Copolymerization with Chain Transfer Monomer. 2. Molecular Weight Distribution

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Received May 30, 1996; Revised Manuscript Received January 9, 1997[⊗]

ABSTRACT: The full molecular weight distribution formed in a batch free-radical copolymerization with chain transfer monomer is considered theoretically. A Monte Carlo simulation algorithm is proposed on the basis of the random sampling technique. Illustrative calculations are conducted for the cases with equal reactivity of all types of double bonds. It was found that even when the probability of possessing a branch point is the same for all units, the formed molecular weight distribution is highly dependent on the chain connection rule. Bimolecular termination by combination may contribute to form extremely large polymer molecules by forming cross-linkages between primary chains. Under the idealized conditions, homogeneously branched polymer molecules are formed, and the analytical solution for the molecular weight distribution can be obtained.

Introduction

In part 1 of this series,[1] we considered the distribution of branch points by focusing our attention on the history of each primary polymer molecule. It was shown that if the reactivities of all types of double bonds are equal, the expected branching density of the primary chain is the same for all chains. It was further proven that such branched structures are not homogeneous, except when the chain transfer constant of the chain transfer monomer is unity if the primary chain length drift during polymerization cannot be neglected. This is because the primary chains born at different conversion levels are not connected randomly. It would be quite interesting to investigate the effect of such a nonrandom nature of the chain connection rule on the statistical properties of the branched polymer systems, such as the full molecular weight distribution (MWD).

To predict the molecular weights formed in polymerization with long-chain branching, notably through chain transfer to polymer, various mathematical methods have been proposed.[2−13] However, most conventional approaches are limited to give only the average molecular weight development, and the full MWDs are obtained only for several limited cases.[10−13] Mathematically, it would be true that the full MWD functions can be obtained, provided the moments of the MWD are given, such as by using the Laguerre polynomials.[11,14] Practically, however, it is very difficult to do so, because the series does not converge rapidly,[13,15] without a priori knowledge of the approximate functional form of the MWD.

Earlier theoretical investigation of the molecular weights of polymers formed in the copolymerization with chain transfer monomer (CTM) was also limited to the average molecular weights.[16,17] In addition, the method proposed in ref 16 is not exact, because the monodisperse primary chains are assumed in estimating the number of branch points on the primary polymer molecule. In ref 17, the Macosko−Miller model[18,19] was used to obtain the weight-average chain lengths; therefore, the full MWD profile cannot be obtained.

In the present report, we use the random sampling technique[20−28] to estimate the full MWD as well as the actual branched structure of each polymer molecule. The basic concept of the random sampling technique is very simple; i.e., we randomly select a large number of polymer molecules from an infinite number of polymeric species in the reaction mixture and determine the statistical properties of the reaction system effectively. When this concept is used as a “thought experiment”, one may obtain analytical solutions for simpler cases.[24−28] For more realistic cases, it is straightforward to combine this concept with the Monte Carlo method.

In this report, we propose a Monte Carlo simulation algorithm based on the random sampling technique. We investigate the effect of nonrandom chain connection statistics on the formed MWD by comparing the analytical solution for the homogeneously branched polymers developed earlier.[25] We further investigate the effect of dead polymer chain formation via bimolecular termination by combination on the formed MWD.

Monte Carlo Simulation Method

We consider a free-radical copolymerization of M_1 and chain transfer monomer (CTM), M_2. The elementary reactions considered are discussed in part 1 of the present series.[1]

In batch polymerizations, the concentration of every reactant may change during polymerization. However, because the lifetime of each primary polymer radical is much smaller than necessary to obtain high conversion of monomer to polymer in the usual free-radical polymerization, it is reasonable to consider that each primary chain is formed instantaneously; i.e., the change in the concentrations of reactants during the formation of a particular primary chain can be neglected. Therefore, the number and weight fraction distribution of the primary polymer radicals at conversion x is given by the following most probable distribution:[28,29]

$$n_p(r,x) = (1-p)p^{r-1} \tag{1a}$$

$$w_p(r,x) = r(1-p)^2 p^{r-1} \tag{2a}$$

where r is the chain length (degree of polymerization) and p is the probability of chain growth for a radical

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

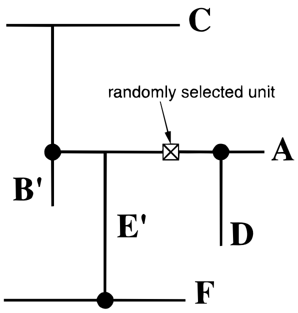

Figure 1. Schematic example of a branched polymer molecule used to elucidate the Monte Carlo simulation method.

center that is defined by

$$p = 1/(1 + \tau + \beta) \tag{3}$$

$$\tau = (v_{fm} + v_{fp} + v_{fT} + v_{td})/v_p \tag{4}$$

$$\beta = v_{tc}/v_p \tag{5}$$

where v_p is the propagation rate, v_{fm}, v_{fp}, and v_{fT} are the rates of chain transfer reactions to monomer, polymer, and chain transfer agents, respectively, and v_{td} and v_{tc} are the rates of bimolecular termination by disproportionation and combination, respectively. The explicit expression for each reaction rate can be found in part 1 of this series.[1]

In the present report, we consider only the cases where long primary chains are formed, as was considered in part 1 of this series,[1] i.e., $\tau + \beta \ll 1$. In such cases, eqs 1a and 2a can be approximated by[28,29]

$$n_p(r,x) = (\tau + \beta) \exp\{-(\tau + \beta)r\} \tag{1b}$$

$$w_p(r,x) = (\tau + \beta)^2 r \exp\{-(\tau + \beta)r\} \tag{2b}$$

In part 1 of this series,[1] we have determined (1) the branching density of primary polymer molecules as a function of the birth conversion, and (2) how the primary chains born at the given conversion level are connected with the primary chains formed at different birth conversions. In addition, we have information on (3) the chain length distribution of the primary polymer molecules formed at each conversion level given by eqs 1 and 2. On the basis of these three pieces of information, the whole molecular constitution can be determined uniquely.

