Random Sampling Technique To Predict the Molecular Weight Distribution in Free-Radical Polymerization That Involves Polyfunctional Chain Transfer Agents

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ABSTRACT: A random sampling technique in which polymer molecules are sampled from an infinite number of polymer molecules in the reaction mixture is used to predict the molecular weight distribution (MWD) development during free-radical polymerization that involves polyfunctional chain transfer agents (P-CTAs). For an ideal case where the chain transfer constant is unity and chain stoppage is dominated by chain transfer reactions, the analytical solutions for the full MWD as well as the average molecular weights can be derived in a straightforward manner. For more complex reaction systems where nonrandom history-dependent kinetics is important due to bimolecular termination reactions and the substitution effect of the P-CTAs, the Monte Carlo simulation on the basis of the random sampling technique enables one to estimate the statistical property development quite effectively. When bimolecular termination reactions and/or the substitution effects are involved, the MWD does not necessarily become narrower with polymerization in contrast with the ideal case. The decreased reactivity of the functional groups in a P-CTA due to the substitution effect may increase or decrease the average molecular weights depending on the magnitude of the chain transfer constant, concentration of P-CTA, the mode of bimolecular termination (disproportionation or combination), and the degree of the substitution effect.

1. Introduction

Nonlinear polymerizations provide an attractive research field combining at the same time fundamental and applied topics of great interest, and various mathematical models have been proposed. In general, however, analytical solutions for the molecular weight development have been obtained only for equilibrium reaction systems; i.e., the most probable connection of primary chains can be assumed.[1−9] On the other hand, however, free-radical polymerization is kinetically controlled; therefore, one has to account for the nonrandom history-dependent nonlinear structure formation properly.

The Monte Carlo method is a versatile technique that can handle complicated phenomena in a straightforward manner, provided each kinetic process, or the transition probabilities, can be defined explicitly. Monte Carlo simulations in a finite reaction system in order to represent an infinite system approximately have been applied extensively to analyze complex reaction systems.[10−18] In this method, a very small part is cut out from the reaction mixture and the kinetic behavior of all of the molecules involved in this small volume is simulated. However, once a very small reaction volume is isolated, a subtle problem concerning the effect of system boundary that does not exist in an infinite system must be considered carefully. Especially, when one needs to calculate the molecular weight distribution (MWD), the system size must be much larger than the largest polymer molecule in the finite reaction system.[19]

A certain type of finiteness is required in Monte Carlo computer simulations due to a limited memory size of a computer. Monte Carlo simulations that employ sampling techniques have been proposed recently in order to make simulations for free-radical and living cross-linking copolymerization,[20−22] random cross-linking and degradation of polymer chains,[9,23,24] and free-radical polymerization with long-chain branching due to chain transfer to polymer and the terminal double bond polymerization.[19,25−28] In this method, the system size considered is infinitely large but instead the number of polymer molecules sampled from the reaction mixture is finite. This simulation method enables one to account for the kinetics of nonrandom history-dependent structure formation quite rigorously and can be applied irrespective of the reactor types used. Another notable advantage of this method is that it is possible to examine the structure of each polymer molecule directly. As a consequence, such statistical properties as the fractal dimensions and the radii of gyration can be determined in a straightforward manner.[22,27,28]

The fundamental idea of the random sampling technique is quite simple; i.e., we select a large number of polymer molecules randomly from the "sea" of polymer molecules. Consider a linear polymer system for simplicity. The number fraction distribution is obtained if one samples polymer molecules by selecting chain ends randomly, as shown in Figure 1a, and the expected chain length is the number-average degree of polymerization. On the other hand, the selection on a weight basis may be visualized as in Figure 1b. Suppose all polymer molecules are embedded into two-dimensional space so that each monomeric unit occupies one measure, and select one measure randomly, such as by throwing a dart. When a monomeric unit bound into a polymer molecule is selected randomly, the polymer molecule that involves this particular unit follows the weight fraction distribution, and the expectation is the weight-average degree of polymerization. We throw a "dart" at the nonlinear polymer mixture a large number of times and take a set of polymer samples to estimate the statistical properties of the reaction system. This concept is useful not only to make Monte Carlo simulations but also to obtain analytical solutions for simpler cases.[24,29]

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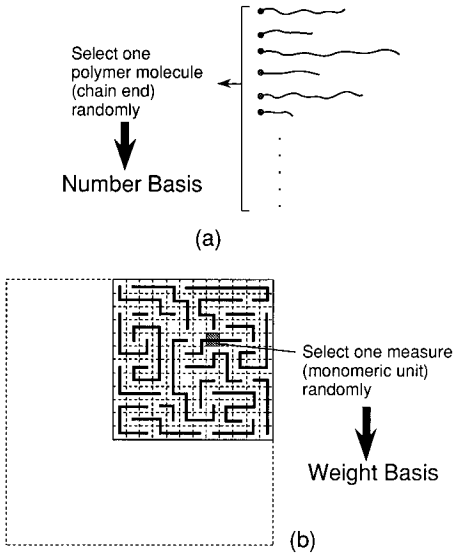

Figure 1. Concept of the molecular weight distribution on the number and weight basis from the point of view of the random sampling technique.

In this paper, we consider the free-radical polymerization that involves a polyfunctional chain transfer agent (P-CTA), which consists of the following elementary reactions, i.e., initiation, propagation (rate constant, k_p), chain transfer to P-CTAs (k_{fT}), bimolecular termination by disproportionation (k_{td}), and that by combination (k_{tc}). By using P-CTA, it is possible to obtain star-shaped polymers in the absence of bimolecular termination by combination. When combination termination is involved, one may obtain cross-linked polymer molecules.

Ullisch and Burchard[30] developed fundamental equations to calculate the average degree of polymerization development during such free-radical polymerizations on the basis of the cascade theory. Unfortunately, however, their use of the average connection probabilities cannot be used for the kinetically controlled systems.[28] Their method is valid only when the link probability is the same for all molecular species; i.e., their predicted structure would be obtained only when all links are cut at a given conversion level and then all polymer molecules are rebuilt on the basis of the most probable connection of molecules, by employing the average link probability. Therefore, their method cannot be applied for the present reaction system.

On the other hand, Yuan et al.[31,32] developed fundamental equations to calculate the full chain length distribution under limited conditions. They considered cases where bimolecular termination reactions can be neglected in terms of the molecular weight development. They obtained analytical solutions for an ideal case[31] in which the chain transfer constant $C_{fT} = k_{fT}/k_p = 1$. They also presented fundamental equations[32] for the cases with $C_{fT} < 1$. In this paper, we propose simulation algorithms that can treat much more general cases that include bimolecular termination reactions and the substitution effect of the functional groups in a P-CTA.

2. Ideal Case

First, we consider an ideal case in which the chain transfer constant, $C_{fT} = 1$ and the chain transfer reactions dominate the dead polymer chain formation, as was considered by Yuan et al.[31] Under these simplified conditions, the formed nonlinear structure is exactly the same as those formed under an equilibrium condition; i.e., nonrandom history-dependent kinetics do not play a role in this simplified reaction system. The analytical solution for the full MWD has already been derived by application of the generating functions.[31] However, consideration of the present reaction system provides a deeper understanding of the concept of the random sampling technique. In this section, we show how the analytical solution can be derived and how the Monte Carlo simulation algorithm can be formulated, and the fundamental concept of the present method is highlighted.

Primary Chain Length Distribution. In the present case, the chain length distribution of the primary polymer molecules is given by the following most probable distribution. The number ($n_p(r)$) and weight ($w_p(r)$) fraction distribution are given by

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

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

where r is the chain length (degree of polymerization), and the probability of chain growth due to propagation, p, is given by

$$p = \frac{R_p}{R_p + R_{fT}} = \frac{k_p[M]}{k_p[M] + k_{fT}[T]} \tag{3}$$

where R_p is the polymerization rate, R_{fT} is the rate of chain transfer to the chain transfer agent (T), [M] is the monomer concentration, and [T] is the concentration of the unreacted functional groups in the P-CTAs. Under the present reaction condition ($C_{fT} = 1$), [T] is simply given by

$$[T] = [T]_0(1-x) \tag{4}$$

where the subscript 0 is used to designate the initial concentration and x is the monomer conversion to polymer. By substituting eq 4 into eq 3, one obtains

$$p = \frac{k_p[M]_0(1-x)}{k_p[M]_0(1-x) + k_{fT}[T]_0(1-x)}$$

$$= \frac{1}{1 + ([T]_0/[M]_0)} \equiv \frac{1}{1+\gamma_0} \tag{5}$$

which means that the probability of growth, p, is unchanged during the whole course of polymerization, and therefore, the primary chain length distribution does not change throughout the polymerization under the present simplified condition.

