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# Random Degradation of Branched Polymers. 2. Multiple Branches

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ABSTRACT: The random sampling technique discussed in part 1 of this series[1] is used to investigate the molecular weight distribution (MWD) change during random scission reactions of the polymers with multiple branches. By application of the concept of the random sampling technique to the Monte Carlo method, one obtains a very powerful simulation method that can be applied to the random degradation of virtually any type of branched polymer. Suppose branched polymers are formed first by randomly combining linear polymer molecules, and then these branched polymer molecules are used for the random degradation reactions (branching → degradation). If the processes of branching and degradation are interchangeable, then the same MWD can be obtained from the sequence of processes, degradation → branching. In contrast with random cross-linking and degradation, the processes are not interchangeable except when all of the primary chains possess the most probable distribution with randomly distributed branch points. The MWDs given by the random branching of primary chains with the most probable distribution provide the limiting distributions to which polymers with multiple branches approach as the extent of the scission reaction increases, irrespective of the initial MWD including nonrandomly branched polymers. An analytical expression for such a limiting MWD is derived by the application of the random sampling technique.

## Introduction

In part 1 of this series,[1] random degradation of star polymers is considered, and the fundamental characteristics of the degradation of branched polymer molecules are investigated. For instance, it was shown that the decrease in the weight-average chain length (degree of polymerization) is slower than for linear polymer systems. In this paper, we consider the random degradation of polymers with multiple branches, which will be of more interest to many readers.

In the present paper, we deal with branched polymers exclusively, i.e., we consider polymers that possess only "T-shaped" junctions,[2] in which only one end of the primary chain can be connected to the backbone polymer chain. In this introduction, however, we briefly discuss the random degradation of homogeneously cross-linked polymers to clarify the differences from branched polymers and to promote a better understanding of the concept of the random sampling technique.

In the case of random cross-linking and degradation, these two processes are interchangeable, i.e., the sequence of the processes, cross-linking → degradation and degradation → cross-linking, gives exactly the same MWD, as long as (1) the ring-free model[3,4] is valid for the cross-linking reaction and (2) these processes are independent of each other.[5,6] Therefore, the process of the random degradation of homogeneously cross-linked polymers (without cycles) reduces to the problem in which the linear polymer molecules that are formed after the random scission process are cross-linked randomly. Therefore, the theory of random cross-linking[3,4,7−10] can be applied to such an investigation directly. The weight-average chain length development during random cross-linking has been known for many years;[3,4] however, we rederive this expression here by using the random sampling technique to highlight the key concepts of the method.

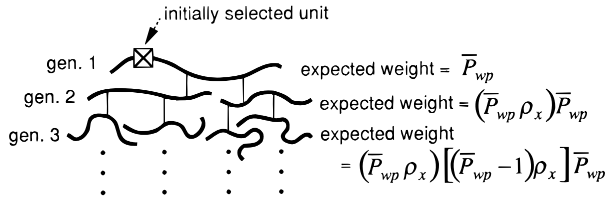

**Figure 1.** Schematic drawing of a cross-linked polymer molecule selected by randomly choosing one unit from a homogeneously cross-linked system consisting of an infinite number of polymer molecules.

Let the weight-average chain length of the primary polymer molecules be $\bar{P}_{wp}$ and the cross-linking density be $\rho_x$. In the random sampling technique, the weight-average chain length of the reaction mixture can be obtained by considering the expected size of a molecule when a polymer molecule is sampled by randomly selecting one unit bound to a polymer molecule, i.e., the sampling is made on a weight basis. When we randomly select one unit, as shown in Figure 1, the primary chain that involves this particular unit follows the weight fraction distribution of the primary polymer molecules, and the expected chain length is $\bar{P}_{wp}$. Let this primary polymer molecule be the first generation (gen. 1 shown in Figure 1). The expected number of cross-link points on this primary polymer molecule is $\bar{P}_{wp}\rho_x$. From the point of view of the connected primary polymer molecules, any unit within the chain can be connected to these cross-link points, i.e., the connected chains are selected on a weight basis. Therefore, the expected weight of the second generation is $(\bar{P}_{wp}\rho_x)\bar{P}_{wp}$. Then, the expected number of cross-link points connected to the third generation is simply given by $(\bar{P}_{xp}\rho_x)(\bar{P}_{wp} - 1)\rho_x$. Here, $(\bar{P}_{wp} - 1)$ is used instead of $\bar{P}_{wp}$, because one unit is used to connect to the primary polymer molecule in the previous generation. Therefore, the expected weight of the third generation is given by $(\bar{P}_{xp}\rho_x)^2(\bar{P}_{wp} - 1)$. The total expected weight, which is the weight-average chain length $(\bar{P}_w)$, is given by

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$$\bar{P}_{w} = \bar{P}_{wp} + (\bar{P}_{wp}\rho_{x})\bar{P}_{wp} + (\bar{P}_{wp}\rho_{x})^2(\bar{P}_{wp} - 1) + (\bar{P}_{wp}\rho_{x})^2 (\bar{P}_{wp} - 1)^2\rho_{x} + (\bar{P}_{wp}\rho_{x})^2(\bar{P}_{wp} - 1)^3(\rho_{x})^2 + ...$$

$$= \bar{P}_{wp} + (\bar{P}_{wp})^2\rho_{x}\sum_{i=0}^{\infty}(\bar{P}_{wp} - 1)^i(\rho_{x})^i$$

$$= \frac{\bar{P}_{wp}(1 + \rho_{x})}{1 - (\bar{P}_{wp} - 1)\rho_{x}} \tag{1a}$$

$$\cong \frac{\bar{P}_{wp}}{1 - \bar{P}_{wp}\rho_{x}} \quad (\bar{P}_{xp} \gg 1 \text{ and } \rho_{x} \ll 1) \tag{1b}$$

In the random sampling technique, the weight-average chain length can be derived arithmetically without using distribution functions. The same derivation method is used to develop the fundamental equation for random branching of primary chains shown in the following section.

As the scission density, $\phi$, increases, the molecular weight distribution (MWD) of the primary polymer molecules approaches the most probable distribution.[5,7,9] Therefore, the MWD formed by the random degradation of homogeneously cross-linked polymer molecules approaches the MWD that is formed by the random cross-linking of the primary chains that follow the most probable distribution. Such a distribution function can be derived in a straightforward manner by the application of the random sampling technique (see Appendix A):

$$W(r) = \frac{r}{(\bar{P}_{np})^2}\exp\left\{-\left(\frac{\bar{P}_{np}\rho_{x} + 1}{\bar{P}_{np}}\right)r\right\} \times \left\{\sum_{k=0}^{\infty}\frac{(\bar{P}_{np}\rho_{x})^k}{(k + 1)!(2k + 1)!}\left(\frac{r}{\bar{P}_{np}}\right)^{3k}\right\} \tag{2}$$

where $r$ is the chain length and $k$ corresponds to the number of cross-linkages, i.e., the distribution obtained from $k = i$ without taking the summation provides the fractional MWD of the polymer molecules that contain $i$ cross-linkages.[10]

The full MWD function for the random branching of primary polymer molecules that conform to the most probable distribution will also be derived later in the same manner as that used for eq 2.

## Average Chain Lengths Formed Due to Random Branching

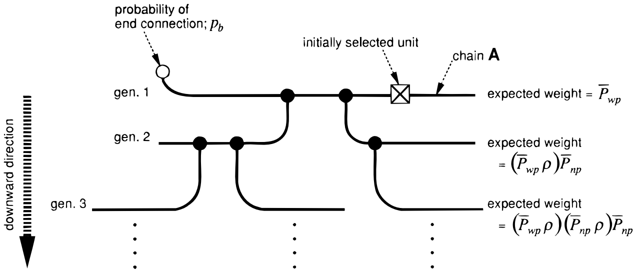

**Figure 2.** Schematic drawing of a part of the branched polymer molecule selected on a weight basis from an infinite system.

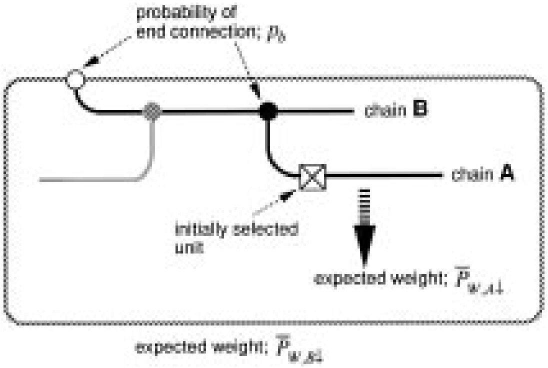

**Figure 3.** Schematic drawing of a branched polymer molecule for the derivation of the weight-average chain length by means of the random sampling technique.

