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Molecular Weight Distribution in Free-Radical Polymerization with Chain-Length-Dependent Bimolecular Termination. 1. Bulk Polymerization

Hidetaka Tobita

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

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ABSTRACT: A new Monte Carlo simulation method for chain-length-dependent kinetics is proposed. This method employs the *segregated microreactor* in which pseudobulk kinetics is valid, and the formation process of all polymer molecules involved in the microreactor is simulated by application of the *competition technique* where only a small number of random numbers are required to generate each polymer molecule stochastically. The necessary volume of the microreactor to simulate the molecular weight distribution (MWD) in homogeneous polymerizations with sufficient accuracy is so small that it may contain about 5 radicals; therefore, the amount of calculation required is rather small. For intermediate to high conversions, bimolecular terminations are likely to be dominated by interactions between radicals with short and long chain lengths. When bimolecular termination by disproportionation is significant, short oligomeric chains that are large in number but small in weight are formed. If bimolecular termination is solely by combination, the instantaneous MWD formed in these conversions may be approximated well with the most probable distribution because all macroradicals are stopped by small molecules including oligomeric radicals via bimolecular termination and monomer molecules as a chain transfer agent. On the other hand, the MWDs formed at low to intermediate conversions are more complex since the probability of chain stoppage for polymer radicals changes rather gradually with chain length. It is straightforward to extend the present simulation to the unsteady state, and it was found that the molecular weight development during the start up period can be significantly different from the predictions based on the assumption of a single constant termination rate coefficient.

Introduction

Textbooks tell us that the bimolecular termination reaction in free-radical polymerization is a typical example of the diffusion-controlled reaction. Since polymer diffusion is a function of polymer chain length, a logical consequence is that the bimolecular termination reactions are chain-length-dependent. However, most kinetic studies in the literature do not account for chain-length-dependent bimolecular termination. The main reason for this would be that the functional form for the termination rate coefficient has not been established yet. However, another reason is that it is not a simple task to connect the microscopic model that accounts for molecular diffusion with the macroscopic quantities that are observable in experiments. This is understandable when one realizes that the termination reactions in homogeneous polymerizations involve an infinite number of combinations of radical pairs simultaneously, each of which possesses a different rate coefficient. Numerical and analytical (for limited cases) techniques to solve a set of an infinite number of differential equations at stationary states have been proposed.[1–7]

On the other hand, 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. Most Monte Carlo simulations employ a finite reaction system to represent an infinite reaction system approximately; i.e., a very small part is cut out from the reaction mixture and the kinetic behavior of all molecules involved in it is simulated. This technique has now become a standard repertoire to study the polymeric network formation.[8–16] Use of a limited reaction volume makes it possible to conduct elaborate simulations that account for diffusion and mobility during reaction[12,13] although such attempts have not succeeded in describing real systems. Once a *microreactor* is used to represent the infinite reaction system, however, one always needs to consider how large the size of the microreactor must be. Recently, O'Driscoll and Kuindersma[17] conducted a Monte Carlo simulation of a pulsed laser polymerization using a microreactor in which 5000 radicals are generated in a single pulse of the laser. Intuitively, the results obtained from a microreactor that contains 5000 radicals are quite persuasive to represent an infinite reaction system, even though the effect of the microreactor size still needs to be considered.

On the other hand, it is well known that pseudobulk kinetics is valid for emulsion polymerization if the polymer particle contains more than 5–10 radicals.[18–22] Recently, we proposed a Monte Carlo simulation method for emulsion polymerization in which the formation processes of all polymer molecules in each polymer particle are simulated.[23,24] In this method, the formation of each polymer molecule is simulated using a small number of random numbers by application of the *competition technique*, and more complex molecular processes such as branching[25] and cross-linking[16] can be accounted for in a straightforward manner. The molecular weight distribution (MWD) formed in emulsion polymerization is very close to that formed in a bulk system even when the polymer particle contains as little as 2 radicals on average,[24] although the chain-length-dependent kinetics were not accounted for in the previous studies.