The number- ($\bar{P}_{np}$) and weight-average ($\bar{P}_{wp}$) chain length of the primary polymer molecules is given by

$$\bar{P}_{np} = \frac{1}{1-p} \tag{6}$$

$$\bar{P}_{wp} = \frac{1+p}{1-p} \tag{7}$$

Weight-Average Degree of Polymerization. When one selects one monomeric unit randomly from all monomeric units bound into polymer chains, the expected degree of polymerization of the polymer molecule that involves this particular unit is the weight-average degree of polymerization, $\bar{P}_W$.

For example, consider the case with the four-functional chain transfer agent ($f = 4$). (See Figure 2.) The probability that the polymer molecule consists of one

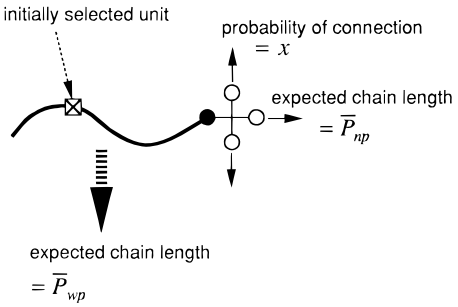

Figure 2. Schematic representation to calculate the weight-average degree of polymerization for the ideal case with four-functional chain transfer agents.

arm, i.e., the given polymer molecule is a linear polymer with a chain transfer agent at the end whose other three functional groups are unreacted, is given by

$$P(1) = \binom{3}{0}(1-x)^3 \tag{8}$$

Note that the probability of the consumption of a functional group in the P-CTA is equal to the monomer conversion, x, in the present case, as shown in eq 4.

The probability that the selected polymer molecule is a two-arm polymer is

$$P(2) = \binom{3}{1}x(1-x)^2 \tag{9}$$

Similarly

$$P(3) = \binom{3}{2}x^2(1-x) \tag{10}$$

$$P(4) = \binom{3}{3}x^3 \tag{11}$$

The expected chain length of the initially selected primary polymer molecule shown in Figure 2 is the weight-average chain length of the primary polymer molecules, $\bar{P}_{wp}$. On the other hand, the primary polymer molecule connected from the four-functional CTA must be selected by the chain end, and therefore, the expected primary chain length is $\bar{P}_{np}$, not $\bar{P}_{wp}$. As a consequence, the expectation of the chain length of the whole polymer molecule is given by

$$\bar{P}_W = \bar{P}_{wp}\binom{3}{0}(1-x)^3 + (\bar{P}_{wp} + \bar{P}_{np})\binom{3}{1}x(1-x)^2 + (\bar{P}_{wp} + 2\bar{P}_{np})\binom{3}{2}x^2(1-x) + (\bar{P}_{wp} + 3\bar{P}_{np})\binom{3}{3}x^3 \tag{12}$$

In general, for an f-functional CTA

$$\bar{P}_W = \sum_{i=0}^{f-1}(\bar{P}_{wp} + i\bar{P}_{np})\binom{f-1}{i}x^i(1-x)^{f-1-i} = \bar{P}_{wp}\sum_{i=0}^{f-1}\binom{f-1}{i}x^i(1-x)^{f-1-i} + \bar{P}_{np}\sum_{i=0}^{f-1}i\binom{f-1}{i}x^i(1-x)^{f-1-i} \tag{13}$$

The first summation in the right-hand side of eq 13 is the sum of the binomial distribution that is equal to unity, while the second summation is the expectation of the binomial distribution that is equal to $(f-1)x$. Therefore

$$\bar{P}_W = \bar{P}_{wp} + (f-1)x\bar{P}_{np} \tag{14}$$

Equation 14 can also be obtained on the basis of the following argument. The expected weight of the initially selected primary chain is $\bar{P}_{wp}$, while that for an additional primary chain connected to the P-CTA molecule is $\bar{P}_{np}$. Because the expected number of the additional branches is $(f-1)x$, the expected weight of the whole polymer molecule ($\bar{P}_W$) is $\bar{P}_{wp} + (f-1)x\bar{P}_{np}$.

In the present case, the number- and weight-average chain length of the primary polymers are given by eqs 6 and 7, and therefore, eq 14 becomes

$$\bar{P}_W = \frac{1+p+(f-1)x}{1-p} \tag{15}$$

Number-Average Degree of Polymerization. The number-average degree of polymerization can be obtained simply by counting the number of polymer molecules in the reaction mixture.

$\bar{P}_N$ = (total no. of monomeric units bound into polymer molecules)/(total no. of polymer molecules)

$$= \frac{[M]_0 x}{[CTA]_0\sum_{i=1}^{f}\binom{f}{i}x^i(1-x)^{f-i}} = \frac{[M]_0 x}{[CTA]_0\{1-(1-x)^f\}}$$

$$= \frac{fpx}{(1-p)\{1-(1-x)^f\}} \tag{16}$$

where $[CTA]_0$ is the initial concentration of P-CTA ($[CTA]_0 = [T]_0/f$) and $\gamma_0 = [T]_0/[M]_0 = (1-p)/p$.

Polydispersity Index ($\bar{P}_W/\bar{P}_N$). The polydispersity index (PDI) is calculated from eqs 15 and 16:

$$\frac{\bar{P}_W}{\bar{P}_N} = \frac{1}{fpx}\{1+p+(f-1)x\}\{1-(1-x)^f\} \tag{17}$$

When $x \to 1$, all polymer molecules are f-armed polymers and the PDI is given by

$$\frac{\bar{P}_W}{\bar{P}_N} = \frac{f+p}{fp} \xrightarrow[p\to 1]{} 1 + \frac{1}{f} \tag{18}$$

Equation 18 was developed for multichain polymers in a condensation reaction a long time ago on the basis of the consideration of the full MWD function.[33] As a more general example, consider the case where the star-shaped polymer molecules with f arms are formed from the primary polymer molecules whose number- and weight-average chain lengths are given by $\bar{P}_{np}$ and $\bar{P}_{wp}$, respectively. First of all, because the connection with f-functional units makes the number-average chain length f times larger than the primary polymer molecules, $\bar{P}_N = f\bar{P}_{np}$. As was shown in Figure 2, because the partner of the coupling process must be selected on the number basis, $\bar{P}_W = \bar{P}_{wp} + (f-1)\bar{P}_{np}$. The PDI for this case is simply given by

$$\frac{\bar{P}_W}{\bar{P}_N} = \frac{1}{f}\left(f - 1 + \frac{\bar{P}_{wp}}{\bar{P}_{np}}\right) \tag{19}$$

When the primary polymer molecules conform to the most probable distribution, $\bar{P}_{wp}/\bar{P}_{np} \cong 2$, and eq 19 reduces to eq 18. Incidentally, Guaita et al.[34] considered the case with $f = 2$ and obtained the polydispersity index

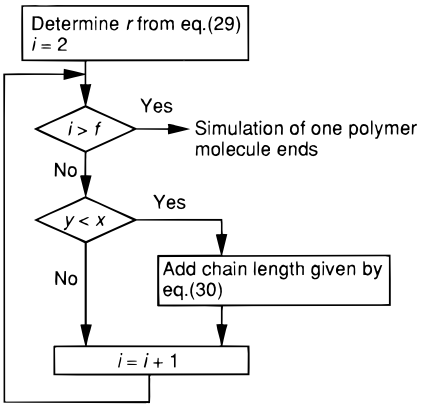

Figure 3. Simulation algorithm for the ideal case.

on the basis of the population balance equations. With the use of the random sampling technique, the derivation is rather straightforward, as shown here.

Weight Fraction Distribution. The whole weight fraction distribution ($W(r)$) consists of the fractional weight fraction distributions containing 1, 2, ..., f arms:

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

Note that every primary chain possesses one P-CTA unit in the present ideal case. First, we consider the fractional weight-based distribution containing i arms, $W_i(r)$.