Let the branching density be $\rho$. Consider the weight-average chain length, which is the expected size of a polymer molecule that is sampled from an infinite system by randomly selecting one unit bound to polymer molecules. When we randomly select one unit, as shown in Figure 2, the expected weight of the primary chain that involves this particular unit is $\bar{P}_{wp}$. First, we consider the expected weight of the chains connected toward the downward direction, including the chain initially selected (see Figure 2). Let the initially selected primary polymer molecule be the first generation. The expected number of branch points on this primary polymer molecule is $\bar{P}_{wp}\rho$. The primary chains in the second generation must be selected on a number basis, because only the chain ends can be connected to the initially selected chain. Therefore, the expected weight of the second generation is $(\bar{P}_{wp}\rho)\bar{P}_{np}$. Next, the expected number of branch points connected to the third generation is simply given by $(\bar{P}_{wp}\rho)(\bar{P}_{np}\rho)$. Therefore, the expected weight of the third generation is given by $(\bar{P}_{wp}\rho)(\bar{P}_{np}\rho)\bar{P}_{np}$. By continuing such processes repeatedly, the total expected weight in the downward direction including A, $\bar{P}_{w,A\downarrow}$, is given by

$$\bar{P}_{w,A\downarrow} = \bar{P}_{wp} + (\bar{P}_{wp}\rho)\bar{P}_{np} + (\bar{P}_{wp}\rho)(\bar{P}_{np}\rho)\bar{P}_{np} + (\bar{P}_{wp}\rho)(\bar{P}_{np}\rho)^2\bar{P}_{np} + ...$$

$$= \bar{P}_{wp}\sum_{i=0}^{\infty}(\bar{P}_{np}\rho)^i = \frac{\bar{P}_{wp}}{1 - \bar{P}_{np}\rho} \tag{3}$$

Up to the present stage, we have not considered chains connected through the chain end of A shown as an open circle in Figure 2. For the random branching of primary chains, the probability that the chain end of A is connected, $p_b$, is given by

$$p_{b} = \frac{\rho}{(1/\bar{P}_{np})} = \bar{P}_{np}\rho \tag{4}$$

If the chain end of A shown in Figure 3 is connected, the backbone chain (B) must be selected on a weight basis, because any unit on chain B can be connected. The expected weight up to chain B toward the downward direction, $\bar{P}_{w,B\downarrow}$, is given by

$$\bar{P}_{w,B\downarrow} = \bar{P}_{w,A\downarrow} + p_{b}\{\bar{P}_{wp} + (\bar{P}_{wp} - 1)(\bar{P}_{np}\rho) + (\bar{P}_{wp} - 1)(\bar{P}_{np}\rho)^2 + (\bar{P}_{wp} - 1)(\bar{P}_{np}\rho)^3 + ...\}$$

$$= \bar{P}_{w,A\downarrow} + \bar{P}_{np}\rho\{1 + (\bar{P}_{wp} - 1)\sum_{i=0}^{\infty}(\bar{P}_{np}\rho)^i\}$$

$$= \bar{P}_{w,A\downarrow} + \bar{P}_{np}\rho\left(1 + \frac{\bar{P}_{wp} - 1}{1 - \bar{P}_{np}\rho}\right) \tag{5}$$

Therefore, the total expected weight, which is the weight-average chain length, $\bar{P}_{\mathrm{w}}$, is given by

$$\bar{P}_{\mathrm{w}} = \bar{P}_{\mathrm{w,A}\downarrow} + \bar{P}_{\mathrm{np}}\rho\left(1 + \frac{\bar{P}_{\mathrm{wp}} - 1}{1 - \bar{P}_{\mathrm{np}}\rho}\right) + (\bar{P}_{\mathrm{np}}\rho)^2\left(1 + \frac{\bar{P}_{\mathrm{wp}} - 1}{1 - \bar{P}_{\mathrm{np}}\rho}\right) + ...$$

$$= \bar{P}_{\mathrm{w,A}\downarrow} + \left(1 + \frac{\bar{P}_{\mathrm{wp}} - 1}{1 - \bar{P}_{\mathrm{np}}\rho}\right)\sum_{i=1}^{\infty}(\bar{P}_{\mathrm{np}}\rho)^i$$

$$= \frac{1}{1 - \bar{P}_{\mathrm{np}}\rho}\left\{\bar{P}_{\mathrm{wp}} + \bar{P}_{\mathrm{np}}\rho\left(1 + \frac{\bar{P}_{\mathrm{wp}} - 1}{1 - \bar{P}_{\mathrm{np}}\rho}\right)\right\} \tag{6a}$$

$$\cong \frac{\bar{P}_{\mathrm{wp}}}{(1 - \bar{P}_{\mathrm{np}}\rho)^2} \qquad (\bar{P}_{\mathrm{wp}} \gg 1) \tag{6b}$$

Equation 6 can be applied to any primary chain distribution as long as the branch points are distributed randomly. Since the average chain length development during random scission reactions for linear polymers has been clarified for various types of initial distributions,[5,7,9] if one assumes that the processes of random branching and degradation are interchangeable, then the weight-average chain length development during the random degradation of homogeneously branched polymer molecules can be calculated from eq 6. By comparing the results obtained from Monte Carlo simulations for the random degradation of branched polymers, one can determine whether or not the processes of branching and degradation are interchangeable.

Incidentally, eq 6 clearly shows that gelation never occurs in the random branching reaction, because of the probability of end connection, $p_{\mathrm{b}} = \bar{P}_{\mathrm{np}}\rho < 1$. Even though nonrandom branching can make the weight-average chain length larger, it is impossible to form an infinitely large molecule without the assistance of cross-linkages (or "H-type" junctions formed, for example, via bimolecular termination by combination with the existence of chain transfer to polymer), as proven earlier.[2,11]

The number-average chain length, on the other hand, can be obtained from the stoichiometric argument regardless of whether the processes are interchangeable. The number of molecules increases by one due to one scission reaction, while it decreases by one through the formation of one branch point, and therefore,

$$\bar{P}_{\mathrm{n}} = \frac{\bar{P}_{\mathrm{np}}{}^0}{1 + (\bar{P}_{\mathrm{np}}{}^0 - 1)\phi - \bar{P}_{\mathrm{np}}{}^0\rho} \tag{7}$$

where $\bar{P}_{\mathrm{np}}{}^0$ is the number-average chain length of the primary polymer molecules before chain scission.

## Degradation of Branched Polymers: Primary Chains with the Most Probable Distribution

When primary chains with the most probable distribution are connected by the randomly distributed branch points, the whole weight fraction distribution can be obtained by following the same procedure as that used for random cross-linking in the context of the random sampling technique, as shown in Appendix B. The whole weight fraction distribution is given by

$$W(r) = \left(\frac{1 - \bar{P}_{\mathrm{np}}\rho}{\bar{P}_{\mathrm{np}}}\right)\exp\left\{-\left(\frac{\bar{P}_{\mathrm{np}}\rho + 1}{\bar{P}_{\mathrm{np}}}\right)r\right\} \times \sum_{k=0}^{\infty}\left(\frac{r}{\bar{P}_{\mathrm{np}}}\right)^{2k+1}\frac{(\bar{P}_{\mathrm{np}}\rho)^k}{k!(k+1)!} \tag{8}$$

where $k$ corresponds to the number of branch points, i.e., the distribution obtained from $k = i$ without taking the summation provides the fractional MWD containing $i$ branch points in each polymer molecule.

In this section, we consider the random degradation of polymer molecules whose primary chains follow the most probable distribution, i.e., the initial polymer distribution is given by eq 8.

As clarified in part 1 of this series,[1] when star-shaped polymers in which the chain length of each arm conforms to the most probable distribution are under random degradation, both the linear fraction and the arms of star polymers follow the same most probable distribution. This fact implies that when randomly branched polymers whose primary chains follow the most probable distribution are severed randomly, the distribution obtained would be the one that is formed via random branching of linear chains after random scission, i.e., the processes of branching and degradation are interchangeable for the present case. To further examine this speculation, we compared the analytical solutions by assuming interchangeability with the Monte Carlo simulation results in which branched polymer molecules are severed. The Monte Carlo simulation method is shown in Appendix C.