In this paper, we propose a Monte Carlo simulation technique in which the molecular buildup process of each molecule in a microreactor can be simulated even

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on a personal computer, and important aspects of the MWD formed in free-radical polymerization with chain-length-dependent bimolecular termination are elucidated.

Theoretical Section

Microreactor Method. We partition a reaction volume into segregated microreactors. The diffusion through the partition wall could be accounted for; however, we prohibit the transfer across the wall in the present study. Suppose radicals are generated stochastically in the microreactor following the initiation rate, R_I. First, in order to clarify the effect of reactor volume on the fluctuation of the radical concentration, let us consider free-radical polymerization with a constant bimolecular termination rate coefficient, k_t. The time evolution of the probability that the microreactor contains n_s radicals is given by

$$\frac{\mathrm{d}P(n_s)}{\mathrm{d}t} = R_I v N_A \{P(n_s-1) - P(n_s)\} + \left(\frac{k_t}{vN_A}\right)\left\{\binom{n_s+2}{2}P(n_s+2) - \binom{n_s}{2}P(n_s)\right\} \quad (1)$$

where v is the volume of a microreactor, and N_A is Avogadro's number. Equation 1 is exactly the same as the equation for the distribution of radicals among the emulsion particles, which is known as the Smith–Ewart equation,[26] without exit of radicals. Stockmayer[18] and O'Toole[19] obtained the exact steady-state solution to the Smith–Ewart equation. In the present case without radical exit, the distribution of the number of radicals and the average number of radicals in a microreactor is given by[19]

$$P(n_s) = \frac{a^{n_s}(2^{\{-(1+3n_s)/2\}})I_{n_s-1}(2^{-0.5}a)}{n_s! I_{-1}(a)} \quad (2)$$

$$\bar{n}_s = \left(\frac{a}{4}\right)\frac{I_0(a)}{I_{-1}(a)} \quad (3)$$

where I denotes the modified Bessel function of the first kind, $a = (8\alpha)^{0.5}$, and $\alpha = 2R_I(vN_A)^2/k_t$. The solution for the case where the radicals are created in pairs within the microreactor, which reminds one of the thermal decomposition of initiators, was also derived.[19] However, we are interested in the region where pseudobulk kinetics is valid, so such differences could be neglected.[19,21]

On the other hand, if the partition walls are removed, the average numbers of radicals involved in the volume v is given by

$$n_v = vN_A(R_I/k_t)^{0.5} \quad (4)$$

Ideally, the number of radicals in the segregated microreactor n_s must be equal to n_v in order to mimic the kinetic behavior in the infinite reaction system. The fluctuation of the radical concentration in the microreactor is shown in Figure 1. The problem of using the segregated microreactor can be restated as how significant the effect of the concentration fluctuation on the polymerization kinetics can be. In this paper, we are mainly interested in the MWD, so it is necessary to know the minimum size of microreactor in which the simulated results with the existence of the concentration fluctuation shown in Figure 1 agree satisfactorily with the system without the fluctuation.

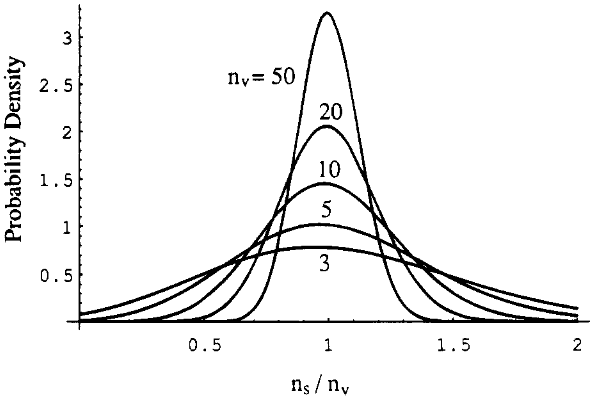

Figure 1. Effect of the volume of the segregated microreactor on the distribution of the number of radicals.