By referring to Figure 2, the initially selected primary polymer molecule follows the weight fraction distribution of the primary polymer molecules given by eq 2. The fractional weight fraction distribution containing only one arm is given by

$$W_1(r) = \binom{f-1}{0}(1-x)^{f-1} w_p(r) = \binom{f-1}{0}(1-x)^{f-1} r p^{r-1}(1-p)^2 \tag{21}$$

If one of the $(f-1)$ functional groups of the P-CTA connected to the initially selected primary polymer molecule is linked to another primary polymer molecule, a two-arm polymer is formed. Suppose our randomly selected unit belongs to a primary polymer whose chain length is s ($s < r$). A polymer molecule with two arms whose degree of polymerization is r can be obtained if the chain length of the connected chain, which is also selected randomly, is $r - s$. Since the connected primary polymer molecule must be selected on the number basis, $W_2(r)$ is given by

$$\begin{aligned} W_2(r) &= \binom{f-1}{1} x(1-x)^{f-2} \sum_{s=1}^{r-1} w_p(s) n_p(r-s) \\ &= \binom{f-1}{1} x(1-x)^{f-2} p^{r-2}(1-p)^3 \sum_{s=1}^{r-1} s \\ &= \binom{f-1}{1} x(1-x)^{f-2} p^{r-2}(1-p)^3 \binom{r}{2} \end{aligned} \tag{22}$$

Similarly, for three-arm polymers

$$\begin{aligned} W_3(r) &= \binom{f-1}{2} x^2(1-x)^{f-3} \times \sum_{s=1}^{r-2} \{ w_p(s) \sum_{t=1}^{r-s-1} n_p(t) n_p(r-s-t) \} \\ &= \binom{f-1}{2} x^2(1-x)^{f-3} p^{r-3}(1-p)^4 \binom{r}{3} \end{aligned} \tag{23}$$

In general, for i-arm polymers

$$W_i(r) = \binom{f-1}{i-1} x^{i-1}(1-x)^{f-i} \times \sum\nolimits_{\sum_{j=1}^{i} s_j = r} w_p(s_1) n_p(s_2) n_p(s_3) \ldots n_p(s_i) \tag{24}$$

where $\sum_{\sum_{j=1}^{i} s_j = r}$ means that the summation is taken for all possible combinations of positive integers s_j under restriction, $\sum_{j=1}^{i} s_j = r$.

$$\sum\nolimits_{\sum_{j=1}^{i} s_j = r} w_p(s_1) n_p(s_2) n_p(s_3) \ldots n_p(s_i) = p^{r-i}(1-p)^{i+1} \sum\nolimits_{\sum_{j=1}^{i} s_j = r} s_1 \tag{25}$$

$$\sum\nolimits_{\sum_{j=1}^{i} s_j = r} s_1 = \sum_{s_1=1}^{r-i+1} s_1 \binom{r-s_1-1}{i-2} = \sum_{s_1=1}^{r-i+1} \binom{s_1}{1} \binom{r-s_1-1}{i-2} = \binom{r}{i} \tag{26}$$

The derivation of eq 26 is shown in Appendix A. From eqs 24−26, one obtains

$$W_i(r) = \binom{f-1}{i-1} x^{i-1}(1-x)^{f-i} p^{r-i}(1-p)^{i+1} \binom{r}{i} \tag{27}$$

The whole distribution can be calculated by using eq 20. Equation 27 was derived by Yuan et al.[31] by using the generating functions (although a typographical error exists in eq A-13 of ref 31). The application of the random sampling technique makes it possible to derive the same equation just arithmetically.

Monte Carlo Sampling Technique. The analytical solution has already been obtained, so that no Monte Carlo simulations are required to predict the MWD. However, in order to clarify the concept of the simulation method especially for more complex cases shown later, we briefly discuss the simulation algorithm for this simple case.

When one selects a monomeric unit bound into polymer molecules randomly, as shown in Figure 2, the primary polymer molecule that includes this particular unit follows the weight-based chain length distribution of the primary polymer molecules, $w_p(r)$. Therefore, the chain length r of the selected primary chain can be determined by solving the following equation:

$$y = \sum_{s=1}^{r} w_p(s) \tag{28}$$

where y is a random number between 0 and 1. When w_p is the most probable distribution, the chain length r can be determined directly from the following transformation by using two random numbers y_1 and y_2 (see Appendix B):

$$r = \text{ceiling}\left[\frac{\ln(y_1)}{\ln(p)}\right] + \text{ceiling}\left[\frac{\ln(y_2)}{\ln(p)}\right] - 1 \tag{29}$$

where celing [a] indicates the closest integer greater than a.

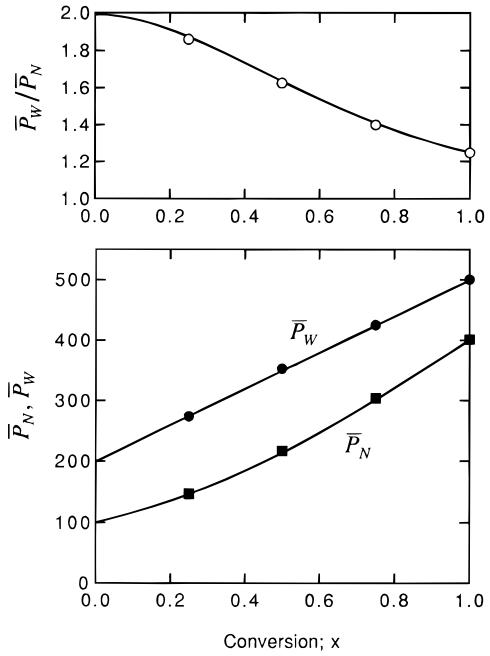

Figure 4. Number- ($\bar{P}_N$) and weight-average ($\bar{P}_W$) degree of polymerization development under the ideal condition with four-functional chain transfer agents. The curves are calculated from eqs 15−17, while the keys are the simulated results.

The probability that a functional group in the P-CTA molecule connected at the end of this primary chain has reacted is equal to the monomer conversion (see eq 4). The chain length distribution of the connected primary chains conforms to the number-based chain length distribution of the primary polymer molecules, because chain ends are selected randomly. Therefore, they can be determined by (see Appendix B)

$$r = \text{ceiling}\left[\frac{\ln(y)}{\ln(p)}\right] \tag{30}$$

The simulation algorithm is shown in Figure 3.

Calculated Results. We examine the ideal case with $f = 4$ and $p = 0.99$. Figure 4 shows the average degree of polymerization development. The solid curves are the analytical solutions that are given by eqs 15−17, while the keys are the simulated results by employing the Monte Carlo sampling technique. The simulation was conducted for 2×10^4 polymer molecules at each conversion level. The accuracy of the simulated results is satisfactory. The present results clearly show that the MWD becomes narrower as the polymerization proceeds.

Figure 5 shows the weight fraction distribution of the whole polymer molecules and the fractional weight-based distribution containing i arms. Again, the agreement is satisfactory, and the Monte Carlo sampling technique can provide an accurate estimation for the infinite reaction system.

3. Effect of Bimolecular Termination

In general, the primary chain length distribution changes during polymerization, which must be accounted for in the simulation. In free-radical polymerization, linear polymer chains are formed within a few seconds, while it usually takes several hours to obtain a high conversion of monomer to polymer. Therefore, it is reasonable to consider that each primary polymer molecule is formed instantaneously and that the probability of connecting the neighboring unit is the same

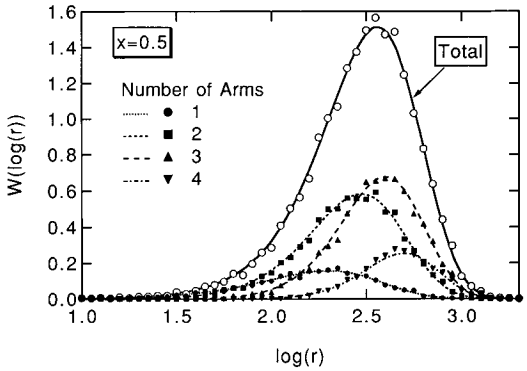

Figure 5. Weight fraction distribution formed under the ideal condition at $x = 0.5$. The curves are calculated from eq 27, while the keys indicate the simulated results.

for all units in the given primary chain. The chain length distribution of the primary polymer radicals that exist at conversion x is given by

$$n^{\bullet}_{p}(r) = p(x)^{r-1}[1 - p(x)] \tag{31}$$

$$w^{\bullet}_{p}(r) = rp(x)^{r-1}[1 - p(x)]^2 \tag{32}$$

where the probability of growth at conversion x, $p(x)$, is given by

$$\begin{aligned} p(x) &= \frac{R_p(x)}{R_p(x) + R_f(x) + R_t(x)} \\ &= \frac{k_p[\mathrm{M}]}{k_p[\mathrm{M}] + k_{fT}[\mathrm{T}] + (k_{td} + k_{tc})[\mathrm{R}^{\bullet}]} \\ &= \frac{1}{1 + C_{fT}\gamma(x) + \tau(x) + \beta(x)} \end{aligned} \tag{33}$$

where $\gamma(x) = [\mathrm{T}]/[\mathrm{M}]$, $\tau(x) = (k_{td}[\mathrm{R}^{\bullet}])/(k_p[\mathrm{M}])$, $\beta(x) = (k_{tc}[\mathrm{R}^{\bullet}])/(k_p[\mathrm{M}])$, and $[\mathrm{R}^{\bullet}]$ is the polymer radical concentration. As long as the chain-length dependence of bimolecular termination reactions is neglected, the probability that a given primary polymer radical stops growing is the same for all polymer radicals that exist at a given moment.