As for the initial polymer distribution, we used the following conditions: (1) the number-average chain length of the primary polymer molecules (before scission) is $\bar{P}_{\mathrm{np}}{}^0 = 500$, and (2) the branching density is $\rho = 0.001$. Since the primary chains possess the most probable distribution, the weight-average chain length

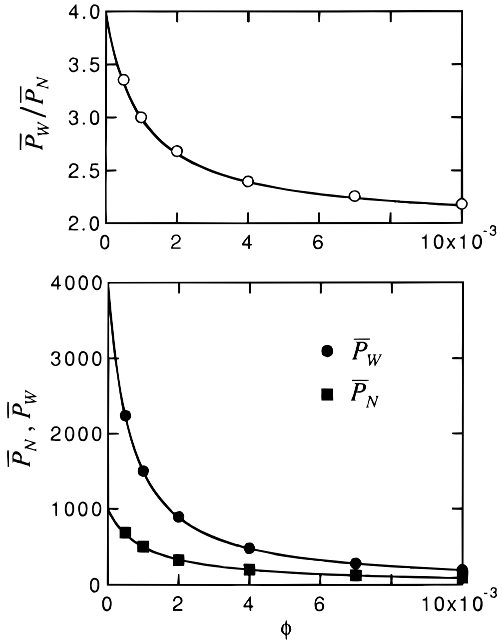

**Figure 4.** Average chain length development during random degradation of branched polymer molecules whose primary chains conform to the most probable distribution, with $\bar{P}_{\mathrm{np}}{}^0 = 500$ and $\rho = 0.001$. The solid curves are the analytical solutions for which degradation is conducted before random branch formation. The symbols are the Monte Carlo simulation results for the random degradation of branched polymers.

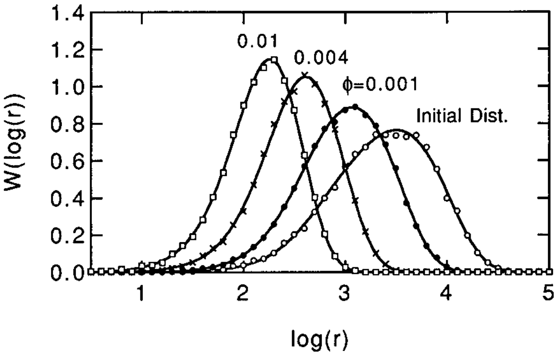

**Figure 5.** Weight fraction distribution development during random degradation of branched polymer molecules whose primary chains conform to the most probable distribution, with $P_{\mathrm{np}}^{\;0} = 500$ and $\rho = 0.001$. The solid curves are the analytical solutions for which degradation is conducted before random branch formation. The symbols are the Monte Carlo simulation results for the random degradation of branched polymers.

of these primary polymer molecules is $\bar{P}_{\mathrm{wp}}^{\;0} = 1000$. From eqs 6 and 7, the number- and weight-average chain lengths for the branched polymer system are $\bar{P}_{\mathrm{n}}^{\;0} = 1000$ and $\bar{P}_{\mathrm{w}}^{\;0} = 4000$.

Figure 4 shows the average chain length development. The symbols indicate the Monte Carlo simulation results in which $2 \times 10^4$ polymer molecules are sampled at each scission density level. On the other hand, the solid curves show the analytical solutions for the process in which primary chains after random scission are connected randomly. As for the number-average chain length, eq 7 can be applied irrespective of the interchangeability of the processes, because it is derived simply from the stoichiometric argument. The weight-average chain length for the process degradation → branching was calculated from the following equations:

$$\bar{P}_{\mathrm{np,deg}} = \frac{\bar{P}_{\mathrm{np}}^{\;0}}{1 + (\bar{P}_{\mathrm{np}}^{\;0} - 1)\phi} \tag{9}$$

$$\bar{P}_{\mathrm{wp,deg}} = \frac{2\bar{P}_{\mathrm{np}}^{\;0}}{1 + (\bar{P}_{\mathrm{np}}^{\;0} - 1)\phi} - 1 \tag{10a}$$

$$\cong \frac{2\bar{P}_{\mathrm{np}}^{\;0}}{1 + \bar{P}_{\mathrm{np}}^{\;0}\phi} \qquad (\bar{P}_{\mathrm{np}}^{\;0} \gg 1 \text{ and } \phi \ll 1) \tag{10b}$$

$$\bar{P}_{\mathrm{W}} = \frac{\bar{P}_{\mathrm{wp,deg}}}{(1 - \bar{P}_{\mathrm{np,deg}}\rho)^2} \tag{11}$$

where $\bar{P}_{\mathrm{np,deg}}$ and $\bar{P}_{\mathrm{wp,deg}}$ are the number- and weight-average chain lengths, respectively, of the primary polymer molecules after random degradation (assuming that all branch points are disconnected), and $\bar{P}_{\mathrm{np}}^{\;0} = 500$ for the present case. Equations 9 and 11 are directly derived from eqs 7 and 6, respectively, while eq 10 shows the weight-average chain length development for the random degradation of linear polymers that conform to the most probable distributions.[5,7]

Figure 4 shows complete agreement for the average chain length development between the processes: branching → degradation and degradation → branching. Figure 5 shows the MWD development during a random scission reaction. The solid curves are calculated from eq 8, while the symbols are the Monte Carlo simulation results. From the results shown in Figures 4 and 5, it is demonstrated that the processes of branching and degradation are interchangeable when the primary chains conform to the most probable distribution. Therefore, eqs 6–8 are valid throughout the degradation reactions.

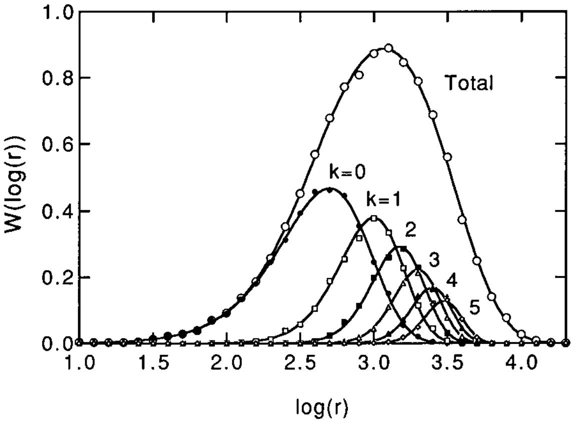

**Figure 6.** Fractional weight-based distribution of polymer molecules containing *k* branch points and the whole weight fraction distribution when $\phi = 0.001$ (primary chains with the most probable distribution). The solid curves are calculated from eq 8, while the symbols are the Monte Carlo simulation results.

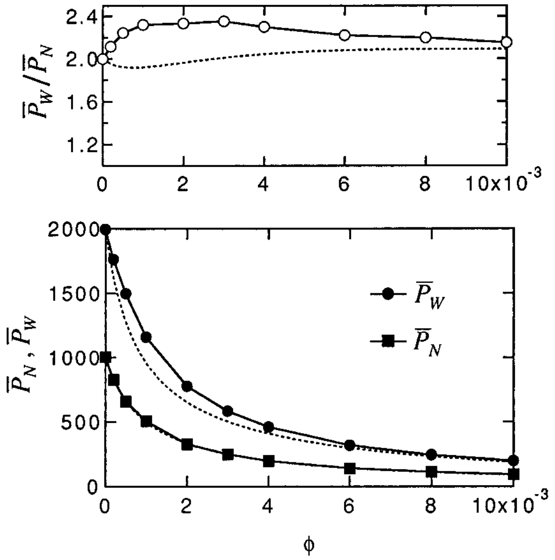

**Figure 7.** Average chain length development during random degradation of homogeneously branched polymer molecules whose primary chains are uniform, with $P_{\mathrm{np}}^{\;0} = 500$ and branching density $\rho = 0.001$. The dashed curves are the analytical solutions for which degradation is conducted before random branch formation.

Figure 6 shows the weight fraction distribution of polymer molecules containing *k* branch points, as well as the whole MWD when the scission density is $\phi = 0.001$. The solid curves are the analytical solutions (eq 8), and the symbols are the simulated results. Complete agreement shown in Figures 4–6 indicates that the Monte Carlo simulations based on the sampling technique can provide quite accurate estimations.

## Degradation of Branched Polymers: Primary Chains with a Uniform Distribution

To examine the effect of the breadth of the primary chain length distribution, we consider a uniform distribution in this section and a broader distribution in the next section.

We consider the random degradation of branched polymer molecules in which all primary chains possess chain length 500, and the branching density is $\rho = 0.001$. From eqs 6 and 7, the number- and weight-average chain lengths for the initial branched polymer system are $\bar{P}_n{}^0 = 1000$ and $\bar{P}_w{}^0 = 2000$. Although the number-average chain length of the primary chains ($\bar{P}_{np}{}^0$) and the branching density are the same as those for the case discussed in the preceding section, the $\bar{P}_w{}^0$ becomes one-half of that for the case for the most probable distribution (for which $\bar{P}_w{}^0 = 4000$). A narrower primary chain length distribution makes the weight-average chain length smaller in the randomly branched system.