In the present Monte Carlo simulation algorithm, we randomly sample polymer molecules from the reaction mixture on a weight basis. The sampling on a weight basis can be conducted by randomly selecting one monomeric unit from all units bound to polymer chains. Suppose we have selected a unit shown in Figure 1, when the conversion at the present time is $x = \psi$. To illustrate the present technique, we now construct this particular polymer molecule by using the Monte Carlo method. This polymer molecule consists of six primary chains, and the primary chains with a prime (B′ and E′) are formed by bimolecular termination by combination. The branch points shown with circles are formed by terminal double-bond polymerization (TDBP). If we use the monomer conversion x as an independent variable, the weight of polymer formed in a fixed conversion interval Δx is the same irrespective of the conversion level. Therefore, the birth conversion of chain A can be determined by randomly selecting the birth conversion θ_A from 0 to ψ. Once the birth conversion of A is settled, then we can determine the chain length of A. The chain length of the primary polymer radical just before dead polymer chain formation, r', conforms to the weight fraction distribution of the primary polymer radicals at $x = \theta_A$, which is given by eq 2, because the selection is made on a weight basis. Therefore, by generating a random number that follows eq 2, we can determine the chain length of A, just before the dead polymer chain formation. A simple algorithm to generate random numbers that follow the weight-based most probable distribution can be found elsewhere.[24,28,30] The probability that chain A is formed by combination termination is given by

$$P_{con}(\theta_A) = \beta/(\tau + \beta) \tag{6}$$

In the present case, chain A does not satisfy the above probability, which means that chain A was formed by means other than combination termination. Therefore, the chain length of A is simply given by $r = r'$.

The probability that the primary chain A started growing from a radical center on a backbone polymer chain resulting from chain transfer to polymer (CTP) is given by

$$P_{fp}(\theta_A) = v_{fp}/(v_{fm} + v_{fT} + v_{fp} + v_{td} + v_{tc}) \tag{7}$$

Chain A does not satisfy the probability given by eq 7 in the present case. On the other hand, the probability that chain A started growing from a monomer radical formed by chain transfer to M_2 is given by

$$P_{fm}(\theta_A) = v_{fm}/(v_{fm} + v_{fT} + v_{fp} + v_{td} + v_{tc}) \tag{8}$$

Chain A falls into this category. Then, this terminal double bond may have reacted until the conversion reaches ψ. Such probability is given by

$$P^*_{react}(\theta_A,\psi) = 1 - \Phi^=(\theta_A,\psi)/\Phi^=(\theta_A,\theta_A) \tag{9}$$

where $\Phi^=(\theta,\psi)$ is the fraction of the unreacted terminal double bonds within the units bound to polymer chains at $x = \theta$, when the present conversion is $x = \psi$. $\Phi^2(\theta,\psi)$ can be obtained by solving eq 30 of ref 1. Chain A satisfies this probability in the present case, and is connected to a backbone polymer chain B′.

The birth conversion of chain B′ can be determined from the following conditional probability; i.e., the probability that the birth conversion of B′ is in the conversion interval $\theta_A < x < \theta_B$, $P^*_a(\theta_B|\theta_A)$, is given by[1]

$$P^*_a(\theta_B|\theta_A) = \frac{1 - \Phi^=(\theta_A,\theta_B)/\Phi^=(\theta_A,\theta_A)}{1 - \Phi^=(\theta_A,\psi)/\Phi^=(\theta_A,\theta_A)} \tag{10}$$

Once the birth conversion of B′ has been determined, then we can determine the chain length of B′. Because the branch point on chain B′ can be located on any unit with equal probability, the selection of chain B′ is considered to be made on a weight basis; i.e., the chain length of B′ follows the weight fraction distribution of the primary chains formed at $x = \theta_B$. Therefore, the primary polymer radical just before dead polymer chain formation, r', follows the distribution given by eq 2. In the present case, chain B′ satisfies the probability $P_{con}(\theta_B)$ given by eq 6 and is formed by combination termination. In the combination termination process, the coupled radical is selected by randomly choosing a chain end (active center) from the polymeric radicals that existed at $x = \theta_B$,[28] if we neglect the chain-length dependence in bimolecular termination reactions. Therefore, the chain length of the coupled radical, r'', follows the number fraction distribution given by eq 1. Then we can determine the chain length of B′ as $r = r' + r''$.

Because chain B′ was formed by combination termination, both chain ends were the starting points for the chain growth. To determine the possibility of connection to other backbone polymer chains via CTP or TDBP, we need to examine the probabilities given by $P_{fp}(\theta_B)$ (eq 7) and $P_{fm}(\theta_B)$ (eq 8), as well as $P^*_{react}(\theta_B,\psi)$ (eq 9), if $P_{fm}(\theta_B)$ is satisfied. In the present example shown in Figure 1, only one chain end satisfies the probability of chain connection given by $P_{fp}(\theta_B)$ and is connected to chain C by CTP.