The Monte Carlo sampling technique for the present reaction system can be conducted as follows. Consider the polymer mixture at the present time when the monomer conversion is $x = \Psi$. We select one unit from all units bound into polymer molecules. If we use the monomer conversion x as an independent variable, the weight of polymer formed in the conversion interval Δx is the same irrespective of the conversion level. The birth conversion of the primary polymer molecule that involves this randomly selected monomeric unit, θ, can simply be determined by selecting the birth conversion θ from 0 to Ψ randomly.

Once the birth conversion of the initially selected primary polymer molecule is determined, the chain length of this primary polymer molecule can be determined from

$$r' = \text{ceiling}\left[\frac{\ln(y_1)}{\ln(p(\theta))}\right] + \text{ceiling}\left[\frac{\ln(y_2)}{\ln(p(\theta))}\right] - 1 \tag{34}$$

If this primary chain is formed via chain transfer or bimolecular termination by disproportionation, the dead primary polymer chain is still equal to r'. The probability for such events to occur is

$$P_\tau(\theta) = \frac{C_{f\mathrm{T}}\gamma(\theta) + \tau(\theta)}{C_{f\mathrm{T}}\gamma(\theta) + \tau(\theta) + \beta(\theta)} \quad (35)$$

On the other hand, if this primary chain is formed via bimolecular termination by combination, whose probability is $P_\beta(\theta) = 1 - P_\tau(\theta)$, the dead primary polymer chain length is given by the following equation, because the coupled polymer radical must be selected on a number basis:

$$r = r' + \mathrm{ceiling}\left[\frac{\ln(y)}{\ln(p(\theta))}\right] \quad (36)$$

The probability that this primary polymer molecule starts growing from a P-CTA is given by

$$P_{\mathrm{CTA}}(\theta) = \frac{R_f(\theta)}{R_\mathrm{I}(\theta) + R_f(\theta)} = \frac{C_{f\mathrm{T}}\gamma(\theta)}{\tau(\theta) + \beta(\theta) + C_{f\mathrm{T}}\gamma(\theta)} \quad (37)$$

where R_I is the initiation rate that is equal to the termination rate at the stationary state. When this particular primary polymer molecule is formed via bimolecular termination by combination, both chain ends are the starting points for the chain growth, so that the above probability must be examined for both chain ends.

Suppose our randomly selected primary chain is connected to a P-CTA molecule. The probability that another functional group in this P-CTA molecule has reacted until the conversion, $x = u$, is given by

$$P_{\mathrm{react}}(u) = ([\mathrm{T}]_0 - [\mathrm{T}])/[\mathrm{T}]_0 = 1 - (1 - u)^{C_{f\mathrm{T}}} \quad (38)$$

Therefore, the conversion at which the given functional group reacts to connect the primary chain can be determined by equating eq 38 to a random number y between 0 and 1, namely

$$u = 1 - y^{(1/C_{f\mathrm{T}})} \quad (39)$$

If $u > \Psi$, the given functional group is unreacted at the present conversion, $x = \Psi$.

The chain length of the primary polymer radical connected to this P-CTA molecule just before dead primary molecule formation conforms to $n^\bullet_\mathrm{p}(r')$; therefore, it can be determined from

$$r' = \mathrm{ceiling}\left[\frac{\ln(y)}{\ln(p(u))}\right] \quad (40)$$

The probability that this primary polymer molecule is formed via bimolecular termination by combination is given by $P_\beta(u)$. If this event occurs, the chain length of the dead primary chain is given by

$$r = r' + \mathrm{ceiling}\left[\frac{\ln(y)}{\ln(p(u))}\right] \quad (41)$$

In such cases, the possibility that the other chain end is connected must be examined by using the probability $P_{\mathrm{CTA}}(u)$.

By repeating the above processes until no more primary chains are connected, the structure of one polymer molecule can be determined. The whole simulation algorithm is shown in Figure 6.

Simulation Results. We investigate the conditions shown in Table 1. The initial molar ratio, $\gamma_0 = [\mathrm{T}]_0/[\mathrm{M}]_0 = 1 \times 10^{-3}$ and $f = 4$ are the same for all conditions.

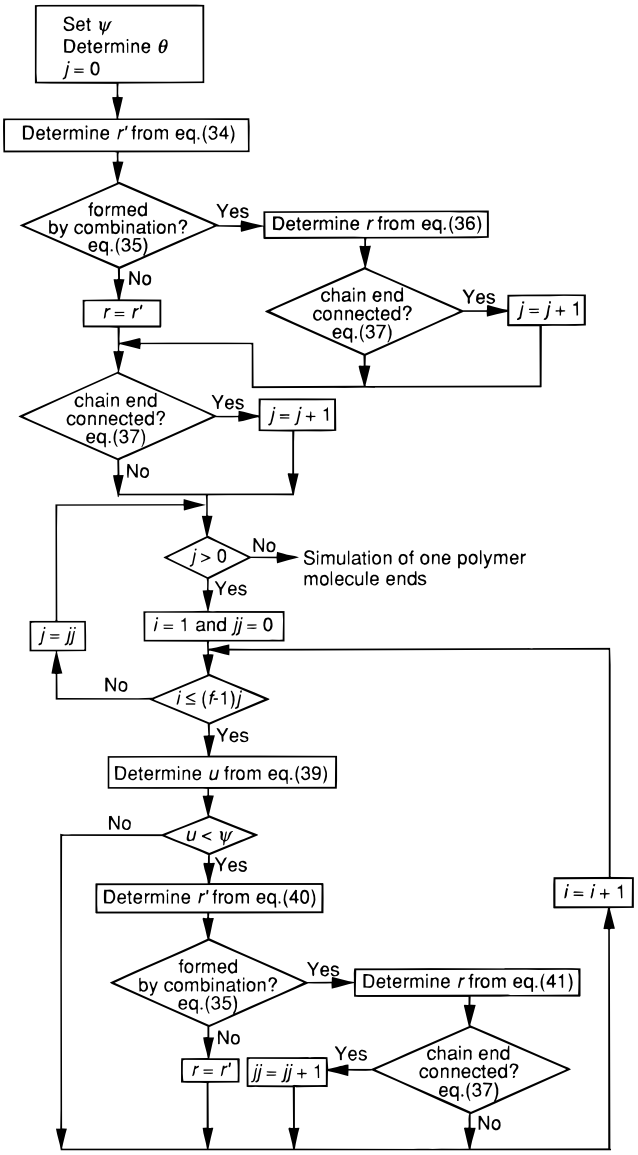

Figure 6. Simulation algorithm that accounts for bimolecular termination reactions.

Table 1. Calculation Conditions Investigated[a]

	$C_{f\mathrm{T}}$	β	τ
C1	1	1×10^{-3}	0
D1	1	0	1×10^{-3}
C2	10	1×10^{-3}	0
D2	10	0	1×10^{-3}

[a] The initial molar ratio is $\gamma_0 = [\mathrm{T}]_0/[\mathrm{M}]_0 = 1 \times 10^{-3}$, and $f = 4$. $C_{f\mathrm{T}} = k_{f\mathrm{T}}/k_\mathrm{p}$, $\beta = R_{\mathrm{tc}}/R_\mathrm{p}$, $\tau = R_{\mathrm{td}}/R_\mathrm{p}$, R_p is the polymerization rate, R_{tc} is the rate of bimolecular termination by combination, and R_{td} is that by disproportionation.

In general, the parameters τ and β change with conversion; however, the change is dependent on the chemical systems used as well as the reaction conditions, especially at high conversions where the gel effect tends to become significant. In this paper, in order to understand the general characteristics of using P-CTAs, we use constant τ and β values, (although it is straighforward to account for the drift of the parameters in the Monte Carlo simulations). Simulations were made for 5×10^3 polymer molecules to calculate the average degree of polymerizations, while 2×10^4 polymer molecules were simulated to estimate the full MWD profile.