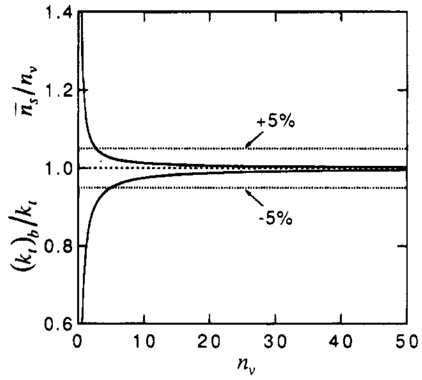

Figure 2. Effect of the microreactor volume on the average number of radicals $\bar{n}_s$ and the termination rate coefficient calculated from the pseudobulk kinetics $(k_t)_b$.

Figure 2 shows the effect of the reactor volume on the average number of radicals in the segregated microreactor. In terms of the average number of radicals, it is shown that we need only a small number of radicals in the microreactor. When the microreactor volume is very small, the kinetics follow that for emulsion polymerization. In the present case where the exit of radicals is prohibited, $\bar{n}_s > 0.5$, so the ratio $\bar{n}_s/n_v$ diverges at the small-volume limit. If one assumes that pseudobulk kinetics is valid, the termination rate coefficient can be determined from

$$(k_t)_b = \frac{R_I(vN_A)^2}{\bar{n}_s^{\,2}} \quad (5)$$

Since $\bar{n}_s$ is squared, the deviation becomes larger than that for the number of radicals as shown in Figure 2.

The segregated microreactor method is approximate by nature; however, it can be a good approximation even when there exist a relatively small number of radicals in the microreactor.

Simulation Method: Competition Technique. In conventional Monte Carlo simulations for the molecular buildup processes in polymers, monomeric units are added to each growing polymer molecule one by one; therefore, a numerous amount of random numbers as well as the calculations are required to simulate the formation of each polymer molecule. Instead, we employ a new concept, what we call the "competition technique", and reduce the amount of calculations drastically.[23,24,27]

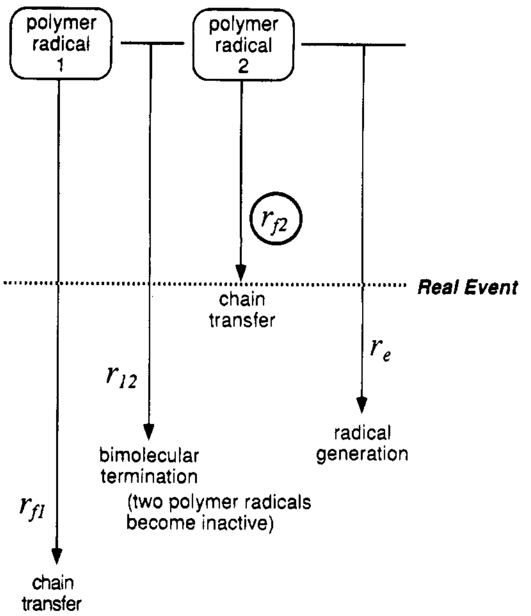

Figure 3. Schematic drawing for the simulation method based on the competition technique.