Chain C must be born before the formation of chain B′, which means the birth conversion of C, θ_C, is smaller than θ_B. The probability that the connected backbone chain was born in the conversion interval $0 < x < \theta_C$, $P_i(\theta_C|\theta_B)$, is given by[1]

$$P_i(\theta_C|\theta_B) = \frac{\int_0^{\theta_C}\{F_2(x) - \rho(x,\theta_B)\}\,dx}{\int_0^{\theta_B}\{F_2(x) - \rho(x,\theta_B)\}\,dx} \tag{11}$$

After determining the birth conversion, we determine the chain length of C. The chain length of the primary polymer radical just before dead polymer chain formation at $x = \theta_C$, r', can be determined from $w_p(r',\theta_C)$ (eq 2). Because chain C was formed by means other than combination termination, the chain length of the dead polymer chain C is equal to r'. Then, we examine the possibility if the chain end of C is connected to another backbone polymer chain, by using $P_{fp}(\theta_C)$, $P_{fm}(\theta_C)$, and $P^*_{react}(\theta_C,\psi)$. No chain was connected in the present example.

Next, we consider the connection to the branch chains. Consider the number of branch chains on the primary chain, A. The branching density formed by CTP, and TDBP, is given by[1]

$$\frac{\partial\rho(\theta_A,\psi)}{\partial\psi} = C_{fp}\frac{F_2(\theta_A) - \rho(\theta_A,\psi)}{1-\psi} \tag{12}$$

$$\rho(\theta_A,\theta_A) = 0 \tag{13}$$

$$\rho^*(\theta_A) = \nu^*(\theta_A)/\nu_p(\theta_A) \tag{14}$$

The number of branch chains on chain A, whose chain length is r, is given by the following binomial distribution. The probability that chain A possesses m branch chains formed by CTP is given by

$$p(m) = \binom{r}{m}\{\rho(\theta_A,\psi)\}^m\{1 - \rho(\theta_A,\psi)\}^{r-m} \tag{15}$$

The probability that chain A possesses n branch chains formed by TDBP is given by

$$p^*(n) = \binom{r}{m}\{\rho^*(\theta_A)\}^n\{1 - \rho^*(\theta_A)\}^{r-n} \tag{16}$$

In the present case, chain A possesses one branch chain formed by CTP (chain E′) and one branch chain by TDBP (D).

The primary chain, D, must be formed before the formation of chain A. The birth conversion of D can be determined from the following equation; i.e., the probability that a branch point of A is connected to a primary chain whose birth conversion is between 0 and θ_D, $P^*_i(\theta_D|\theta_A)$, is given by[1]

$$P^*_i(\theta_D|\theta_A) = \frac{\int_0^{\theta_D}\Phi^=(x,\theta_A)\,dx}{\int_0^{\theta_A}\Phi^=(x,\theta_A)\,dx} \tag{17}$$

After determining the birth conversion of D, we then determine the chain length of D. This branch point is formed during the formation of chain A by consuming the terminal double bond located at the chain end. Because the chain end is selected randomly at the time of branch chain formation, the primary chain D is selected on a number basis from the dead primary chain formed at $x = \theta_D$. Therefore, the chain length of D conforms to the number fraction distribution of the primary chains, *not* the weight fraction distribution. The chain length of the primary polymer radical just before dead polymer chain formation at $x = \theta_D$, r', can be determined, therefore, from $n_p(r',\theta_D)$ (eq 1). Because chain D was formed, by means other than combination termination, the chain length of dead polymer chain D is equal to r'.

The primary chain, E′, formed by CTP, must be born after the formation of chain A, i.e., $\theta_A < \theta_E$. The probability that a branch point on primary chain A is connected to a branch chain formed in the conversion interval $\theta_A < x < \theta_E$, $P_a(\theta_E|\theta_A)$, is given by[1]

$$P_a(\theta_E|\theta_A) = \frac{\rho(\theta_A,\theta_E)}{\rho(\theta_A,\psi)} \tag{18}$$

The chain length of the primary polymer radical just before dead polymer chain formation at $x = \theta_E$, r', can be determined, therefore, from $n_p(r',\theta_E)$. In the present example, chain E′ was formed by combination termination. The chain length of the coupled radical, r'', also follows the number fraction distribution, $n_p(r'',\theta_E)$, because the radical center exists only at the chain end.[28] The chain length of E′ is, therefore, given by $r = r' + r''$.

Because chain E′ was formed by combination termination, we need to consider the possibility that the other chain end of E′ is connected to some other backbone polymer chain by using $P_{fp}(\theta_E)$ (eq 7) and $P_{fm}(\theta_E)$ (eq 8), as well as $P^*_{react}(\theta_E,\psi)$ (eq 9), if $P_{fm}(\theta_E)$ is satisfied. In the present case, chain F is connected by TDBP. The birth conversion of F can be determined from $P^*_a(\theta_F|\theta_E)$ given by eq 10. The chain length of F can be determined from the weight fraction distribution, $w_p(r,\theta_F)$. Then, we need to examine the possibility that the chain end of F is connected to another backbone polymer chain by using eqs 7−9. However, no backbone chain is connected in the present case. Obviously, we need to examine the number of branch chains on every polymer chain by using eqs 15 and 16, i.e., we further examine the number of branch chains on B′, C, D, E′, and F; however, no further branch chains exist in the branched polymer molecule shown in Figure 1.