Figure 7 shows the average chain length development. The solid lines with symbols are the Monte Carlo simulation results in which branched polymer molecules are severed randomly. Again, $2 \times 10^4$ polymer molecules are simulated. On the other hand, the dashed curves show the calculated results where linear polymer chains are severed first, and then these chains are connected randomly, i.e., the process degradation → branching. Equations 9, 11, and 12 are used for the degradation → branching process:

$$\bar{P}_{wp,deg} = \frac{\{1 - (1-\phi)^2\}\bar{P}_{np}{}^0 - 2(1-\phi) + 2(1-\phi)^{\bar{P}_{np}{}^0+1}}{\bar{P}_{np}{}^0\phi^2} \tag{12a}$$

$$\cong \frac{2}{\bar{P}_{np}{}^0\phi^2}\{\bar{P}_{np}{}^0\phi - 1 + \exp(-\bar{P}_{np}{}^0\phi)\} \qquad (\phi \ll 1) \tag{12b}$$

Equation 12 shows the weight-average chain length development for the random degradation of linear polymer molecules whose chain lengths are uniform.[7,9]

As clearly shown in Figure 7, the processes are not interchangeable for this case. The weight-average chain length decreases more slowly than the estimated values when assuming an interchangeable process. This phenomenon can be understood as follows. Since all primary chains possess the same chain length initially, all linear polymer chains after scission must possess a chain length smaller than 500 ($=\bar{P}_{np}{}^0$). For example, small linear chains with $r = 10$ and 20 may be cut out from the same primary chain. If the scission process comes first and then the chains are connected, both $r = 10$ and 20 may become a part of branched polymers instead of connecting longer ones, which clearly makes the chain length of the branched fraction smaller. Because the branched polymers tend to possess larger chain lengths than the linear fraction, and the polymers with larger chain lengths possess dominant effects on the weight-average chain length, $\bar{P}_w$ becomes smaller if the scission process comes first.

When the scission reaction is conducted first, the polydispersity index ($\bar{P}_w/\bar{P}_n$) decreases at a low scission density level. On the contrary, it increases if branching comes first, as shown in Figure 7. The differences are quite significant.

Figure 8 shows the weight fraction distribution development. The initial distribution is discontinuous, because only multiples of 500 ($=\bar{P}_{np}{}^0$) are allowed for the present case. However, the distribution becomes a smooth curve as the scission density increases.

## Degradation of Branched Polymers: Primary Chains with a Broad Distribution

In this section, we consider the random degradation of branched polymer molecules whose primary chains possess a broad MWD. When the Monte Carlo simulations are employed, one can use virtually any type of distribution, including an experimentally determined one. For simplicity, however, we use the Schulz–Zimm distribution[12,13] for the initial primary chain length distribution, which is given by

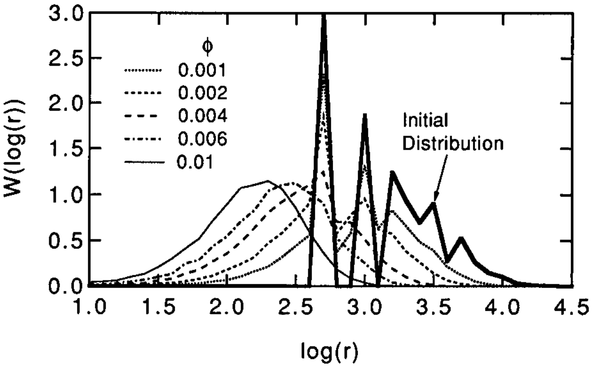

**Figure 8.** Weight fraction distribution development during random degradation of branched polymer molecules in which all primary chains possess the same chain length, $\bar{P}_{np}{}^0 = 500$ and $\rho = 0.001$. The simulation results are plotted with respect to the chain length interval, $\Delta \log(r) = 0.1$.

$$w_p(r) = \frac{\sigma^\sigma}{\bar{P}_{np}{}^0\Gamma(\sigma)}\left(\frac{r}{\bar{P}^0_{np}}\right)^\sigma \exp(-\sigma r/\bar{P}_{np}{}^0) \tag{13}$$

where $\sigma$ is a parameter indicating the narrowness of the distribution breadth, namely,

$$\sigma = \frac{\bar{P}_{np}{}^0}{\bar{P}_{wp}{}^0 - \bar{P}_{np}{}^0} \tag{14}$$

To make a comparison with an imaginary process where chain scission comes first, we used eqs 9, 11, and 15 for the random degradation of linear chains whose MWD is given by the Schulz–Zimm distribution:[7,9]

$$\bar{P}_{wp,deg} = \frac{1}{\bar{P}_{np}{}^0\phi^2}\left\{\bar{P}_{np}{}^0[1 - (1-\phi)^2] - 2(1-\phi) + 2(1-\phi)\left(\frac{\sigma}{\sigma - \bar{P}_{np}{}^0\ln(1-\phi)}\right)^\sigma\right\} \tag{15a}$$

$$\cong \frac{2}{\bar{P}_{np}{}^0\phi^2}\left\{\bar{P}_{np}{}^0\phi - 1 + \left(1 + \frac{\bar{P}_{np}{}^0\phi}{\sigma}\right)^{-\sigma}\right\} \qquad (\phi \ll 1) \tag{15b}$$

In this section we use the number-average chain length of the primary polymer molecules before scission, $\bar{P}_{np}{}^0 = 500$, and the branching density, $\rho = 0.001$. These conditions are the same as for the cases considered in the previous two sections. In the Schulz–Zimm distribution, the most probable distribution is obtained when $\sigma = 1$, and a uniform distribution is obtained when $\sigma = \infty$. To examine a case with a broad distribution, we use $\sigma = 0.1$, which results in $\bar{P}_{wp}{}^0 = 5500$. From eqs 6 and 7, the number- and weight-average chain lengths of the initial branched polymer system are $\bar{P}_n{}^0 = 1000$ and $\bar{P}_w{}^0 = 2.2 \times 10^4$. The weight-average chain length, $\bar{P}_w{}^0$, is much larger than in previous cases ($\bar{P}_w{}^0 = 4000$ for the most probable distribution, and $\bar{P}_w{}^0 = 2000$ for the uniform distribution). A broader primary chain length distribution makes the weight-average chain length

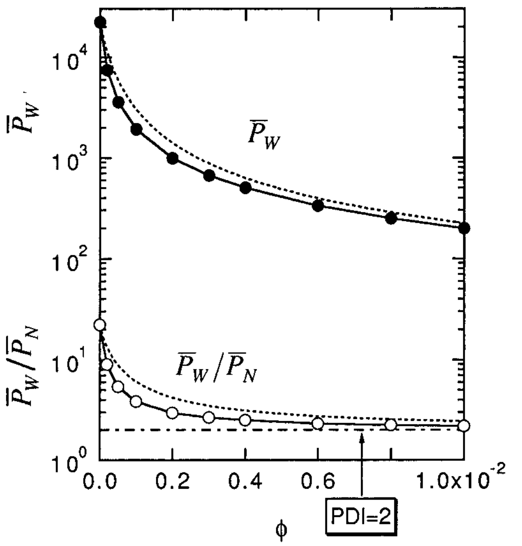

**Figure 9.** Average chain length development during random degradation of homogeneously branched polymer molecules whose primary chains follow a broad Schulz−Zimm distribution, with $\bar{P}_{np}{}^0 = 500$, $\sigma = 0.1$, and branching density $\rho = 0.001$. The dashed curves are the analytical solutions for which degradation is conducted before random branch formation.

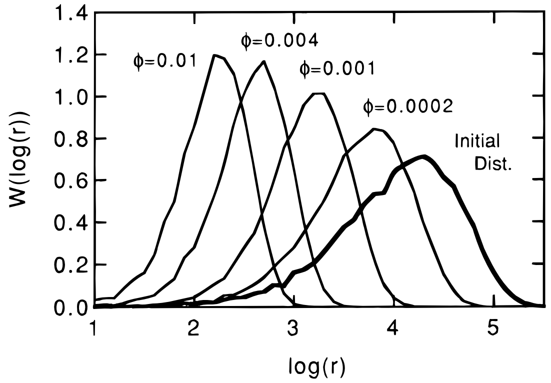

**Figure 10.** Weight fraction distribution development during random degradation of branched polymer molecules whose primary chains follow a broad Schulz−Zimm distribution, with $\bar{P}_{np}{}^0 = 500$, $\sigma = 0.1$, and $\rho = 0.001$.

larger in the randomly branched system, similar to the case for random cross-linking.

Figure 9 shows the average chain length development. The solid lines with symbols are the Monte Carlo simulation results in which branched polymer molecules are severed randomly ($2 \times 10^4$ polymer molecules are simulated). On the other hand, the dashed curves show calculated results where the scission process is conducted first. As clearly shown in Figure 9, the processes are not interchangeable. The weight-average chain length decreases faster than the estimated values for the process degradation → branching. This phenomenon may be explained qualitatively as follows. Within the branched polymer molecules, long primary chains are very important for forming large polymer molecules, because these long chains significantly improve the connectivity to other primary chains. In the random degradation process, these longer chains have a better chance of being severed, and longer primary chains tend to become a type of chain whose chain ends are not connected. With this process, the size of larger polymer molecules would decrease quite rapidly. On the other hand, if the scission process comes first, longer primary chains whose ends are not connected (in the branching → degradation process) may be bound to a backbone polymer chain, which clearly contributes to form larger polymer molecules. Therefore, $\bar{P}_w$ would become larger if the scission process is conducted first.