Figure 3 illustrates the case where two polymer radicals exist in a microreactor after a certain event, radical generation, chain transfer, or bimolecular termination, occurs. Then one calculates the "imaginary chain lengths" for each event. For example, the probability density that a polymer radical adds r_f monomeric units until it ceases growing by chain transfer reaction is given by the following most probable distribution:

$$P_f(r_f) = C_f \exp(-C_f r_f) \tag{6}$$

where $C_f = R_f/R_p$, R_p is the polymerization rate, and R_f is the rate of chain transfer to monomer and small molecules. The random numbers that follow the most probable distribution can simply be generated on the basis of the inverse function of the cumulative distribution; i.e., the chain length, r_f, can be determined by using a random number y between 0 and 1 as follows:

$$r_f = (1/C_f) \ln(1/y) \tag{7}$$

On the basis of eq 7, r_{f1} and r_{f2} are determined. Similarly, the imaginary chain length for bimolecular termination, r_{12}, and that for radical generation, r_e, can be determined.[23,24,27] (Note that the transformation between time t and the number of added monomer units to a radical center r is simply given by $dr/dt = k_p[M]$, where k_p is the propagation rate constant and [M] is the monomer concentration.) At this stage, a kind of competition of events is considered; namely, the event with the shortest "imaginary chain length" is chosen as the "real event". In the figure, r_{f2} is chosen as the real event, which means that the events given by the imaginary chain lengths, r_{f1}, r_{12}, and r_e, never happened in reality and are rejected. The polymer radical 1 shown in the figure simply grows to add r_{f2} monomeric units during that period and still possesses an active center after the growth. (Note that the Gaussian distribution could be used for the number of added monomeric units to the polymer radical 1. However, such statistical deviation is neglected in the present simulation, because the variance is small enough as long as r_{f2} is large.) This method is called the competition technique, and the simulation of polymerization can be conducted by reiterating the above processes. In order to follow the time evolution of polymerization, a large number of microreactors are employed to obtain statistically valid results.[23] On the other hand, in order to obtain the instantaneous properties, such as the instantaneous MWD (formed in a very small time interval), we consider a single imaginary microreactor in which all concentrations except the radical concentration do not change after the formation of polymer chains; i.e., the reaction environment is kept constant except that the number and chain lengths of the macroradicals are changed stochastically.[24] By producing a large number of polymer molecules consecutively with this imaginary microreactor after the attainment of the steady state, the instantaneous properties can be determined.

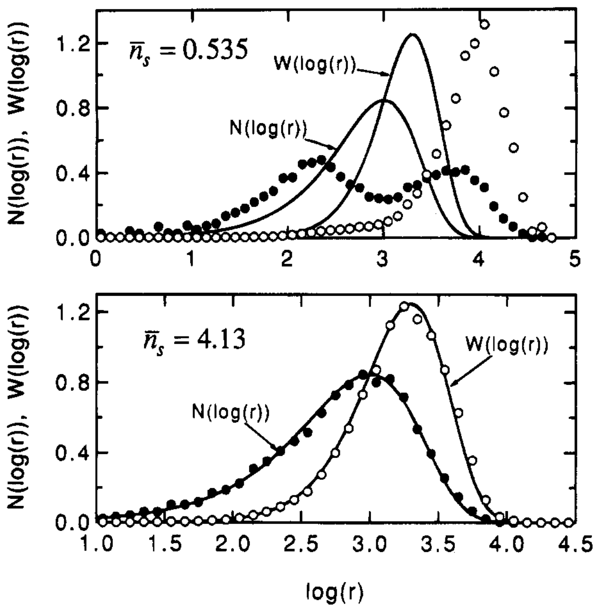

Figure 4. Comparison of the chain length distribution formed in the microreactor (circles; Monte Carlo simulation) and in an infinitely large reactor (solid curves; theoretical results).

Each imaginary chain length follows the most probable distribution if the chain-length-dependent kinetics is neglected.[23,24] We examine the effect of reactor volume on the MWD. If one uses a single constant bimolecular termination rate coefficient independent of chain length, the instantaneous weight fraction distribution (formed within a very small time interval) in homogeneous polymerization is given by[28]

$$W(r) = (\tau + \beta)\left\{\tau + \frac{\beta}{2}(\tau + \beta)(r - 1)\right\} r \exp\{-(\tau + \beta) r\} \tag{8}$$

where $\tau = [R_f + R_{td}]/R_p$, $\beta = R_{tc}/R_p$, R_{td} is the rate of termination by disproportionation, and R_{tc} is the rate of termination by combination.

