the star polymers whose arms conform to the most probable distribution and to a uniform distribution. The Monte Carlo simulations can be used to investigate any initial MWD with sufficient accuracy. Compared with the random degradation of the initial linear polymer molecules, the decrease in the weight-average molecular weight is slower; however, such a difference becomes smaller as the initial MWD becomes broader. As the degradation reaction proceeds, the linear polymer fraction approaches the most probable distribution, while the branched fraction approaches the morphology in which the MWD of each arm follows the most probable distribution.

Glossary of Symbols

f	number of functional groups in a multifunctional unit
N	chain length of the arm for the uniform distribution (eq 32)
$N'_b(r)$	number fraction distribution of the branched polymers
$N_s(s)$	probability density that the scission occurs at the $(s + 1)$th bonding (eq 2)
n	locaton of the *base* unit (Figure 1)
$n_{arm}(r)$	number fraction distribution of the arms after scission
$n_p(r)$	number fraction distribution of the primary polymer molecules (before chain scission)
$P_b(n)$	probability that the nth unit from the f functional unit still belongs to the branched fraction after scission (eq 8)
$\bar{P}_n$, $\bar{P}_w$	number- and weight-average chain lengths
$\bar{P}_n^0$, $\bar{P}_w^0$	number- and weight-average chain lengths before chain scission
$\bar{P}_{n,b}$, $\bar{P}_{w,b}$	number- and weight-average chain lengths of the branched polymer fraction
$\bar{P}_{n,l}$, $\bar{P}_{w,l}$	number- and weight-average chain lengths of the linear polymer fraction
$\bar{P}_{np}$	number-average chain length of the primary polymer molecule before scission
$\bar{P}_{n,arm}$, $\bar{P}_{w,arm}$	number- and weight-average chain lengths of the arms after scission
p	probability of connection in the most probable distribution (eqs 6 and 7)
r	chain length (degree of polymerization)
r'	chain length of the initially selected primary chain after scission ($r' = r'_R + r'_L$)
r_i	chain length of the ith arm before chain scission
r'_i	chain length of the ith arm after chain scission
r_R, r_L	number of units bound to the primary chain on the right- (r_R) and left-hand (r_L) sides of the base unit before chain scission (Figure 1)

r'_R, r'_L number of units bound to the primary chain on the right- (r'_R) and left-hand (r'_L) sides of the base unit after chain scission (Figure 1)

s_i estimated location of the scission point for the ith arm (eq 5)

s_R, s_L estimated number of units on the right- (s_R) and left-hand (s_L) sides of the base unit when chain scission occurs (Figure 1)

$W(r)$ weight fraction distribution

$W_b(r)$ fractional distribution of branched polymer molecules in the whole MWD after scission ($=\Phi_b W'_b(r)$)

$W'_b(r)$ weight fraction distribution of the branched polymers after scission ($\sum_{r=1}^{\infty} W'_b(r) = 1$)

$W_i(r)$ fractional weight-based distribution containing i arms (eq 20)

$W_l(r)$ fractional distribution of linear polymer molecules in the whole MWD after scission [$=(1 - \Phi_b)W'_l(r)$]

$W'_l(r)$ weight fraction distribution of the linear polymers after scission ($\sum_{r=1}^{\infty} W'_l(r) = 1$)

$w_{arm}(r)$ weight fraction distribution of the arms after scission

$w_p(r)$ weight fraction distribution of the primary polymer molecules (before chain scission)

y random number between 0 and 1

Greek Letters

α average number of scission points per initial polymer molecule ($=\phi \bar{P}_n^0$)

σ parameter for the Schulz−Zimm distribution (eq 29)