Figure 10 shows the weight fraction distribution development. The MWD becomes significantly narrower as the random degradation proceeds.

## Degradation of Heterogeneously Branched Polymers

In this section, we consider the degradation of branched polymers that are formed due to free-radical polymerization that involves chain transfer to polymer (CTP) as a branching reaction. In general, this type of polymerization reaction does not produce homogeneously branched polymers. For example, consider a batch polymerization. The primary chains formed in the earlier stages of polymerization are subjected to branching reactions for a longer period of time; therefore, the branching density of these chains would be larger than those formed in the later stages of polymerization. Such history-dependent processes result in the formation of a heterogeneously branched structure, and the branching density distribution was developed to describe such history-dependent nonlinear structure formation.[14]

As a matter of fact, the random sampling technique employed in the present series of papers was originally developed for a Monte Carlo simulation method to describe such history-dependent cross-linking[15] and branching.[11] By combining the Monte Carlo algorithms for nonrandom branching[2,11,16−18] and random degradation,[1,5] one can investigate the random degradation of heterogeneously branched polymers in a straightforward manner, as shown in Appendix D.

In this section, to investigate the effect of the heterogeneity of the branched structure on the random degradation reactions, we consider the branched polymer molecules formed in free-radical polymerization that involves CTP, whose elementary reactions are as follows: initiation, propagation (rate constant, $k_p$), chain transfer to small molecules including monomer ($k_{fT}$), bimolecular termination by disproportionation ($k_{td}$), and chain transfer to polymer ($k_{fp}$). We use an ideally micromixed, continuous stirred-tank reactor (CSTR) at steady state. Due to the very large residence time distribution in a CSTR, the branched structure formed is highly heterogeneous.[14] Furthermore, if the bimolecular termination does not involve combination, the primary chain length distribution is given by the most probable distribution as long as the chain length-dependent kinetics[19] is neglected. Therefore, the effect of the difference in the MWD of the primary polymer molecules can be removed to compare the results for homogeneously branched polymers whose MWD is given by eq 8. The weight fraction distribution of the primary polymer molecules is given by

$$w_p(r) = \tau^2 r \exp(-\tau r) \tag{16}$$

where $\tau = (R_{td} + R_f + R_{fp})/R_p$, $R_{td}$ is the rate of termination by disproportionation, $R_f$ is the rate of chain transfer to small molecules, $R_{fp}$ is the rate of chain transfer to polymer, and $R_p$ is the polymerization rate.

The average branching density, $\bar{\rho}$, is given by[14]

$$\bar{\rho} = C_{fp}x/(1 - x) \tag{17}$$

where $C_{fp}$ is polymer transfer constant ($=k_{fp}/k_p$) and $x$ is the monomer conversion to polymer at steady state.

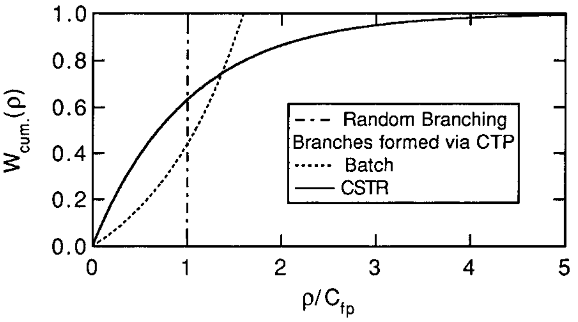

**Figure 11.** Comparison of the distribution of the branching density formed in a batch reactor and a CSTR with polymer transfer constant $C_{fp} = 0.001$ and average branching density $\bar{\rho} = 0.001$.

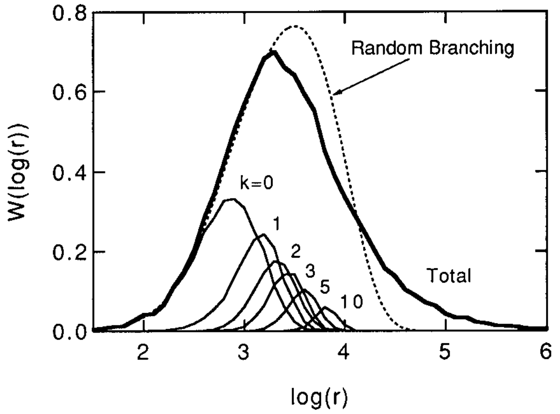

**Figure 12.** Initial weight fraction distribution of nonrandomly branched polymers. The weight fraction distribution of random branching when the average branching density is the same is shown by a dashed curve.

Figure 11 shows the comparison of the distribution of branching density, when $C_{fp} = 0.001$ and $\bar{\rho} = 0.001$. The $y$-axis shows the weight fraction of the primary polymer molecules whose branching density is smaller than $\rho$. In the calculation, the primary chain lengths are assumed to be large enough to neglect the statistical deviations due to finite chain lengths. The fundamental equations to calculate the branching density distribution can be found elsewhere.[14] The branched polymer molecules formed in a CSTR possess a very large variation in branching density due to a large residence time distribution.

To compare with the results obtained in the section on Degradation of Branched Polymers: Primary Chains with the Most Probable Distribution, we use the following calculation conditions: the number-average chain length of the primary polymer molecules before scission is $\bar{P}_{np}{}^0 = 1/\tau = 500$, and the average branching density is $\bar{\rho} = 0.001$.

Figure 12 shows the MWD before chain scission as well as the fractional distributions containing $k$ branch points. The dashed curve shows the MWD for random branching calculated from eq 8. The weight-average chain length of the polymer molecules formed in a CSTR, which was obtained from the Monte Carlo simulation, is $\bar{P}_w{}^0 = 1.68 \times 10^4$, which is much larger than that for random branching ($\bar{P}_w{}^0 = 4000$). The heterogeneous structure may make the weight-average chain length larger, because the chain connectivity can be improved substantially due to the regions with larger branching densities.[5,23]

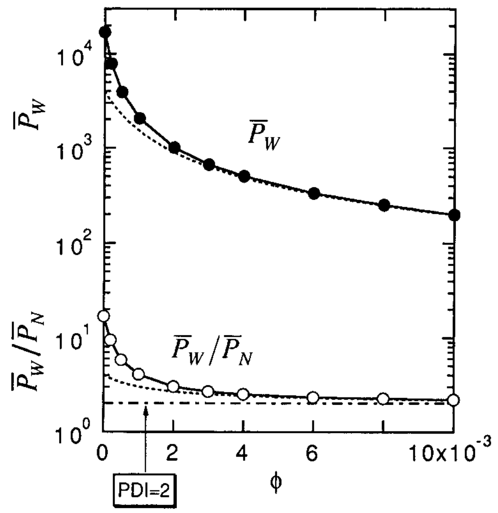

**Figure 13.** Average chain length development during random degradation of nonrandomly branched polymer molecules that are formed in a CSTR with $\bar{P}_{np}{}^0 = 500$ and $\bar{\rho} = 0.001$. The dashed curves are the results for randomly branched polymers.

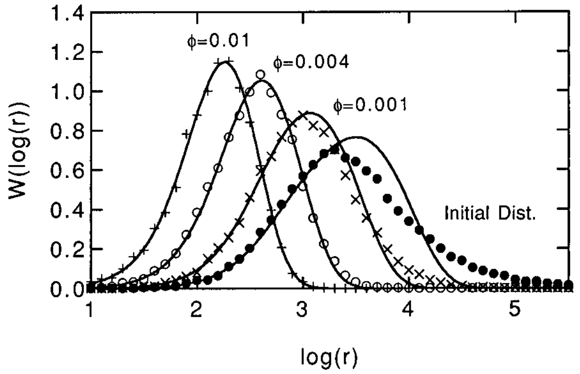

**Figure 14.** Weight fraction distribution development during the random degradation of nonrandomly branched polymer molecules that are formed in a CSTR (shown by the symbols) and that for homogeneously branched polymers. The primary polymer chain length distribution before scission follows the same most probable distribution for both systems, with $\bar{P}_{np}{}^0 = 500$ and $\bar{\rho} = 0.001$.

Figure 13 shows the average chain length development during random scission reactions. The comparison was made with the homogeneously branched polymers. The weight-average chain length decreases very fast in the heterogeneous system, and the differences from a homogeneous system soon become negligible. Figure 14 shows the MWD development both for the heterogeneous (given by symbols in the figure) and homogeneous (curves) systems. Because larger polymer molecules have a better chance of being severed, the high molecular weight tail for the heterogeneous system decreases very rapidly, and the MWDs become close to those for the homogeneous system at larger $\phi$ values.