Figure 4 shows the simulated chain length distribution in the microreactor and the distribution for an infinite reaction system that is obtained from eq 8. In the simulation, 10^4 polymer molecules are simulated after the attainment of the steady state (i.e., the simulation is started from $n_s = 0$, and 500 polymer molecules are discarded as the transient state[24]). The shown distributions are for $\tau = 1 \times 10^{-3}$ and $R_f = \beta = 0$; namely, the dead polymer formation is fully via bimolecular termination by disproportionation. If k_t is independent of chain length, the MWD formed without bimolecular termination by combination ($\beta = 0$) is equal to the MWD for polymer radicals. It is well known that

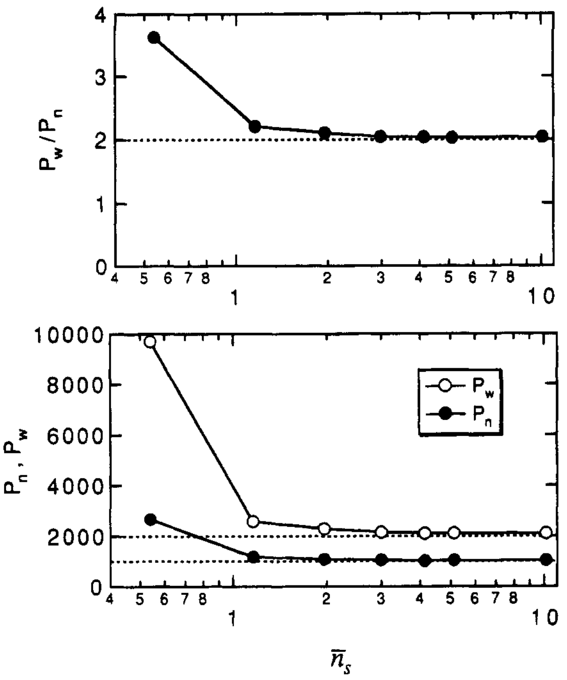

Figure 5. Effect of the microreactor volume on the average chain lengths.

the distribution shape is different significantly whether the independent variable is the chain length r or the logarithm of the chain length $\log(r)$. The logarithm of the chain length is important due to the formal relationship with the elution volume in size exclusion chromatography (SEC) and is used as an independent variable for the chain length distribution throughout the present paper.

When the microreactor volume is very small, $\bar{n}_s$ approaches 0.5, where the emulsion polymerization kinetics is valid. If the microreactor possesses a macroradical in it, the bimolecular termination occurs before the newly generated radical grows to a sufficient chain length; therefore, a peak with smaller chain lengths is formed in the number fraction distribution ($N(\log(r))$) when $\bar{n}_s = 0.535$. Though large in number, such smaller polymers constitute only a small weight fraction, and therefore, the peak with smaller chain lengths can be barely observed in the weight fraction distribution ($W(\log(r))$). The obtained distribution is completely different from that for an infinite system (solid curve).

By increasing the number of radicals in the microreactor, the MWD approaches the infinite system, and when $\bar{n}_s = 4.13$, the agreement appears to be satisfactory as shown in the lower figure of Figure 4. Figure 5 shows the effect of the microreactor volume on the simulated average chain lengths and the polydispersity index (P_w/P_n). For a constant k_t, a microreactor with only about 3 radicals can give satisfactory predictions.