Figure 7 shows the average degree of polymerization development under condition C1 and D1 where $C_{f\mathrm{T}} =$

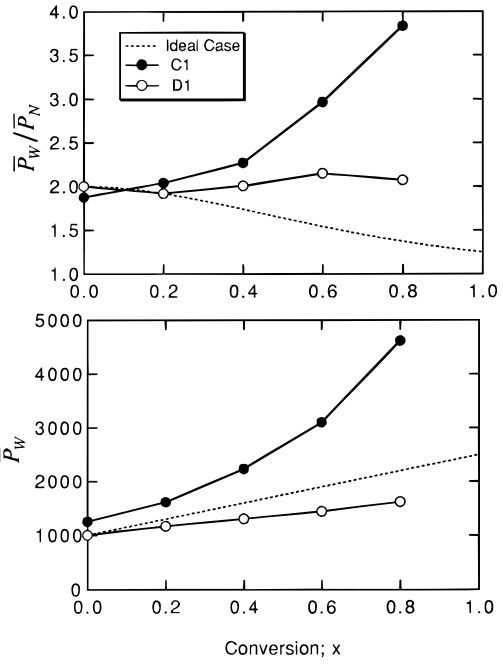

Figure 7. Number- ($\bar{P}_N$) and weight-average ($\bar{P}_W$) degree of polymerization development under conditions C1 (lines with closed circles) and D1 (lines with open circles) as well as the ideal case (broken curves).

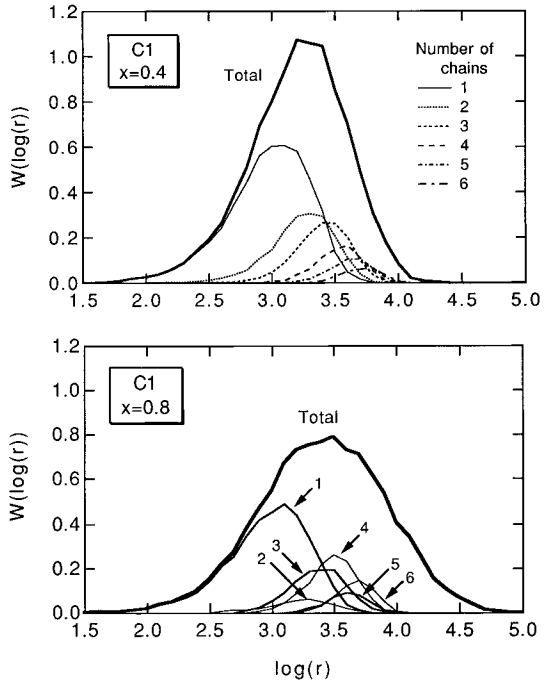

Figure 8. Weight fraction distribution formed under condition C1 at conversion, $x = 0.4$ and 0.8.

1. The broken curves show the ideal case with $C_{fT} = 1$, $\tau = \beta = 0$, and $\gamma_0 = 2 \times 10^{-3}$. Under condition D1, the weight average degree of polymerization is smaller than the ideal case due to the formation of linear polymer chains that start growing from the initiator fragments rather than the P-CTA molecules. Production of linear polymer chains makes the distribution broader, as shown in the larger polydispersity index.

Under condition C1 in which bimolecular termination by combination is involved, the weight-average degree of polymerization increases significantly as the reaction proceeds. This is due to the formation of cross-linking via combination termination of polymer radicals that both started growing from the P-CTA molecules. As a consequence, the polydispersity index becomes much larger than 2. Figure 7 clearly shows that when bimolecular termination reactions are involved, the MWD becomes broader than the ideal case irrespective of the mode of termination.

Figure 8 shows the weight fraction distribution formed under condition C1. A large weight fraction of linear polymers exists throughout the polymerization. The polymer molecules that consist of more than four arms must involve more than one P-CTA molecule, which means that they possess chains that form cross-linkage between P-CTA molecules. At the higher conversion with $x = 0.8$, the weight fraction of polymers that consist of two chains is smaller than that for both one-chain and three-chain polymers, and the weight fraction of polymers with five chains is smaller than that for both four-chain and six-chain polymers. This type of disordering with respect to the number of chains is caused by a higher conversion of functional groups in the P-CTA molecules; i.e., it is unlikely to form branched polymers carrying a large number of unreacted functional groups.

A notable advantage of conducting the present computer simulation is that one can observe the structure of each polymer molecule directly. An example of the two-dimensional structure of the polymer molecule that exists at $x = 0.8$ under condition C1 is shown in Figure

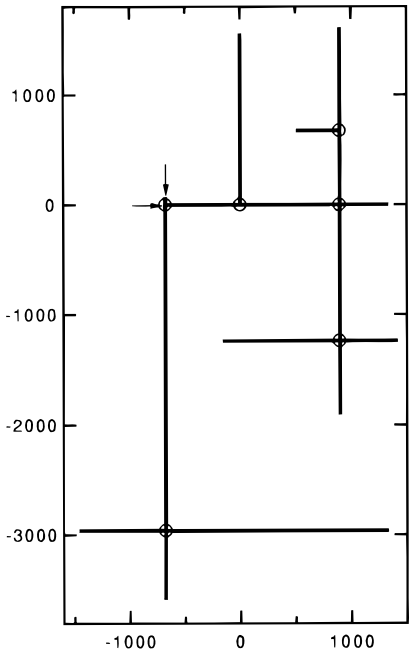

Figure 9. Example of a branched polymer molecule embedded in the two-dimensional space formed under condition C1 at $x = 0.8$. The length of one monomeric unit is drawn as a unit length in the figure. The arrows are used to help find the locations of the chains whose lengths are smaller than 100. This polymer molecule consists of 17 chains with 6 P-CTA molecules (shown by the circles), and the degree of polymerization is 15 315.

9. This polymer molecule contains 6 P-CTA molecules with 17 primary chains. Under this calculation condition, the chain length distribution of the primary polymer molecules is unchanged throughout the polymerization; however, it can be seen that primary chains with significantly different chain lengths are incorporated into the branched polymer molecule. On the basis of the simulated spatial distributions, it is straightforward to investigate such properties as the radii of gyration and the fractal dimensions by using the present simulation method.[22,27,28]

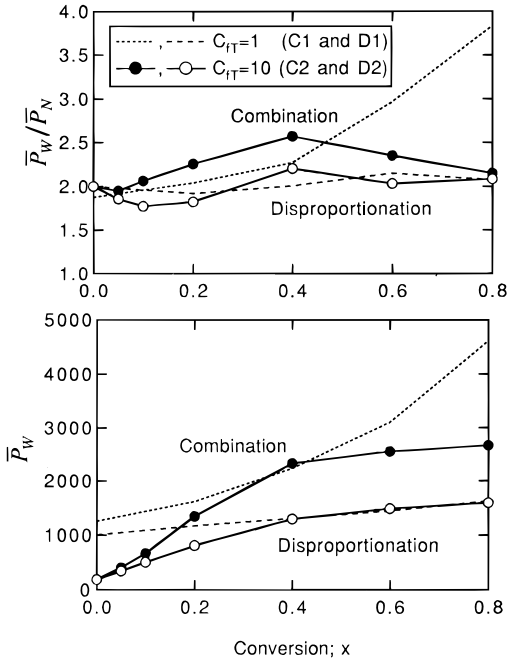

Figure 10. Number- ($\bar{P}_N$) and weight-average ($\bar{P}_W$) degree of polymerization development under conditions C2 (lines with closed circles) and D2 (lines with open circles) as well as those for C1 and D1 (broken lines).

Figure 10 shows the simulation results when the chain transfer constant is changed to $C_{fT} = 10$ (C2 and D2). The broken lines show the cases for $C_{fT} = 1$ (C1 and D1). At the initial stages of polymerization, much smaller chains compared with the cases for $C_{fT} = 1$ are formed due to a larger chain transfer constant. Around the conversion, $x \approx 0.4$, the weight-average degree of polymerization catches up with that for $C_{fT} = 1$. At higher conversions, $\bar{P}_W$ is almost the same as that for $C_{fT} = 1$ under condition D2 (disproportionation termination). On the other hand, under condition C2, $\bar{P}_W$ is much smaller than that for $C_{fT} = 1$. Note that more than 99% of T groups have been consumed before the monomer conversion reaches $x = 0.37$ and that the weight-average chain length of the primary polymer molecules formed via bimolecular termination after the depletion of T is 2×10^3 for D2 and 3×10^3 for C2.

In summary, when bimolecular termination reactions are significant, (1) a large weight fraction of linear polymer molecules is produced and (2) the polydispersity index does not become much smaller than 2 in contrast with the ideal case where the effect of bimolecular termination is negligible.

4. Substitution Effect

After some of the functional groups in a P-CTA molecule have reacted, the reactivity of the rest of the functional groups may change due to both chemical and physical effects.[30] In this part, we consider the cases where the reactivity of the functional group is dependent on the number of unreacted functional groups in a P-CTA molecule.