## Conclusions

By the application of the random sampling technique to a homogeneously branched polymer system, the analytical solutions were derived for (1) the weight-average chain length that is valid irrespective of the primary polymer chain length distribution and (2) the full MWD function as well as the fractional MWD containing $k$ branch points for the primary chains with the most probable distribution. These solutions are used to investigate whether or not the processes of branching and degradation are interchangeable by comparing the Monte Carlo simulation results where branched polymer molecules are severed randomly. In

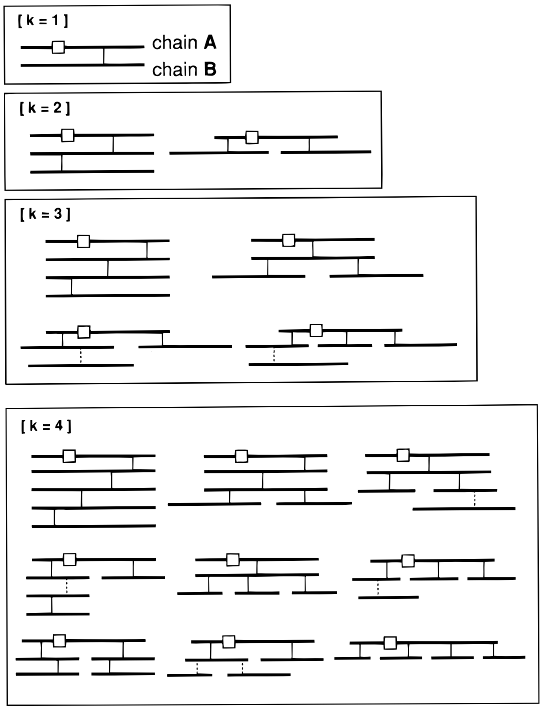

**Figure 15.** Possible types of morphology of cross-linked polymers that must be considered to derive the MWD function. Squares show the location of the initially selected unit. The cross-linkages drawn as dashed lines indicate that other possible locations of cross-linkage exist with the same probability.

contrast with random cross-linking and degradation, the processes are not interchangeable except when all primary chains possess the most probable distribution with randomly distributed branch points. When the primary chain length distribution is narrow, the process branching → degradation gives a larger weight-average chain length ($\bar{P}_w$) than the process degradation → branching. On the other hand, when the primary chain length distribution is broad, the process of branching → degradation provides a smaller $\bar{P}_w$ than the process of degradation → branching. The decrease in $\bar{P}_w$ during random scission reactions for heterogeneously branched polymer molecules can be very fast, and the differences from the homogeneously branched system may become negligible even at a relatively small scission density level.

## Appendix A: MWD Formed via Random Cross-Linking of Primary Chains

On the basis of the integrodifferential equation developed by Saito,[7,20] the MWD development during random cross-linking of polymer chains whose initial MWD is given by the Schultz–Zimm distribution (therefore, the most probable distribution is included) has already been derived.[10,21,22] However, here we develop the MWD by using the random sampling technique. For simplicity, we restrict ourselves to the initial most probable distribution, i.e., the primary chain length distribution is given by

$$w_p(r) = \frac{r}{(\bar{P}_{np})^2} \exp(-r/\bar{P}_{np}) \qquad \text{(A1)}$$

The MWD of cross-linked polymer molecules is the sum of the fractional MWDs containing 0, 1, 2, 3, ... cross-linkages, i.e., the weight fraction distribution, $W(r)$, is

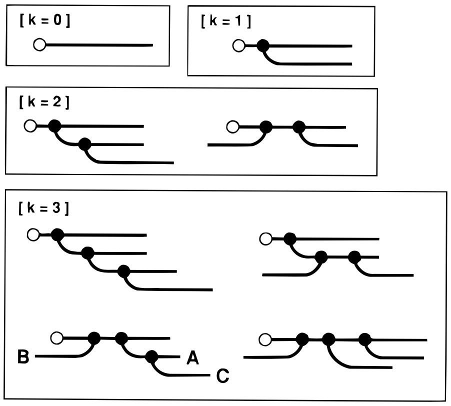

**Figure 16.** Possible types of morphology of branched polymer molecules.

given by

$$W(r) = \sum_{k=0}^{\infty} W_k(r) \qquad \text{(A2)}$$

To obtain a polymer molecule without cross-linkages ($k = 0$) by random sampling, the selected primary chain (that follows the weight fraction distribution given by eq A1) must not possess any cross-link points. The fractional weight-based distribution, $W_0(r)$, is given by

$$\begin{aligned} W_0(r) &= (1-\rho_x)^r w_p(r) \cong \exp(-\rho_x r) w_p(r) \qquad (\rho_x \ll 1) \\ &= \frac{r}{(\bar{P}_{np})^2} \exp\left\{-\left(\frac{\bar{P}_{np}\rho_x + 1}{\bar{P}_{np}}\right) r\right\} \qquad \text{(A3)} \end{aligned}$$

Next, consider $W_1(r)$, i.e., $k = 1$. When one unit is selected as shown in Figure 15, the chain length that contains this particular unit (chain A) follows eq A1. In the cross-linking reaction, the connected chain is also selected on a weight basis, because any unit within chain B can be connected. Therefore, a polymer molecule with chain length $r$ that contains one cross-linkage can be formed by connecting primary chains with $v$ and $r - v$. Chain A shown in Figure 15 must possess one cross-linked unit within $v$ units and $(v - 1)$ un-cross-linked units. On the other hand, chain B must possess $(r - v - 1)$ un-cross-linked units, and therefore,

$$\begin{aligned} W_1(r) &= \sum_{v=1}^{r-1} \left( w_p(v) \binom{v}{1} \rho_x (1-\rho_x)^{v-1} \right) (w_p(r-v) \times (1-\rho_x)^{r-v-1}) \\ &= \rho_x (1-\rho_x)^{r-2} \sum_{v=1}^{r-1} v w_p(v) w_p(r-v) \\ &\cong \rho_x (1-\rho_x)^{r-2} \int_0^r v w_p(v) w_p(r-v)\, dv \\ &= \frac{\rho_x (1-\rho_x)^{r-2}}{(\bar{P}_{np})^4} \exp(-r/\bar{P}_{np}) \int_0^r v^2 (r-v)\, dv \\ &\cong \frac{r}{(\bar{P}_{np})^2} \exp\left\{-\left(\frac{\bar{P}_{np}\rho_x + 1}{\bar{P}_{np}}\right) r\right\} \left(\frac{\bar{P}_{np}\rho_x}{2!3!}\right) \left(\frac{r}{\bar{P}_{np}}\right)^3 \qquad \text{(A4)} \end{aligned}$$

There are two types of morphology, which must be distinguished in the sampling technique, for the connection of three primary chains by two cross-linkages ($k = 2$) as shown in Figure 15:

$$W_2(r) = \sum_{v_1=1}^{r-2} \left\{ \left( w_p(v_1) \binom{v_1}{1} \rho_x (1-\rho_x)^{v_1-1} \right) \times \sum_{v_2=1}^{r-v_1-1} \left( w_p(v_2) \binom{v_2-1}{1} \rho_x (1-\rho_x)^{v_2-2} \times w_p(r-v_1-v_2)(1-\rho_x)^{r-v_1-v_2-1} \right) \right\} + \sum_{v_1=1}^{r-2} \left\{ \left( w_p(v_1) \binom{v_1}{2} {\rho_x}^2 (1-\rho_x)^{v_1-2} \right) \sum_{v_2=1}^{r-v_1-1} \left( w_p(v_2) \times (1-\rho_x)^{v_2-1} w_p(r-v_1-v_2)\,(1-\rho_x)^{r-v_1-v_2-1} \right) \right\}$$
$$\cong \frac{{\rho_x}^2}{(\bar{P}_{np})^6} \exp\left\{ -\left( \frac{\bar{P}_{np}\rho_x + 1}{\bar{P}_{np}} \right) r \right\} \{ \int_0^r {v_1}^2 \int_0^{r-v_1} {v_2}^2 (r - v_1 - v_2)\, dv_2\, dv_1 + \int_0^r {v_1}^3/2 \int_0^{r-v_1} v_2 (r - v_1 - v_2)\, dv_2\, dv_1 \}$$
$$= \frac{r}{(\bar{P}_{np})^2} \exp\left\{ -\left( \frac{\bar{P}_{np}\rho_x + 1}{\bar{P}_{np}} \right) r \right\} \frac{(\bar{P}_{np}\rho_x)^2}{3!5!} \left( \frac{r}{\bar{P}_{np}} \right)^6 \tag{A5}$$

For $k = 3$, four types of morphology (and nine types for $k = 4$ shown in Figure 15) must be considered. In general, the fractional weight fraction distribution containing $k$ cross-linkages, $W_k(r)$, is given by

$$W_k(r) = \frac{r}{(\bar{P}_{np})^2} \exp\left\{ -\left( \frac{\bar{P}_{np}\rho_x + 1}{\bar{P}_{np}} \right) r \right\} \times \frac{(\bar{P}_{np}\rho_x)^k}{(k+1)!(2k+1)!} \left( \frac{r}{\bar{P}_{np}} \right)^{3k} \tag{A6}$$