When k_t is dependent on chain length, the imaginary chain length for the bimolecular termination, r_{ij}, cannot be determined from the most probable distribution. Suppose the chain length of the ith radical in the microreactor is r_i and that of the jth radical is r_j. The probability that a pair of radicals with chain lengths r_i and r_j cause bimolecular termination rather than any other event, $\xi(r_i,r_j)$, is given by

$$\xi(r_i,r_j) = \frac{k_t(r_i,r_j)}{k_p[\mathrm{M}]vN_A} \qquad (9)$$

The probability that this pair of radicals continue to add more than r_{ij} monomeric units without causing bimolecular termination between them is given by

$$P_t(r_{ij}) = \prod_{s=0}^{r_{ij}} \{1 - \xi(r_i+s,r_j+s)\} \qquad (10)$$

Therefore, r_{ij} can be determined stochastically by solving eq 10 on the basis of $P_t(r_{ij})$, which is given by a random number between 0 and 1.

Since the multiplication in eq 10 could take a long time if r_{ij} is very large, one may need to adopt the following strategy to reduce the amount of calculations. (1) Our purpose is to determine the event with the shortest time interval, not to determine r_{ij} for every pair of radicals. One should determine r_{fi} and r_e, which can be determined simply from the most probable distribution, and determine the shortest one r_s prior to tackling r_{ij}. If r_{ij} exceeds r_s, one need not continue the multiplication. Furthermore, examination of r_{ij} should start from the shortest radical. (2) If k_t is a constant, the number of the added monomeric units before termination $(r_{ij})_c$ can be determined from the simple most probable distribution. Because of the relationship $\xi(r_i,r_j) > \xi(r_i+s,r_j+s)$, $(r_{ij})_c < r_{ij}$. Therefore, if $(r_{ij})_c$ exceeds the chain length for the shortest event (r_s), such bimolecular termination can never be a real event, and one need not continue the calculation for such a radical pair.

Functional Form of the Bimolecular Termination Rate Coefficient. Various functional forms for the chain length dependence of the termination reaction rate coefficient have been proposed.[1-7,29-35] For example, an empirical relationship based on the geometric mean assumption is given by[1-5,29,30]

$$k_t(l,m) = k_t^0(lm)^{-z} \qquad (11)$$

where z is a constant usually about the order of 10^{-1} and l and m are chain lengths of macroradicals. Although the functional forms are different depending on the theory employed, a unanimous feature is that $k_t(l,m)$ decreases with chain length and the obtained trend for the chain length dependence does not differ much whichever model is used.

Recently, Russell summarized the necessary parameters of their model for the bulk polymerization of styrene.[7] In this paper, we use the model and parameters reported by Russell. The outline of their model is as follows.[6,7] On the basis of the Smoluchowski equation,[36] $k_t(l,m)$ is given by

$$k_t(l,m) = 4\pi(D_l + D_m)\sigma N_A \qquad (12)$$

where D_l and D_m are the diffusion coefficients for chain ends of a macroradical of chain lengths l and m, respectively, and σ is the separation of radical sites at which the actual chemical reaction of termination takes place. D_l is given by the sum of a center-of-mass diffusion coefficient $D_{l,\mathrm{com}}$ and the reaction-diffusion D_{rd}; namely

$$D_l = D_{l,\mathrm{com}} + D_{\mathrm{rd}} \qquad (13)$$

The functional forms for $D_{l,\mathrm{com}}$ and D_{rd} are given by

Table 1. Parameters Reported for the Bulk Polymerization of Styrene[7]

	C1	C4
conditions	50 °C, $w_p = 0.76^a$	20 °C, $w_p = 0^a$
[M] (mol·L^{-1})	2.30	8.70
σ (Å)	6.02	3
D_{mon} (cm^2·s^{-1})	7.4×10^{-8}	1.5×10^{-5}
a	1	0.487
b	2	0.584
X_c	5.5	86.4
A (Å)	7.4	7.4
k_p (L·mol^{-1}·s^{-1})	255	60.3
C_m	3.53×10^{-5}	2.92×10^{-5}
R_I (mol·L^{-1}·s^{-1})	8.6×10^{-10}	1.26×10^{-9}

[a] Weight fraction of polymer.