Concentration of CTA. The number of the unreacted functional groups in a P-CTA may vary from f to 0. Let $[T_i]$ be the concentration of the P-CTA molecule with i unreacted functional groups in it. For example, the time evolution of T_f is given by

$$\frac{d[T_f]}{dt} = -fk_{fT,f}[T_f][R^\bullet] \tag{42}$$

where $k_{fT,i}$ is the transfer rate constant of a functional group within the P-CTA molecule containing i unreacted functional groups. By using the relationship for the polymerization rate

$$dx/dt = k_p(1 - x)[R^\bullet] \tag{43}$$

The independent variable in eq 42 can be transformed into conversion as follows:

$$\frac{d[T_f]}{dx} = -\frac{C_f[T_f]}{1 - x} \tag{44}$$

where $C_i \equiv ik_{fT,i}/k_p$. Similarly, one can set up the balance equation for each type of CTA, and one obtains the following set of differential equations:

$$\begin{cases} \dfrac{d[T_f]}{dx} = -\dfrac{C_f[T_f]}{1 - x} \\ \dfrac{d[T_{f-n}]}{dx} = \dfrac{C_{f-n+1}[T_{f-n+1}] - C_{f-n}[T_{f-n}]}{1 - x} \qquad (0 < n < f) \\ \dfrac{d[T_0]}{dx} = \dfrac{C_1[T_1]}{1 - x} \end{cases} \tag{45}$$

The solutions for the above equations are given by

$$\begin{cases} \dfrac{[T_f]}{[T_f]_0} = (1 - x)^{C_f} \\ \dfrac{[T_{f-n}]}{[T_f]_0} = (-1)^n \left(\prod_{j=f-n+1}^{f} C_j \right) \left\{ \sum_{j=f-n}^{f} \dfrac{(1 - x)^{C_j}}{\prod_{\substack{i=f-n \\ (i \neq j)}}^{f} (C_j - C_i)} \right\} \qquad (0 < n < f) \\ \dfrac{[T_0]}{[T_f]_0} = 1 + (-1)^f \sum_{j=1}^{f} \left\{ (1 - x)^{C_j} \prod_{\substack{i=1 \\ (i \neq j)}}^{f} \dfrac{C_i}{C_j - C_i} \right\} \end{cases} \tag{46}$$

Key Equation for the History-Dependent Kinetics. Consider the history of the P-CTA molecules that change from T_{i+1} to T_i at conversion $x = \theta$. Let the total number of such P-CTAs be $n_i(\theta)$. Now, we consider the probability that such a P-CTA molecule still possesses i unreacted functional groups at conversion $x = \Psi$ ($\theta < \Psi$), $P_i(\theta,\Psi)$. The time evolution of $P_i(\theta,\Psi)$ is given by the following balance equation:

$$n_i(\theta)\{P_i(\theta,\Psi) - P_i(\theta,\Psi + \Delta\Psi)\} = ik_{fT,i}n_i(\theta)P_i(\theta,\Psi)[R^\bullet]\Delta t \tag{47}$$

Using eq 43, one obtains

$$\frac{\partial P_i(\theta,\Psi)}{\partial \Psi} = -\frac{C_i P_i(\theta,\Psi)}{1 - \Psi} \tag{48}$$

Equation 48 can be solved to give

$$P_i(\theta,\Psi) = \left(\frac{1 - \Psi}{1 - \theta}\right)^{C_i} \tag{49}$$

Equation 49 is the key equation that describes the history-dependent kinetics when the substitution effect is considered. Incidentally, because of the T_i-type CTAs that exist at $x = \Psi$, $[T_i]_\Psi$ must be formed in the

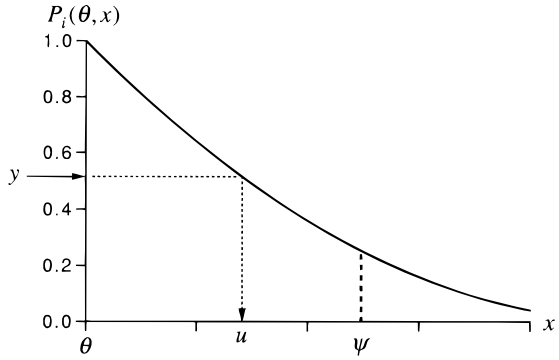

Figure 11. Schematic drawing for the determination method of the birth conversion of the connected chain, u ($\theta < u < \Psi$). By generation of a random number, y ($0 < y < 1$), u can be determined, as shown in the figure.

conversion range from 0 to Ψ, $[T_i]_\Psi$ ($0 < i < f$) can be obtained from

$$[T_i]_\Psi = \int_0^\Psi \left(\frac{C_{i+1}[T_{i+1}]_\theta}{1-\theta}\right) P_i(\theta,\Psi)\, d\theta \qquad (50)$$

It is straightforward to show that the same solutions as eq 46 are obtained from eq 50, which confirms the validity of the present theory.

Connection Probabilities. The probability that the selected primary polymer molecule that is born at $x = \theta$ starts growing from a P-CTA molecule that possessed i unreacted functional groups just before forming this particular arm, $P_i(\theta)$, is given by

$$P_i(\theta) = \frac{ik_{fT,i}[T_i]_\theta}{R_t(\theta) + R_f(\theta)} = \frac{\left(\frac{[T_f]_0}{[M]_0(1-\theta)}\right)\left(C_i\frac{[T_i]_\theta}{[T_f]_0}\right)}{\tau(\theta) + \beta(\theta) + \left(\frac{[T_f]_0}{[M]_0(1-\theta)}\right)\sum_{j=1}^{f}\left(C_j\frac{[T_j]_\theta}{[T_f]_0}\right)} \qquad (51)$$

Suppose the selected primary polymer chain is the mth chain of the P-CTA ($m = f - i + 1$). Before this primary molecule is formed, ($m - 1$) functional groups must have already reacted before conversion reaches $x = \theta$. On the basis of eq 50, the probability that this P-CTA molecule changes from T_{i+1}-type to T_i-type within the conversion interval $0 < z < \theta$ is given by

$$P_{i,i+1}(z|\theta) = \frac{\int_0^z \left(\frac{C_{i+1}[T_{i+1}]_x}{1-x}\right)\left(\frac{1-\theta}{1-x}\right)^{C_i} dx}{[T_i]_\theta} \qquad (52)$$

By using eq 52 iteratively, one can determine the birth conversions for all ($m - 1$) branch chains. Now, we can determine the connection of the given P-CTA molecule toward primary polymer molecules formed in the conversion interval, 0 to θ.

Next, consider the connection of primary chains formed between θ and Ψ. On the basis of eq 49, the probability that the CTA that becomes the T_i-type at $x = \theta$ is still the T_i-type at $x = u$ ($\theta < u$) is given by

$$P_i(\theta,u) = \left(\frac{1-u}{1-\theta}\right)^{C_i} \qquad (53)$$

As illustrated in Figure 11, one can determine u by

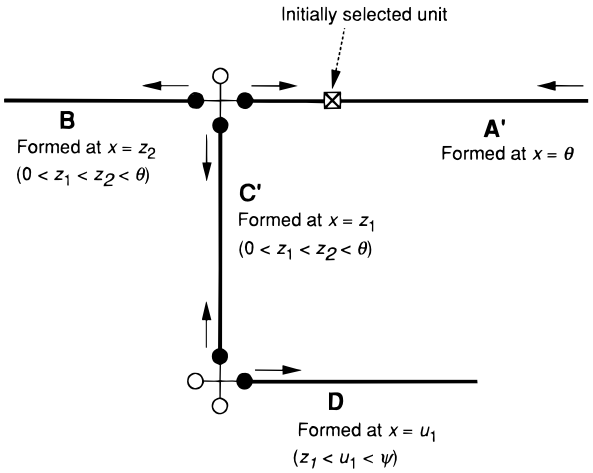

Figure 12. Schematic drawing of a polymer molecule selected from the reaction mixture at the present conversion, $x = \Psi$. The arrows show the direction of growth for each chain. When a primary chain is formed via bimolecular termination by combination, both chain ends are the starting points for chain growth.

solving the following equation:

$$y = \left(\frac{1-u}{1-\theta}\right)^{C_i} \qquad (54)$$

Therefore, u can be determined from the following transformation:

$$u = 1 - (1-\theta)y^{(1/C_i)} \qquad (55)$$

If $\Psi < u$, the rest of the functional groups in the given CTA are unreacted. On the other hand, if $u < \Psi$, one determines the birth conversion of the connected chain.

Simulation Method. In order to illustrate the simulation method, we consider the case with the functionality of the P-CTA is $f = 4$. We consider the various molecular species that exist at the present conversion $x = \Psi$; i.e., no primary chains formed at $x > \Psi$ exist in this reaction system. Suppose our randomly selected polymer molecule possesses the structure shown in Figure 12. The primary polymer molecules shown with a prime (A′ and C′) are formed via bimolecular termination by combination. The arrows indicate the direction of growth for each primary chain. When the primary polymer molecule is formed by combination termination, both chain ends are the starting points for propagation. The conversion at which each primary polymer molecule is formed is also shown in the figure. We generate this polymer molecule using the Monte Carlo sampling technique as follows.