At this point, we have determined the size and structure of one polymer molecule. By generating a large number of polymer molecules in this way, we can determine the statistical properties of a branched polymer system effectively. One can write down the whole diagram for the simulation algorithm in a straightforward manner by referring to the flowcharts shown in refs 22 and 23.

Method of Moments

In the absence of bimolecular termination by combination, Nagasubramanian and Graessley[5] derived the moment equations for vinyl acetate polymerization in which both CTP and TDBP occur simultaneously, by assuming that (1) the stationary-state hypothesis is valid for all types of polymer radicals and that (2) all polymer radicals possess only one active center. The moment equations for the homopolymerization case[5] can be extended to the copolymerization systems considered here as follows:

$$\frac{\mathrm{d}Q_0^{=}}{\mathrm{d}x} = C_{\mathrm{fm}}f_2 - \frac{KQ_0^{=}}{1-x} \tag{19}$$

$$\frac{\mathrm{d}Q_0'}{\mathrm{d}x} = \frac{\nu_{\mathrm{fT}} + \nu_{\mathrm{td}}}{\nu_{\mathrm{p}}} \tag{20}$$

$$\frac{\mathrm{d}Q_1^{=}}{\mathrm{d}x} = [C_{\mathrm{fp}}Q_1^{=}(\bar{F}_2 - \bar{\rho}) + C_{\mathrm{fm}}f_2(1-x) - KQ_1^{=}\{(\nu_{\mathrm{fT}} + \nu_{\mathrm{td}})/\nu_{\mathrm{p}} + C_{\mathrm{fp}}Q_1'(\bar{F}_2 - \bar{\rho})/(1-x)\}]/Z \tag{21}$$

$$\frac{\mathrm{d}Q_1'}{\mathrm{d}x} = \left(1 + \frac{KQ_1^{=}}{1-x}\right)\left(\frac{(1-x)(\nu_{\mathrm{fT}} + \nu_{\mathrm{td}})/\nu_{\mathrm{p}} + C_{\mathrm{fp}}Q_1'(\bar{F}_2 - \bar{\rho})}{Z}\right) \tag{22}$$

$$\frac{\mathrm{d}Q_2}{\mathrm{d}x} = \left(\frac{2}{1-x}\right)\left(\frac{(1-x+KQ_1^{=})\{1-x+KQ_1^{=} + C_{\mathrm{fp}}Q_2(\bar{F}_2 - \bar{\rho})\}}{Z}\right) \tag{23}$$

where $Q_{\mathrm{i}}^{=}$ is the ith moment of the polymers that possess a terminal double bond, Q_i' is the ith moment of the polymers without a terminal double bond, and Q_i is the ith moment of the total polymers ($Q_i = Q_i^{=} + Q_i'$). The grouped parameter Z is defined by

$$Z = (1-x)\{\nu_{\mathrm{fm}} + \nu_{\mathrm{fp}} + \nu_{\mathrm{fT}} + \nu_{\mathrm{td}}\}/\nu_{\mathrm{p}} \tag{24}$$

Note that we assume that the terminal double bonds formed by disproportionation termination are inactive toward free-radical polymerization, as discussed in part 1 of this series.[1] By using the moments of distribution, the number- and weight-average chain lengths are given by

$$\bar{P}_{\mathrm{n}} = Q_1/Q_0 \tag{25}$$

$$\bar{P}_{\mathrm{w}} = Q_2/Q_1 \tag{26}$$

Results and Discussion

In order to examine the detailed structural differences on the formed MWD, we use the calculation conditions C1 and C2 shown in Table 2 of ref 1; i.e., the reactivity ratios $r_1 = r_2 = 1$ and the terminal double-bond reactivity $K = 1$ for both conditions, while the initial mole fraction of M_2 is $f_2^0 = 0.001$ and the reactivity of the chain transfer functional group is $C_{\mathrm{fm}} = C_{\mathrm{fp}} = 10$ for C1, and $f_2^0 = 0.1$ and $C_{\mathrm{fm}} = C_{\mathrm{fp}} = 0.01$ under condition C2. Note that for both cases, the expected branching density is the same for all chains at any stage of polymerization. Figure 2 shows the average branching density development formed by CTP and TDBP.

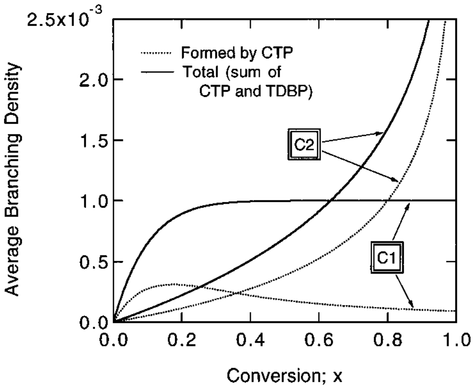

Figure 2. Average branching density development during polymerization. The dotted curves show the contribution by CTP.

Under condition C1, the average branching density formed by CTP takes a maximum at $x = 0.174$, because the chain transfer functional groups on both polymer and monomer are consumed in the earlier stage of polymerization due to a high chain transfer constant. (Note that the decrease in branching density does not mean the number of branch points is decreased, because the branching density is the *fraction* of units that bear a branch point.)