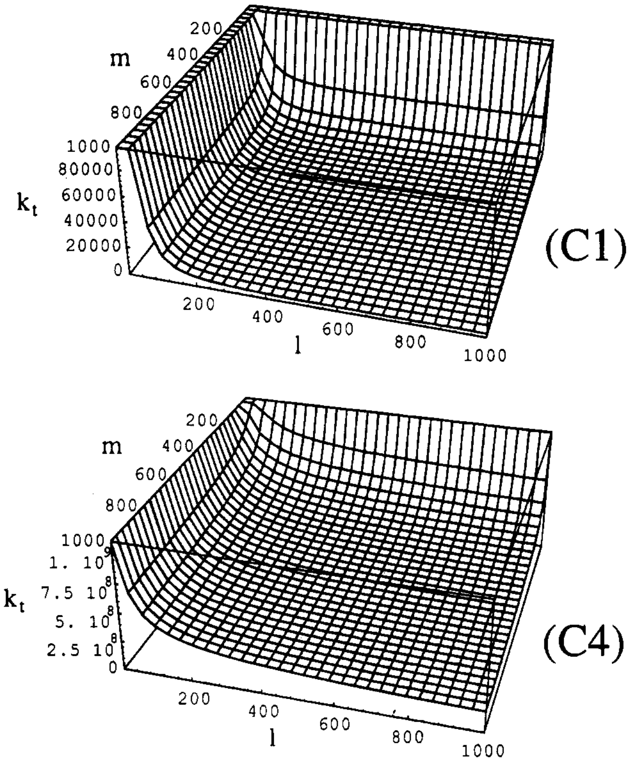

Figure 6. Functional form of the termination rate coefficient as a function of chain lengths, l and m.

$$D_{l,\text{com}} = \frac{D_{\text{mon}}}{l^a} \qquad \text{for } l \le X_c$$

$$= \frac{D_{\text{mon}}(X_c)^{b-a}}{l^b} \qquad \text{for } X_c \le l \qquad (14)$$

$$D_{\text{rd}} = \frac{k_p[\text{M}]A^2}{6} \qquad (15)$$

where D_{mon} is the diffusion coefficient of a monomeric species, and A is an index of unperturbed chain dimensions.

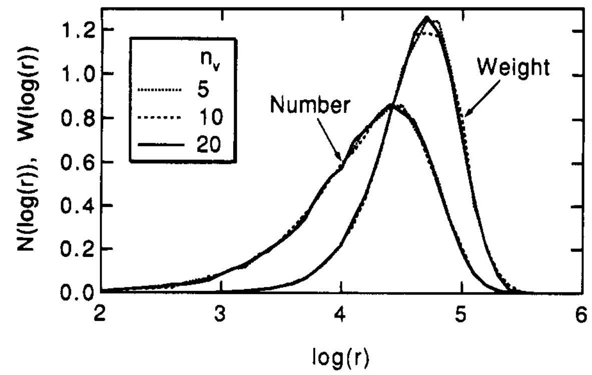

Figure 7. Effect of the reactor volume on the chain length distribution.