Suppose our initially selected monomeric unit is located on the primary chain A′; the birth conversion of this chain, θ, can be determined by selecting the birth conversion θ from 0 to Ψ randomly. Once the birth conversion of the initially selected primary chain is settled, we determine the chain length of this primary polymer radical just before chain stoppage by using eq 34. The probability of growth, $p(\theta)$, for the present reaction system is given by

$$p(\theta) = \frac{1}{1 + \tau(\theta) + \beta(\theta) + \left(\frac{[T_f]_0}{[M]_0(1-\theta)}\right)\sum_{j=1}^{f}\left(C_j\frac{[T_j]_\theta}{[T_f]_0}\right)} \qquad (56)$$

The probability that the primary chain A′ is formed via bimolecular termination by combination is given by

$$P_\beta(\theta) = \frac{\beta(\theta)}{\tau(\theta) + \beta(\theta) + \left(\frac{[T_f]_0}{[M]_0(1-\theta)}\right)\sum_{j=1}^{f}\left(C_j\frac{[T_j]_\theta}{[T_f]_0}\right)} \quad (57)$$

In the present case, A′ falls in with this event given by eq 57, so that the chain length of this dead primary chain is given by eq 36.

The probability that the chain end of A′ is not connected to a P-CTA is given by

$$P_{\mathrm{noCTA}}(\theta) = \frac{\tau(\theta) + \beta(\theta)}{\tau(\theta) + \beta(\theta) + \left(\frac{[T_f]_0}{[M]_0(1-\theta)}\right)\sum_{j=1}^{f}\left(C_j\frac{[T_j]_\theta}{[T_f]_0}\right)} \quad (58)$$

Because both chain ends of A′ are the starting point for propagation, we have to examine the above probability twice. In the present case, one of the chain ends satisfies eq 58.

On the other hand, the other end (left end) of A′ starts growing from a P-CTA molecule. The number of functional groups in this P-CTA just before the formation of A′ can be determined from eq 51, $P_i(\theta)$. In the present example, the P-CTA satisfies the event given by the probability $P_2(\theta)$; i.e., A′ is formed due to the chain transfer reaction to the P-CTA molecule that possesses two unreacted functional groups in it (T_2-type). Therefore, two functional groups in this P-CTA molecule have already reacted before $x = \theta$, and one functional group is unreacted just after the formation of A′. This unreacted functional group may react during the conversion interval θ to Ψ. The conversion at which this functional group reacts, u, can be determined from eq 55. However, because $u > \Psi$ in the present case, this functional group stays unreacted at the present conversion $x = \Psi$ and no primary chain formed in the conversion interval θ to Ψ is connected to it.

On the other hand, two primary chains have already been formed on the given P-CTA molecule until $x = \theta$. The birth conversion of B, which is the second arm in the P-CTA, z_2, can be determined from eq 52, $P_{2,3}(z_2|\theta)$. Because B is formed by a method other than bimolecular termination by combination, i.e., formed by the events that satisfy the probability $P_\tau(z_2) = 1 - P_\beta(z_2)$, the chain length is directly given by eq 40.

The first arm of this P-CTA, C′, must be formed before conversion reaches z_2. The birth conversion of C′, z_1, can be determined from eq 52, $P_{3,4}(z_1|z_2)$. The chain C′ satisfies the probability $P_\beta(z_1)$ and is formed via bimolecular termination by combination. The chain length of C′ can be determined from eqs 40 and 41. When a primary chain is formed by combination termination, the possibility of connection to a P-CTA at the other chain end must be examined. In the present case, the other end of C′ also started growing from a P-CTA, whose event is determined from eq 58, $P_{\mathrm{noCTA}}(z_1)$.

With the probabilities given by eq 51, $P_i(z_1)$, the type of this P-CTA just before the formation of C′ can be determined and is shown to be T_4 in the present example; i.e., no additional arms exist on this P-CTA molecule at $x = z_1$. On the other hand, however, the three unreacted functional groups at $x = z_1$ may react before the conversion reaches the present conversion, Ψ. In the present example shown in Figure 12, one chain is formed at $x = u_1$ ($z_1 < u_1 < \Psi$). The conversion, u_1, can be determined from eq 55. The chain length of the connected chain, D, can be determined from eq 40, because D is formed via a method other than bimolecular termination by combination. At $x = u_1$, two unreacted functional groups are still left and the possibility of reaction for these functional groups until the present conversion, Ψ, must be considered. This conversion can also be determined from eq 55, i.e., $u_2 = 1 - (1 - u_1)y^{(1/C_2)}$. However, $u_2 > \Psi$ in the present case, and no additional chains are shown to be formed at least until $x = \Psi$. The whole simulation algorithm is schematically shown in Figure 13.

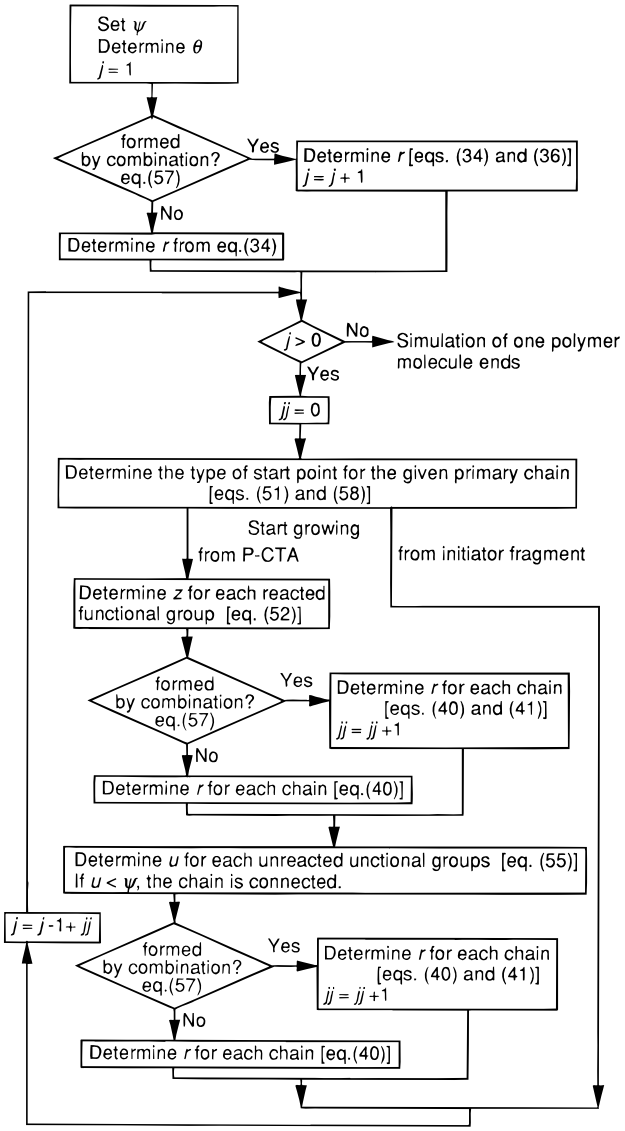

Figure 13. Simulation algorithm that accounts for the substitution effects.

Simulation Results. We investigate the substitution effect (SE) by decreasing the reactivity of the unreacted functional groups once some functional groups in the same P-CTA have reacted. We employ conditions C2 and D2 as an illustrative purpose. We use $C_4 = 4C_{f\mathrm{T}}$, $C_3 = 3C_{f\mathrm{T}} \times 0.4$, $C_2 = 2C_{f\mathrm{T}} \times 0.2$, $C_1 = C_{f\mathrm{T}} \times 0.1$, and $C_{f\mathrm{T}} = 10$. The change of the type of the starting point for chain growth during polymerization is shown in Figure 14. Without the substitution effect (C2 and D2), almost all chains formed with $x > 0.6$ started growing from the initiator fragments rather than P-CTAs. On the other hand, a significant amount of primary chains start growing from P-CTAs with one unreacted func-

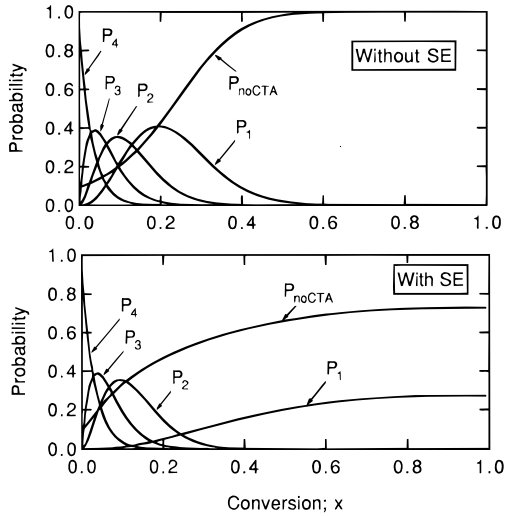

Figure 14. Probability that the randomly selected primary polymer molecule formed at conversion x starts growing from a P-CTA molecule that possessed i unreacted functional groups just before forming this arm, P_i, under the condition with or without (C2 and D2) the substitution effect for $C_{fT} = 10$.