In order to examine the effect of bimolecular termination reactions, we considered two types of cases: (a) bimolecular termination is solely by disproportionation, $\nu_{\mathrm{td}}/\nu_{\mathrm{p}} = 1 \times 10^{-3}$, and (b) bimolecular termination is solely by combination, $\nu_{\mathrm{tc}}/\nu_{\mathrm{p}} = 1 \times 10^{-3}$. Obviously, the values of these parameters would change during polymerization in real systems, and such changes can be accounted for in a straightforward manner in the present simulation method. However, we used constant values for simplicity. Further, note that the bimolecular termination by disproportionation can be replaced by chain transfer reactions to chain transfer agents without changing the whole molecular constitution; i.e., the condition with $\nu_{\mathrm{td}}/\nu_{\mathrm{p}} = 1 \times 10^{-3}$ and $\nu_{\mathrm{fT}}/\nu_{\mathrm{p}} = 0$ gives the same MWD as with $\nu_{\mathrm{td}}/\nu_{\mathrm{p}} = 0$ and $\nu_{\mathrm{fT}}/\nu_{\mathrm{p}} = 1 \times 10^{-3}$.

Figure 3 shows the change in the weight-average chain length of the primary polymer molecules. The solid curves show the weight-average chain lengths of all primary chains, while the dotted curves show those of the primary chains formed at a given conversion level instantaneously. Under condition C1, the primary chain lengths are smaller in the earlier stages due to high chain transfer reaction rates, and the chain lengths increase as chain transfer functional groups are consumed. In the later stages of polymerization, a large function of primary chains are formed by bimolecular termination.

Under condition C2, the chain transfer functional groups are preserved until the later stages of polymerization due to a lower reactivity of the functional groups. The primary chain length decreases with polymerization because of an increasing contribution of chain transfer reactions.

Figure 4 shows the simulated results for the weight-average chain length development. The Monte Carlo simulations were conducted to generate 2×10^4 polymer molecules at each conversion level. The solid curves indicate the calculated results by using the moment equations shown in eqs 21–23, which can be applied only for the cases without combination termination. The Monte Carlo simulation results agree satisfactorily

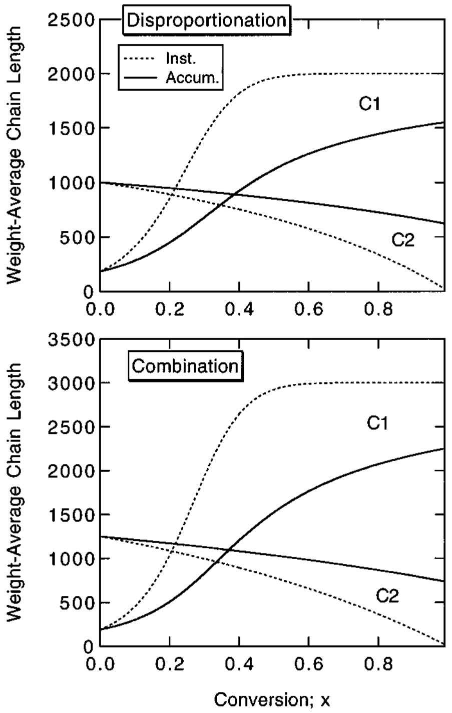

Figure 3. Primary chain length drift during polymerization. The solid curves show the accumulated weight-average chain length of the primary polymer molecules, while the dotted curves indicate the instantaneous weight-average chain length.

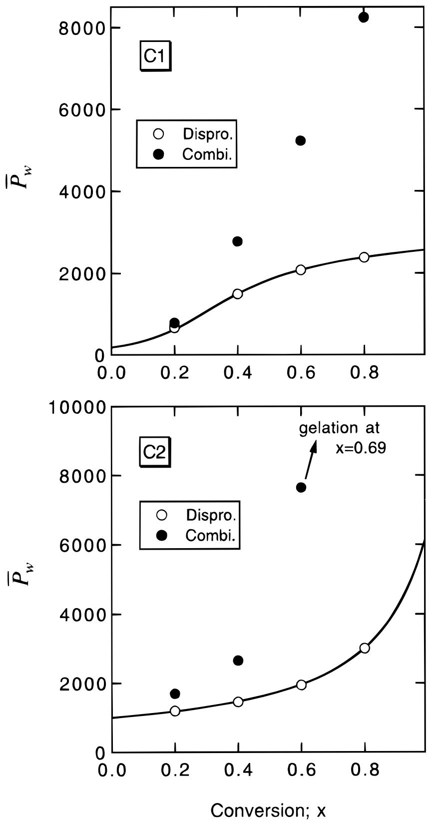

Figure 4. Weight-average chain length development. The symbols show the Monte Carlo simulation results, and the solid curves are the calculated results by using the moment equations (disproportionation termination only). The Monte Carlo simulations are conducted for the cases with disproportionation termination (open circles) and combination termination (closed circles).

with the moment equations derived by employing the method of moments.

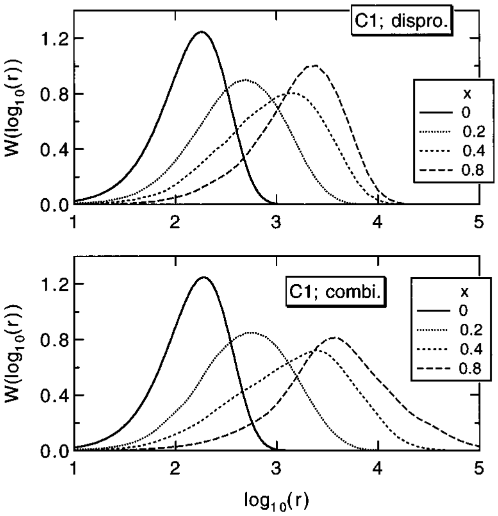

Figure 5. Weight fraction distribution development under condition C1.