## Appendix B: MWD Formed via Random Branching of Primary Chains with the Most Probable Distribution

Reasoning similar to that shown for random cross-linking can be extended to the random branching reaction. Again, let us consider the case where the primary chain length distribution is given by the most probable distribution shown in eq A1. The random sampling technique can be applied on both a weight and number basis. Because the derivation on a number basis is more straightforward than that on a weight basis for the present case, we show the derivation of the MWD on a number basis. Derivation on a weight basis can be found elsewhere.[23]

Figure 16 shows various types of morphology of branched polymer molecules. (Note that the present figure is shown only for the purpose of illustrating the derivation method, and the real structures of randomly branched polymer molecules are quite different from those shown in Figure 16; they tend to possess a large number of relatively shorter branch chains.[18,23]) There are two types of primary chains in a branched polymer system: those with both chain ends not connected to the backbone polymer chain (primary chains with open circles in Figure 16) and those with one chain end connected to the backbone polymer chain (primary chains with closed circles). When primary chains are classified into these two types, such a classification is made on a number basis because only the chain end can be connected to the backbone polymer chain; therefore, both types of primary chains follow the same most probable distribution, whose number fraction distribution is given by

$$n_p(r) = \frac{1}{\bar{P}_{np}} \exp(-r/\bar{P}_{np}) \tag{A7}$$

Furthermore, it is obvious from the figure that every polymer molecule possesses one primary chain whose chain ends are not connected, i.e., the primary chain with an open circle. Let us call the chain end shown by an open circle the “head group”. Within a randomly branched polymer system, one can select a polymer molecule on a number basis by randomly selecting one head group.

Suppose our randomly selected head group belongs to a linear polymer molecule without any branch point, whose chain length is $r$ as shown in Figure 16 ($k = 0$). We consider the probability of selecting such a polymer molecule with chain length $r$, which is equal to the fractional number-based distribution containing no branch points ($k = 0$). Because no units are connected to the branch chain, $N_0(r)$ is given by

$$N_0(r) = (1-\rho)^r n_p(r) \cong \frac{1}{\bar{P}_{np}} \exp\left\{ -\left( \frac{\bar{P}_{np}\rho + 1}{\bar{P}_{np}} \right) r \right\} \tag{A8}$$

Next, consider the probability that we select a polymer molecule with two chains containing one branch point ($k = 1$), as shown in Figure 16. This type of polymer molecule can be selected with the following probability, $N_1(r)$:

$$N_1(r) = \sum_{v=1}^{r-1} n_p(v) \binom{v}{1} \rho (1-\rho)^{v-1} n_p(r-v)(1-\rho)^{r-v}$$
$$\cong \frac{\rho}{(P_{np})^2} \exp\left\{ -\left( \frac{\bar{P}_{np}\rho + 1}{\bar{P}_{np}} \right) r \right\} \int_0^r v\, dv$$
$$= \frac{1}{\bar{P}_{np}} \left( \frac{r}{\bar{P}_{np}} \right)^2 \frac{\bar{P}_{np}\rho}{1!2!} \exp\left\{ -\left( \frac{\bar{P}_{np}\rho + 1}{\bar{P}_{np}} \right) r \right\} \tag{A9}$$

There are two types of morphology for the connection of three primary chains by two branch points ($k = 2$), as shown in Figure 16. $N_2(r)$ is given by

$$N_2(r) \cong \frac{\rho^2}{(P_{np})^3} \exp\left\{ -\left( \frac{P_{np}\rho + 1}{P_{np}} \right) r \right\} \times \{ \int_0^r v_1 \int_0^{r-v_1} v_2\, dv_2\, dv_1 + \int_0^r {v_1}^2/2 \int_0^{r-v_1} dv_2\, dv_1 \}$$
$$= \frac{1}{\bar{P}_{np}} \left( \frac{r}{\bar{P}_{np}} \right)^4 \frac{(\bar{P}_{np}\rho)^2}{2!3!} \exp\left\{ -\left( \frac{\bar{P}_{np}\rho + 1}{\bar{P}_{np}} \right) r \right\} \tag{A10}$$

For $k = 3$, four types of morphology must be considered. Note that primary chain C can be connected to A and B with equal probability, so that this type of morphology must be counted twice. $N_3(r)$ is given by

$$N_3(r) \cong \frac{\rho^3}{(P_{\rm np})^4} \exp\left\{-\left(\frac{P_{\rm np}\rho + 1}{P_{\rm np}}\right)r\right\} \times$$
$$\{\int_0^r v_1 \int_0^{r-v_1} v_2 \int_0^{r-v_1-v_2} v_3 \, dv_3 \, dv_2 \, dv_1 +$$
$$\int_0^r v_1 \int_0^{r-v_1} {v_2}^2/2 \int_0^{r-v_1-v_2} dv_3 \, dv_2 \, dv_1 +$$
$$2 \int_0^r {v_1}^2/2 \int_0^{r-v_1} v_2 \int_0^{r-v_1-v_2} dv_3 \, dv_2 \, dv_1 +$$
$$\int_0^r {v_1}^3/6 \int_0^{r-v_1} \int_0^{r-v_1-v_2} dv_3 \, dv_2 \, dv_1\}$$
$$= \frac{1}{\bar{P}_{\rm np}} \left(\frac{r}{\bar{P}_{\rm np}}\right)^6 \frac{(\bar{P}_{\rm np}\rho)^3}{3!4!} \exp\left\{-\left(\frac{\bar{P}_{\rm np}\rho + 1}{\bar{P}_{\rm np}}\right)r\right\} \quad \text{(A11)}$$

In general, the fractional weight-based distribution that contains $k$ branch points is given by

$$N_k(r) = \frac{1}{\bar{P}_{\rm np}} \left(\frac{r}{\bar{p}_{\rm np}}\right)^{2k} \frac{(\bar{P}_{\rm np}\rho)^k}{k!(k+1)!} \exp\left\{-\left(\frac{\bar{P}_{\rm np}\rho + 1}{\bar{P}_{\rm np}}\right)r\right\} \quad \text{(A12)}$$

The total number fraction distribution, $N(r)$, is given by

$$N(r) = \sum_{k=0}^{\infty} N_k(r) = \left(\frac{I_1(2r\sqrt{\rho/\bar{P}_{\rm np}})}{r\sqrt{\bar{P}_{\rm np}\rho}}\right) \exp\left\{-\left(\frac{\bar{P}_{\rm np}\rho + 1}{\bar{P}_{\rm np}}\right)r\right\} \quad \text{(A13)}$$

where $I_m$ is the modified Bessel function of the first kind.

The weight fraction distribution given by eq 8 in the text can be obtained from $W(r) = (r/\bar{P}_{\rm n})N(r)$. The number-average chain length, $\bar{P}_{\rm n}$, can be obtained from eq 7 by substituting $\phi = 0$. It can also be obtained directly from the distribution function as follows:

$$\bar{P}_{\rm n} = \sum_{k=0}^{\infty} \int_0^{\infty} rN_k(r) \, dr = \frac{\bar{P}_{\rm np}}{1 - \bar{P}_{\rm np}\rho} \quad \text{(A14)}$$

Incidentally, the random sampling technique can also be used to obtain $\bar{P}_{\rm n}$ similar to the argument shown in the text to derive the weight-average chain length. In the present case, the selection of the primary chain is made on a number basis, so that $\bar{P}_{\rm n}$ is given by

$$\bar{P}_{\rm n} = \bar{P}_{\rm np} + (\bar{P}_{\rm np}\rho)\bar{P}_{\rm np} + (\bar{P}_{\rm np}\rho)^2\bar{P}_{\rm np} + ...$$
$$= \bar{P}_{\rm np} \sum_{i=0}^{\infty} (\bar{P}_{\rm np}\rho)^i = \frac{\bar{P}_{\rm np}}{1 - \bar{P}_{\rm np}\rho} \quad \text{(A15)}$$

## Appendix C: Monte Carlo Simulation Method for the Random Degradation of Homogeneously Branched Polymers on the Basis of the Random Sampling Techinque

The Monte Carlo simulation algorithm based on the random sampling technique can be developed by combining the method for the formation of branched polymer molecules[2,11,16−18] and that for the random degradation reactions.[1,5] Here, we show the simulation method by using a simple example. Consider the reaction mixture when the scission density is $\phi$. Suppose that our randomly selected polymer molecule possesses the structure shown in Figure 17. This molecule was generated as follows. The chain length of the primary polymer molecule that involves the initially selected unit can be determined from the weight fraction distribution of the primary polymer molecules, $w_{\rm p}(r)$. By looking from the randomly selected unit toward the right-hand side, the chain length until scission occurs can be determined from the following distribution:[1,5]