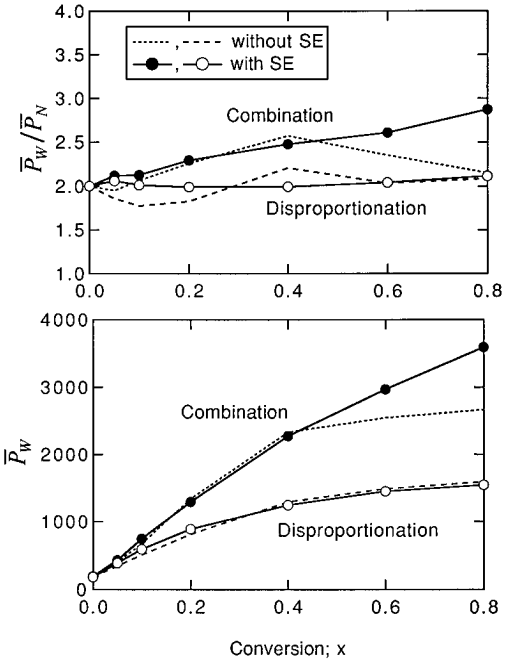

Figure 15. Number- ($\bar{P}_N$) and weight-average ($\bar{P}_W$) degree of polymerization developments with the substitution effect (lines with circles) and those without the substitution effect (broken lines; C2 and D2).

tional group left at high conversions with the substitution effect.

Figure 15 shows the simulated average degree of polymerization development. Simulations were made for 5000 polymer molecules at each conversion level. When the bimolecular terminations are by disproportionation, the substitution effect on the formed MWD is rather small, at least for the present calculation conditions, and it would be very difficult to determine the substitution effect experimentally.

On the other hand, when the bimolecular terminations are by combination, the decreased reactivity of the rest of the functional groups increases the weight-average degree of polymerization at higher conversions. Contrary to the usual speculation that the deceased reactivity of the functional groups in P-CTA molecules due to the substitution would decrease the weight-

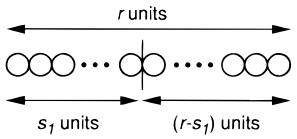

Figure 16. Sequence of r units divided into two groups in which the first group consists of s_1 units.

average molecular weights,[30] $\bar{P}_W$ becomes larger due to the substitution effect. Especially when the cross-linking reactions due to the combination termination are involved, the probability of cross-link formation is affected by a delicate balance between chain transfer to P-CTA and bimolecular termination. As a consequence, the weight-average molecular weights may become larger or smaller due to the decreased reactivity of the functional groups, depending on (1) the magnitude of chain transfer constant, C_{fT}, and that of the bimolecular termination rate, β, (2) the concentration of P-CTA used, $\gamma_0 = [T]_0/[M]_0$, and (3) the significance of the substitution effect.

When the cross-link formation due to bimolecular termination by combination is involved, one may need to consider the effect of the chain-length-dependent bimolecular termination coefficient, especially at high-conversion regions. It is widely accepted that the bimolecular termination reactions are diffusion controlled and, therefore, are chain-length-dependent. The chain-length-dependent kinetics could be handled by application of the Monte Carlo simulations in a finite system (what we call the microreactor method[18]) in a straightforward manner as long as the system size is chosen properly.[18,19]

5. Conclusions

The random sampling technique is applied to the free-radical polymerization that involves polyfunctional chain transfer agents. The random sampling technique can be used to obtain analytical solutions for the MWD under simplified conditions. This technique is particularly useful to conduct Monte Carlo simulations, and the substitution effects of the functional groups in the P-CTA molecule as well as bimolecular terminations can be accounted for in a straightforward manner. The present simulation technique would be a powerful tool to analyze the complex behavior of the real systems.

Under the ideal case where $C_{fT} = 1$ and the effects of bimolecular terminations are negligible, the MWD becomes narrower as the polymerization proceeds. However, this is not the case when bimolecular terminations are involved and/or $C_{fT} \neq 1$. The decreased reactivity of the functional groups in a P-CTA due to the substitution effect may increase or decrease the average molecular weights depending on the magnitude of the chain transfer constant, the concentration of P-CTA, the mode of bimolecular termination (disproportionation or combination), and the degree of the substitution effect.

Appendix

A. Derivation of Equation 26. Calculating $\sum_{\sum_{j=1}^{i} s_j = r}$ is equivalent to counting the total number of ways to separate a sequence of r units into i separate groups. When s_1 units shown in Figure 16 form the first group, the rest of the $(i - 1)$ groups can be made by inserting $(i - 2)$ partitions into $(r - s_1 - 1)$ spacings between units. Therefore

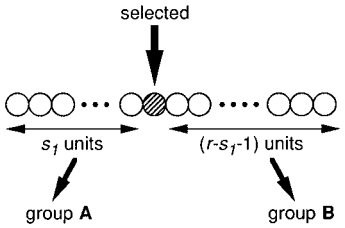

Figure 17. Sequence of r units divided into three groups in which group A consists of the first s_1 units, the second group consists of one unit, and the rest of the units belonging to group B.

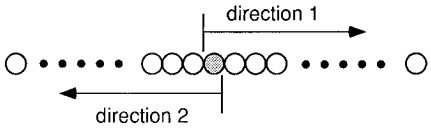

Figure 18. Primary polymer molecule that involves the randomly selected unit (shown as a shadowed circle). The probability of connection between units is the same for all units in this polymer molecule; therefore, the chain length distribution in both directions 1 and 2 follows the number fraction distribution given by eq a4.

$$\sum_{\Sigma_{j=1}^{i} s_j = r} s_1 = \sum_{s_1=1}^{r-i+1} s_1 \binom{r-s_1-1}{i-2} = \sum_{s_1=1}^{r-i+1} \binom{s_1}{1}\binom{r-s_1-1}{i-2} \tag{a1}$$

Now, we consider the right-hand side of eq a1 as follows. Suppose that we separate a sequence of r units into three groups, as shown in Figure 17. Consider the selection process in which we select one unit from group A and $(i - 2)$ units from group B, given that the $(s_1 + 1)$th unit shown as a shadowed circle has already been selected. As a consequence of this process, we obtain i units from r units. The total number of ways to make such a selection is $\binom{s_1}{1}\binom{r-s_1-1}{i-2}$. By changing s_1 from 1 to $r - i + 1$, one can count the total number of ways to select i units from r units, which is equal to $\binom{r}{i}$.

B. Generation of the Random Numbers That Follow the Weight-Based Most Probable Distribution. The chain lengths that follow the number-based most probable distribution (eq 1) can simply be obtained by solving

$$y = \sum_{s=1}^{r} n_p(s) = 1 - p^r \tag{a2}$$

Therefore, the following transformation can be used to generate the random numbers that conform to the number-based most probable distribution:

$$r = \text{ceiling}\left[\frac{\ln(1-y)}{\ln(p)}\right] \tag{a3}$$

or equivalently

$$r = \text{ceiling}\left[\frac{\ln(y)}{\ln(p)}\right] \tag{a4}$$

When $p \rightarrow 1$, eq a4 can be approximated by

$$r = \text{ceiling}\left[\bar{P}_{np} \ln\left(\frac{1}{y}\right)\right] \tag{a5}$$

Next, consider the method to generate the random numbers that follow the weight-based most probable distribution (eq 2). The most probable distribution is formed when the probability of connecting the neighboring unit is the same for all units. When one unit is selected randomly from the polymer molecules that follow the most probable distribution, as shown in Figure 18, the chain length distribution in direction 1 is given by the number-based most probable distribution; therefore, it can be determined from eq a4. Similarly, the chain length distribution in direction 2 from the selected unit is also determined from eq a4. Because the selected unit is counted twice, the chain length of this selected primary chain can be determined by eq 29 in the text. When $p \rightarrow 1$, the following approximation can be employed:

$$r = \text{ceiling}\left[\bar{P}_{np} \ln\left(\frac{1}{y_1}\right)\right] + \text{ceiling}\left[\bar{P}_{np} \ln\left(\frac{1}{y_2}\right)\right] - 1 \tag{a6}$$

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