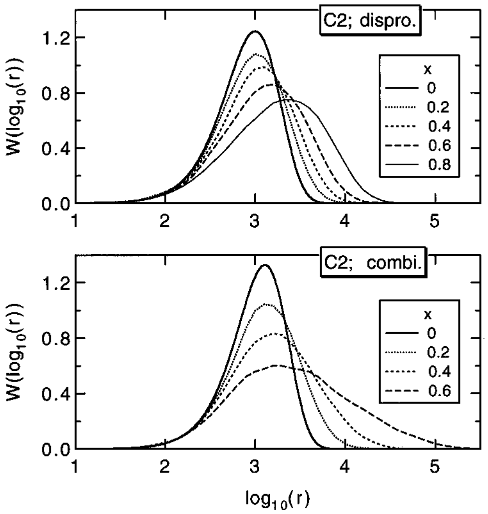

Figure 6. Weight fraction distribution development under condition C2.

As clearly shown in Figure 4, the combination termination makes the weight-average chain length significantly larger than the cases with disproportionation termination. In particular, gelation occurs at $x = 0.69$ under condition C2. The full MWD development is shown in Figures 5 and 6. The independent variable is taken as the logarithm of chain length, as usually used in a size exclusion chromatography (SEC) analysis. Combination termination reactions increase the high molecular weight tails significantly.

Figure 7 shows an example of the 2-dimensional structure of a branched polymer molecule formed under condition C2 at $x = 0.6$ with the existence of combination termination. The bold lines indicate the primary chains that form the H-shaped junctions, which can be considered cross-linkages.[23] The existence of cross-linkage increases the polymer size significantly even when its occurrence is not frequent. In the polymerization that involves cross-link formation, gelation may occur.

On the other hand, however, bimolecular termination in free-radical polymerization is a typical example of the diffusion-controlled reaction. Because the polymer diffusion is a function of polymer chain length, a logical consequence is that the bimolecular termination reac-

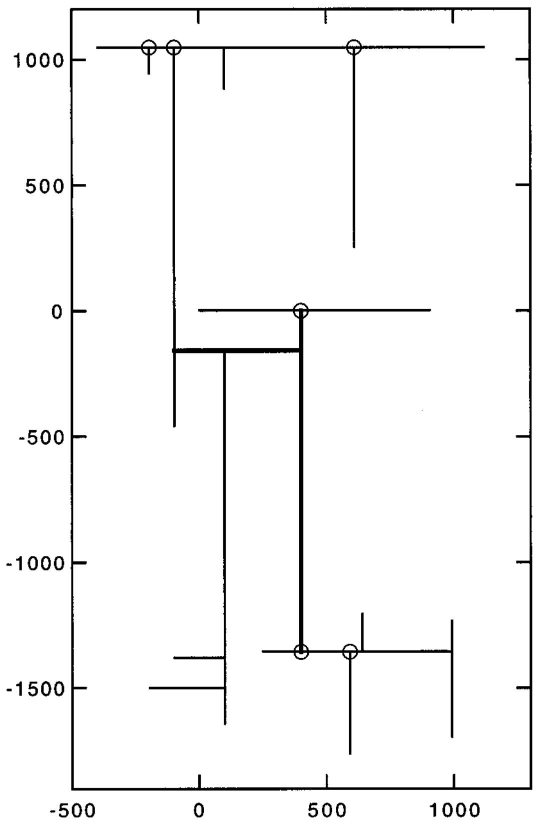

Figure 7. Example of a branched polymer molecule formed under condition C2 at $x = 0.6$ with the existence of combination termination. Both axes indicate the length in terms of the number of monomeric units. The branch points with circular symbols indicate those formed by TDBP. This polymer molecule consists of 16 primary chains, and the total chain length is 11 528.

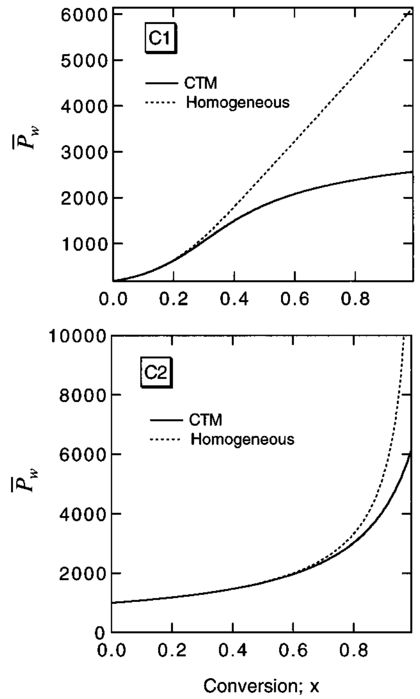

Figure 8. Weight-average chain length development under condition C1 and C2 in the absence of combination termination. The dotted curves show the weight-average chain length for the homogeneously branched polymers, when the branching density and the primary chain length distribution are the same as for C1 and C2, respectively.

tions are chain-length-dependent. When bimolecular terminations are chain-length-dependent, bimolecular termination events tend to be dominated by the interaction between short and long polymer radicals.[31−34] Therefore, the occurrence of the bimolecular termination events between large polymer radicals, which is very important to form large polymer molecules, might be reduced significantly. The present reaction system could be used to reveal the fundamental characteristics of the chain-length-dependent bimolecular termination reactions in nonlinear polymer systems.