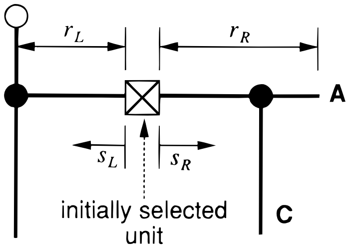

**Figure 17.** Schematic drawing of a branched polymer molecule.

$$N_s(s_{\rm R}) = \phi(1 - \phi)^{s_{\rm R}} \quad \text{(A16)}$$

By comparing $s_{\rm R}$ and the chain length actually located in the right-hand side direction, $r_{\rm R}$, the shorter one is chosen as the chain length after scission. In the molecule shown in Figure 17, if $s_{\rm R} > r_{\rm R}$, no scission reaction occurs in the right-hand side direction. The chain length after scission in the left-hand side can be determined similarly. If $r_{\rm L} < s_{\rm L}$, then one examines the possibility of connection at the chain end by using the probability, $p_{\rm b} = \bar{P}_{\rm np}\rho$ (see eq 4 in the text). In the present case, a backbone chain B is connected. The chain length of this primary chain can again be determined from $w_{\rm p}(r)$, because any unit on chain B can be connected. The chain length after scission is determined by considering imaginary chain lengths $s_{\rm R}$ and $s_{\rm L}$. In the present case, the chain end of B is not connected to another backbone polymer chain, because $s_{\rm L} < r_{\rm L}$ or the chain end is not connected in the original form (before scission), whose probability is given by $1 - p_{\rm b}$.

The number of branch chains connected to A and B can be determined from the following binomial distribution, i.e., the number of branch points $m$ on a primary chain with chain length $r$ is given by

$$p(m) = \binom{r}{m} \rho^m (1 - \rho)^{r-m} \quad \text{(A17)}$$

In the present example, only one branch chain is connected to chain A. The chain length of C can be determined from the number fraction distribution of the primary polymer molecules ($n_{\rm p}(r)$), because only the chain end can be connected. The chain length of C after scission can be determined by considering an imaginary chain length $s$ that follows the same distribution function as eq A16.

When no further chains are connected, the simulation for one polymer molecule ends. By generating a large number of polymer molecules, the statistical properties can be determined effectively.

## Appendix D: Monte Carlo Simulation Method for the Random Degradation of Heterogeneously Branched Polymers

In the case of nonrandom, history-dependent branching reactions, one has to consider the residence time of each primary polymer molecule, because the branching probability is dependent on how long the primary polymer molecule is subjected to the branching reaction. In the case of batch polymerization, the conversion at which the given primary polymer molecule is formed (birth conversion) can be used for such a purpose. On the other hand, for continuous polymerizations, one needs to consider the residence time to describe the history of the branching reaction for a particular primary polymer molecule.

In this section, we consider the branched polymer molecules formed in a continuous stirred-tank reactor (CSTR) at steady state via a free-radical polymerization whose elementary reactions are listed in the text. Suppose that our randomly selected polymer molecule possesses the structure shown in Figure 17. When one unit is selected randomly, we first have to determine the length of time for the primary polymer molecule to come out of the reactor after it is formed, because the connection probabilities are different depending on the residence time. This can be determined from the residence time distribution, $E(\xi)$, of a continuous stirred-tank reactor (CSTR):

$$E(\xi) = \mathrm{e}^{-\xi} \tag{A18}$$

where $\xi = t/\bar{t}$ and $\bar{t}$ is the mean residence time.

The chain length of A can be determined from the weight fraction distribution of primary chains, $w_p(r)$, given by eq 16 in the text. Then, the chain length of A after chain scission can be determined in the same manner as shown in Appendix C. In the present case, $r_L < s_L$, so we examine the possibility of connection at the chain end. This probability, $p_b$, for the present case is given by[17]

$$p_{\mathrm{b}} = \frac{C_{\mathrm{fp}}x}{\tau(1-x)} \tag{A19}$$

Note that, in a CSTR at steady state, both $w_p(r)$ and $p_b$ are the same for all primary chains. As shown in Figure 17, a backbone chain B is connected. The primary chain B must be formed before chain A is formed. The conditional probability that the primary polymer molecule with residence time $\xi$ started growing from the primary polymer molecule formed in the residence time interval $z$ to $\infty$ ($\xi < z$) is given by[17]

$$CP_i(z|\xi) = \mathrm{e}^{\xi - z} \tag{A20}$$

The chain length of this primary chain can again be determined from $w_p(r)$, because any unit on chain B can be connected. The chain length after scission can be determined by considering the imaginary chain lengths $s_R$ and $s_L$.

The expected branching density of the primary polymer molecules whose residence time is $\xi$ is given by[14,17]

$$\rho(\xi) = C_{\mathrm{fp}}\left(\frac{x}{1-x}\right)\xi \tag{A21}$$

The number of branch chains connected to A can be determined from the following binomial distribution, i.e., the probability that a primary polymer molecule with chain length $r$ possesses $m$ branch points is given by

$$p(m) = \binom{r}{m}\rho(\xi)^m\{1-\rho(\xi)\}^{r-m} \tag{A22}$$

The number of branch points on chain B can also be determined from eq A22 by using the residence time $z$, although $m = 0$ for B in the present example.

The primary chain C must be formed after the formation of chain A. The conditional probability that the primary polymer molecules with residence time $\xi$ is connected to the branch chain with the residence time interval 0 to $u$ ($0 < u < \xi$), $CP_a(u|\xi)$, is given by[17]

$$CP_{\mathrm{a}}(u|\xi) = u/\xi \tag{A23}$$

The chain length of C can be determined from the number fraction distribution of the primary polymer molecules ($n_p(r)$), which is given by

$$n_{\mathrm{p}}(r) = \tau\exp(-\tau r) \tag{A24}$$

The chain length of C after scission can be determined by considering an imaginary chain length $s$ that follows the same distribution function as eq A16.

## Glossary of Symbols

| | |
|---|---|
| $C_{fp}$ | polymer transfer constant ($=k_{fp}/k_p$) |
| $k_{fT}$, $k_{fp}$ | rate constants for chain transfer reactions to small molecules (including monomer) and to polymer |
| $k_p$ | rate constant for the propagation reaction |
| $k_{td}$ | rate constant for bimolecular termination by disproportionation |
| $N_k(r)$ | fractional number-based distribution containing $k$ branch points (Appendix B) |
| $N_s(s)$ | probability density that the scission occurs at the $(s + 1)$th bonding (eq A16) |
| $n_p(r)$ | number fraction distribution of the primary polymer molecules |
| $\bar{P}_n$, $\bar{P}_w$ | number- and weight-average chain lengths |
| $\bar{P}_n^0$, $\bar{P}_w^0$ | number- and weight-average chain lengths before chain scission |
| $\bar{P}_{np}$, $\bar{P}_{wp}$ | number- and weight-average chain lengths of the primary polymer molecules |
| $\bar{P}_{np}^0$, $\bar{P}_{wp}^0$ | number- and weight-average chain lengths of the primary polymer molecules before chain scission |
| $\bar{P}_{np,deg}$, $\bar{P}_{wp,deg}$ | number- and weight-average chain lengths of the primary polymer molecules after chain scission (assuming that all branch points are disconnected) |
| $P_b$ | probability that the chain end of a primary polymer molecule is connected to a backbone polymer chain |
| $p(m)$ | probability that the primary polymer molecule possesses $m$ branch points (eq A17) |
| $R_f$, $R_{fp}$ | rates of chain transfer to small molecules (including monomer) and to polymer |
| $R_p$ | polymerization rate |
| $R_{td}$ | rate of bimolecular termination by disproportionation |
| $r$ | chain length (degree of polymerization) |
| $r_R$, $r_L$ | 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 17) |
| $s_R$, $s_L$ | estimated number of units on the right ($s_R$) and left-hand ($s_L$) sides of the base unit when chain scission occurs (Figure 17) |
| $t$ | time |
| $\bar{t}$ | mean residence time |
| $W(r)$ | weight fraction distribution |
| $W_k(r)$ | fractional weight-based distribution containing $k$ cross-linkages (eq A2) or $k$ branch points |
| $w_p(r)$ | weight fraction distribution of the primary polymer molecules |

| | |
|---|---|
| $x$ | monomer conversion |

*Greek Letters*

| | |
|---|---|
| $\xi$ | dimensionless residence time ($=t/\bar{t}$) |
| $\rho$ | branching density |
| $\bar{\rho}$ | average branching density for heterogeneously branched polymers (eq 17) |
| $\rho_x$ | cross-linking density |
| $\sigma$ | parameter for the Schulz–Zimm distribution (eq 14) |
| $\tau$ | probability of chain stoppage due to chain transfer and termination by disproportionation in free-radical polymerization (eq 16) |
| $\phi$ | probability of chain scission for each bond |

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