Φ_b weight fraction of the branched polymers

ϕ probability of chain scission for each bond

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(2) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.
(3) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
(4) Saito, O. *J. Phys. Soc., Jpn.* **1958**, *13*, 198.
(5) Charlesby, A. *Atomic Radiation of Polymers*; Pergamon Press: Oxford, UK, 1960.
(6) Kimura, T. *J. Phys. Soc., Jpn.* **1962**, *17*, 1884.
(7) Inokuti, M.; Dole, M. *J. Chem. Phys.* **1963**, *38*, 3006.
(8) Saito, O. In *The Radiation Chemistry of Macromolecules*; Dole, M., Ed.; Academic Press: New York, 1972; Vol. 1, p 223.
(9) David, C.; Baeyens-Volant, D. *Eur. Polym. J.* **1978**, *14*, 29.
(10) Demjanenko, M.; Dusek, K. *Macromolecules* **1980**, *13*, 571.
(11) Suwanda, D.; Lew, R.; Balke, S. T. *J. Appl. Polym. Sci.* **1988**, *35*, 1033.
(12) Hamielec, A. E.; Gloor, P. E.; Zhu, S. *Can. J. Chem. Eng.* **1991**, *69*, 611.
(13) Tobita, H.;Yamamoto, Y.; Ito, K. *Macromol. Theory Simul.* **1994**, *3*, 1033.
(14) Tobita, H. *J. Polym. Sci., Polym. Phys.* **1995**, *33*, 1191.
(15) Kotliar, A. M.; Podgor, S. *J. Polym. Sci.* **1961**, *55*, 423.
(16) Kotliar, A. M. *J. Polym. Sci., Part A* **1963**, *1*, 3175.
(17) Malac, J. *J. Polym. Sci., Part C* **1971**, *33*, 223.
(18) Tobita, H. *Polymer* **1995**, *36*, 2585.
(19) McDermott, J. B.; Libanati, C.; LaMarca, C.; Klein, M. T. *Ind. Eng. Chem. Res.* **1990**, *29*, 22.
(20) Huang, C.; Tzoganakis, C.; Duever, T. A. *Polym. React. Eng.* **1995**, *3*, 43.
(21) Guaita, M.; Chiantore, O.; Luda, M. P. *Macromolecules* **1990**, *23*, 2087.
(22) Basedow, A. M.; Ebert, K. H.; Ederer, H. J. *Macromolecules* **1978**, *11*, 774.
(23) Ballauff, M.; Wolf, B. A. *Macromolecules* **1981**, *14*, 654.
(24) Ziff, R. M.; McGrady, E. D. *Macromolecules* **1986**, *19*, 2513.
(25) Meddings, P. J.; Potter, O. E. *Adv. Chem. Ser.* **1972**, *109*, 96.
(26) Giudici, R.; Hamielec, A. E. A Simulation Study on Random Scission of Branched Chains. *Polym. React. Eng.*, in press.
(27) Saito, O. *Kobunshi no Tokeiteki Seishitu (Statistical Properties of Polymers)*; Chuo University Press: Tokyo, 1992; p 225.
(28) Tobita, H. Degradation of Branched Polymers. 2. Multiple Branches. *Macromolecules* **1996**, *29*, 3010.
(29) Tobita, H. Ph.D. Thesis, McMaster University, 1990, p 274.
(30) Grest, G. S.; Kremer, K.; Duering, E. R. *Europhys. Lett.* **1992**, *19*, 195.
(31) Tobita, H. *Polymer* **1994**, *35*, 3023, 3032.
(32) Tobita, H. *Macromolecules* **1993**, *26*, 836, 5427.
(33) Tobita, H. *Makromol. Chem. Theory Simul.* **1993**, *2*, 761.
(34) Tobita, H. *Macromolecules* **1994**, *27*, 5413.
(35) Tobita, H. *J. Polym. Sci., Polym. Phys.* **1993**, *31*, 1363.
(36) Tobita, H. *J. Polym. Sci., Polym. Phys.* **1994**, *32*, 901, 911.
(37) Tobita, H.; Hatanaka, K. *J. Polym. Sci., Polym. Phys.* **1995**, *33*, 841.
(38) Tobita, H.; Hatanaka, K. Branched Structure Formation in Free-Radical Polymerization of Vinyl Acetate. *J. Polym. Sci., Polym. Phys.*, in press.
(39) Tobita, H. Random Sampling Technique to Predict the Molecular Weight Distribution in Free-Radical Polymerization that Involves Polyfunctional Chain Transfer Agents. *Macromolecules*, in press.
(40) Miyatake, O.; Wakimoto, K. *Ransu to Monte Carlo Ho (Random Numbers and Monte Carlo Method)*; Morikita Shuppan: Tokyo, 1978; Chapter 2.
(41) Schaefgen, J. R.; Flory, P. J. *J. Am. Chem. Soc.* **1948**, *70*, 2709.
(42) Schulz, G. V. *Z. Phys. Chem. (Leipzig)* **1939**, *B43*, 25.
(43) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.

MA950971C