Formation of Homogeneously Branched Polymers

In this section, we consider the cases without cross-link formation, i.e., polymerization without combination termination reactions. For homogeneously branched polymers, the weight-average chain length is given by[25]

$$\bar{P}_{w} = \frac{\bar{P}_{wp}}{(1 - \rho_{T}\bar{P}_{np})^{2}} \qquad (27)$$

where $\bar{P}_{np}$ and $\bar{P}_{wp}$ are the number- and weight-average chain length of the primary polymer molecules, respectively.

In the present simulation conditions, C1 and C2, the probability of possessing a branch point is the same for all units bound to polymer chains; however, the connections among primary chains are not random with respect to the birth conversions, as was discussed in part 1 of this series.[1] Because the primary chain length drift during polymerization is significant in the present reaction systems, the formed MWD is expected to be different from those formed in a random branching of primary chains.

Figure 8 shows the comparison of the weight-average chain length development. Equation 27 was used to calculate the weight-average chain length development for the homogeneously branched polymers (shown by dotted curves). When applying eq 27, we used the same primary chain length distribution and branching density as those for the corresponding copolymerizations; however, the nonrandom chain connection rule changes the $\bar{P}_w$ development significantly, as clearly shown in Figure 8. In the present examples, nonrandom connection among primary chains makes $\bar{P}_w$ smaller than the homogeneously branched structures for both cases.

As shown in part 1 of this series,[1] the homogeneously branched polymers are formed when the chain transfer constant is unity, i.e., $C_{fm} = C_{fp} = 1$. We now consider the following ideal conditions: $f_2^0 = 0.01$, $r_1 = r_2 = K = 1$, and $C_{fm} = C_{fp} = 1$. In the present case, if $(\nu_{td} + \nu_{tc})/\nu_p \ll C_{fm}f_2^0$, the effect of bimolecular terminations on the dead polymer chain formation can be neglected. Furthermore, the number-average chain length of the primary chains is always given by $\bar{P}_{np} = 1/(C_{fm}f_2^0)$ at any stage of polymerization, and the primary chain length drift during polymerization does not occur. The primary chain length distribution is given by the most probable distribution. Here, we consider such an ideal condition.

When the primary chains with the most probable distribution are connected randomly to form homogeneously branched polymers, the analytical solution for the full weight fraction distribution ($W(r)$) is

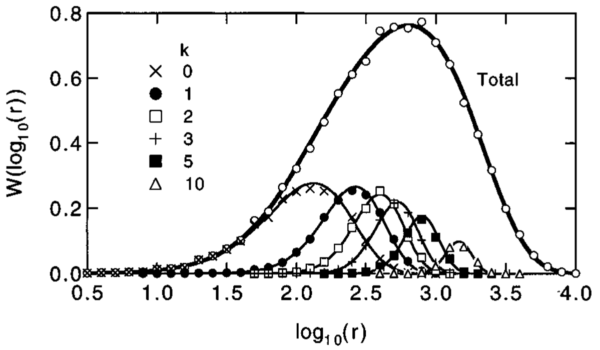

Figure 9. Weight fraction distribution formed under the ideal condition where homogeneously branched polymer molecules are formed, when the branching density is $\rho = 0.005$. The solid curves show the analytical solution given by eqs 28 and 29. The k values shown in the figure indicate the number of branch points in a polymer molecule.

given by[25,27]

$$W(r) = \left(\frac{1-\rho\bar{P}_{\mathrm{np}}}{\bar{P}_{\mathrm{np}}}\right)\left(\frac{I_1(2r\sqrt{\rho/\bar{P}_{\mathrm{np}}})}{\sqrt{\rho\bar{P}_{\mathrm{np}}}}\right)\exp\left\{-\left(\frac{\rho\bar{P}_{\mathrm{np}}+1}{\bar{P}_{\mathrm{np}}}\right)r\right\} \tag{28}$$

where I_m is the modified Bessel function of the first kind. Furthermore, the above equation can be fractionated by the number of branch points in each polymer to obtain the fractional weight-based distribution containing k branch points ($W_k(r)$), as shown below:[25,27]

$$W_k(r) = \left(\frac{1-\rho\bar{P}_{\mathrm{np}}}{\bar{P}_{\mathrm{np}}}\right)\exp\left\{-\left(\frac{\rho\bar{P}_{\mathrm{np}}+1}{\bar{P}_{\mathrm{np}}}\right)r\right\}\left(\frac{r}{\bar{P}_{\mathrm{np}}}\right)^{2k+1}\frac{(\rho\bar{P}_{\mathrm{np}})^k}{k!(k+1)!} \tag{29}$$

Obviously, $W(r)$ is given by

$$W(r) = \sum_{k=0}^{\infty} W_k(r) \tag{30}$$

Note that eqs 28 and 29 can be used only when the primary polymer molecules conform to the most probable distribution. Therefore, eqs 28 and 29 describe just one type of the homogeneously branched polymer systems.

Figure 9 shows the weight fraction distribution formed under the ideal conditions and the analytical solutions given by eqs 28 and 29. The k values shown in the figure indicate the number of branch points in a polymer molecule. The Monte Carlo simulation was conducted to produce 4×10^4 polymer molecules. The complete agreement shown here confirms that the branched structure formed under the ideal conditions gives a homogeneously branched polymer system.[35]

The homogeneously branched polymer molecules whose MWD is given by eqs 28 and 29 would be quite useful, because the analytical solution for the radius of gyration is given by the Zimm–Stockmayer equation.[36] Because very detailed structural information can be obtained, such polymer systems would be regarded as polymers with a well-defined branched structure and could be used as a polymer standard, for example, to prepare a calibration curve for the SEC analysis for branched polymer molecules.

In order to produce such a homogeneously branched polymer system, however, the condition $C_{\mathrm{fm}} = C_{\mathrm{fp}} = 1$ is not always required, because one obtains homogeneously branched polymers by preventing the primary chain length drift[37] under the conditions $r_1 = r_2 = K = 1$ and $C_{\mathrm{fm}} = C_{\mathrm{fp}}$. In the present system, the instantaneous primary chain length distribution is given by the most probable distribution in the absence of bimolecular termination by combination. For such cases, the whole primary chain length distribution conforms to the most probable distribution, if the primary chain length drift can be prevented. Without the primary chain length drift, the discrimination of primary chains with respect to the birth conversion is immaterial from the point of view of the resulting branched polymers.[38] In principle, the primary chain length drift could be suppressed, for example, by controlling the amount of chain transfer agents (not CTM) during polymerization. However, such reactor control may be difficult to carry out in real systems.

Another method to obtain a homogeneously branched polymer system would be to use a continuous stirred tank reactor. We have found that the homogeneously branched polymers that satisfy the distribution functions given by eqs 28 and 29 could be formed, at least approximately, irrespective of the reactivity ratios (r_1 and r_2) and terminal double-bond reactivity (K), provided the chain transfer constant is large enough.[39] Such reactor operations promise to produce the homogeneously branched polymers in real systems.

Conclusions

A new Monte Carlo simulation algorithm for the free-radical copolymerization with chain transfer monomer is proposed. The calculated results show that the bimolecular termination by combination can contribute to form very large polymer molecules, and even gelation may occur under certain conditions.

When the reactivity of all types of double bonds are equal, one may obtain branched polymer molecules whose branching densities are the same for all primary chains, irrespective of the magnitude of chain transfer constants. The MWD is, however, different from the homogeneously branched polymer molecules, except when $C_{\mathrm{fm}} = C_{\mathrm{fp}} = 1$ if the primary chain length drift cannot be neglected. On the other hand, in the absence of the primary chain length drift and combination termination, one obtains a homogeneously branched polymer system under the conditions $r_1 = r_2 = K = 1$ and $C_{\mathrm{fm}} = C_{\mathrm{fp}}$. The analytical solutions for both the fractional MWD containing k branch points and the full MWD can be obtained for such ideal cases.

Acknowledgment. I acknowledge financial support from the Ministry of Education, Science, Sports, and Culture, Japan, and the wonderful hospitality at the School of Chemistry, University of Sydney.

Glossary of Principal Symbols

C_{fm}	monomer chain transfer constant
C_{fp}	polymer chain transfer constant
F_2	instantaneous mole fraction of CTM bound to polymer chains by propagation reactions
f_1, f_2	mole fraction of M_1 and M_2, respectively
f_2^0	initial mole fraction of M_2
K	terminal double-bond reactivity
M_1	monomer whose chain transfer constant is much smaller than for the chain transfer monomer

M_2	chain transfer monomer (CTM)
[M]	total monomer concentration (=$[M_1] + [M_2]$)
$n_p(r,x)$	instantaneous number fraction distribution of the primary polymer radicals at conversion x
$P_{con}(\theta)$	probability that a primary polymer molecule born at $x = \theta$ is formed by combination termination
$P_{fm}(\theta)$	probability that a primary polymer molecule born at $x = \theta$ started growing from a monomer radical resulting from chain transfer to monomer
$P_{fp}(\theta)$	probability that a primary polymer molecule born at $x = \theta$ started growing from a radical center located on a backbone polymer chain resulting from chain transfer to polymer
$\bar{P}_n$, $\bar{P}_w$	number- and weight-average chain length, respectively
$\bar{P}_{np}$, $\bar{P}_{wp}$	number- and weight-average chain length of the primary polymer molecules, respectively
$Q_i^{=}$, Q_i'	*i*th order moment of polymers with and without a terminal double bond, respectively
Q_i	*i*th order moment of total polymers, $Q_i = Q_i^{=} + Q_i'$
$[R^{\bullet}]$	total radical concentration
r_1, r_2	reactivity ratios, $r_1 = k_{p,11}/k_{p,12}$ and $r_2 = k_{p,22}/k_{p,21}$
v_{fm}, v_{fp}, v_{fT}	rates of chain transfer reactions to monomer, polymer, and chain transfer agents, respectively
v_p, v^*	propagation (polymerization) rate and the rate of terminal double-bond polymerization, respectively
v_{td}, v_{tc}	rates of bimolecular termination by disproportionation and by combination, respectively
$w_p(r,x)$	instantaneous weight fraction distribution of the primary polymer radicals at conversion x
$W(r)$	weight fraction distribution
x	conversion

Greek Letters

$\Phi^{=}(\theta,\psi)$	fraction of terminal double bonds within the units bound to polymer chains at $x = \theta$, when the present conversion is $x = \psi$
θ	conversion at which the given primary polymer molecule was born (birth conversion)
$\rho(\theta,\psi)$	expected branching density of the primary polymer molecules born at $x = \theta$ formed by CTP, when the present conversion is $x = \psi$
$\rho^*(\theta)$	expected branching density of the primary chains born at $x = \theta$ formed by TDBP
ψ	conversion at the present time (present conversion)

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MA960781H