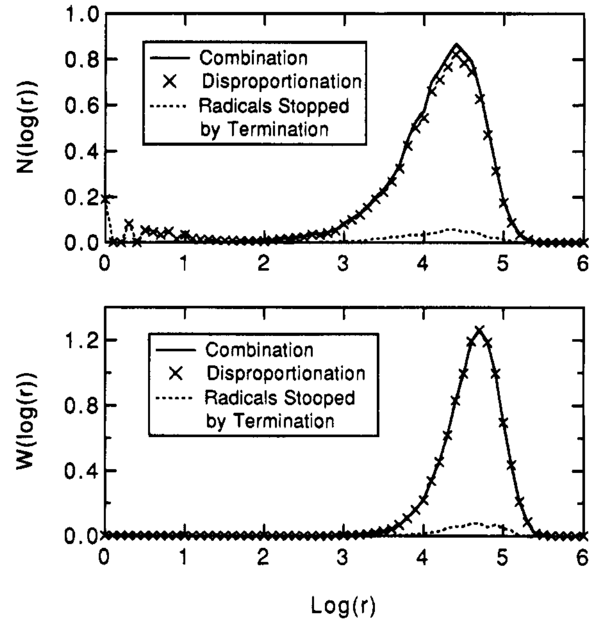

Figure 8. Instantaneous number and weight fraction distributions formed under condition C1 with bimolecular termination by combination (solid curve) and by disproportionation (crosses). The distribution of radicals that caused bimolecular termination is shown by the broken curves. The distributions are plotted for the interval $\Delta\log(r) = 0.1$.

The parameters for styrene polymerization reported by Russell[7] are summarized in Table 1. Figure 6 shows the termination rate coefficient as a function of l and m. Since l and m are interchangeable, the function is symmetric. At an intermediate conversion (C1; $w_p = 0.76$), k_t decreases significantly in a smaller chain length region. In the figure, k_t values for very small chain lengths are cut out because they are extremely large compared with those for larger chain length; for example, $k_t(1,1) = 6.74 \times 10^7$ and $k_t(1,1000) = 3.37 \times 10^7$, while $k_t(1000,1000) = 859$ in L·mol^{-1}·s^{-1}. On the other hand, at a low conversion (C4; $w_p = 0$), k_t decreases rather gradually with chain length.

Results and Discussion

Instantaneous MWD Formed with Chain-Length-Dependent k_t. First, we investigate the effect of the microreactor volume on the simulated results using the condition C1. The simulation was continued until 2×10^4 polymer molecules were formed. Since the parameters used are intended to be germane to styrene polymerization, the bimolecular termination reaction is assumed to be by combination. Figure 7 shows the effect of the microreactor volume on the simulated chain length distribution. There is virtually no difference for $n_v = 5$, 10, and 20. The necessary number of radicals in the microreactor can be as small as 5 radicals for the prediction of the overall MWD profile.

In the case of styrene polymerization, the bimolecular terminations are considered to be by combination. However, by assuming the termination mode to be disproportionation, one can investigate the size of radicals just before chain stoppage. Figure 8 shows the effect of the termination mode on the instantaneous

Table 2. Comparison of the Obtained Average Termination Rate Coefficients (in L·mol^{-1}·s^{-1}) and the Average Chain Lengths

	C1			C2	C3	C4
	$n_v = 5$	$n_v = 10$	$n_v = 20$	$n_v = 20$	$n_v = 20$	$n_v = 20$
$(\bar{k}_t)_R$[a]		8994		12046	16940	3.82×10^8
$(\bar{k}_t)_b$	8228	8255	8992	11761	16031	3.82×10^8
$(\bar{k}_t)_e$	8652	8460	9106	11909	16230	3.86×10^8
$P_n/(P_n)_R$[b]	1.002	1.008	0.996	1.008	0.999	0.995
P_w	5.28×10^4	5.39×10^4	5.25×10^4	4.24×10^4	2.71×10^4	2631
P_w/P_n	1.98	2.02	1.99	2.00	2.00	1.83

[a] The termination rate coefficients determined by Russell $(\bar{k}_t)_R$ for conditions C1 and C4 are "completely exact", while those for C2 and C3 are approximations that are called the "coarse-grained overall termination coefficients".[7] [b] $(P_n)_R$ is the number-average chain length calculated by using $(\bar{k}_t)_R$.

chain length distribution. When the termination mode is shifted to disproportionation, discrete peaks appear at very small chain lengths in the number fraction distribution, which correspond to the chain length with 1, 2, 3, etc. These peaks are formed because the bimolecular termination reactions are dominated by interactions between radicals with short and long chain lengths. In Figure 8, the distribution of radicals that cause bimolecular termination is also plotted (broken curve), which confirms that the oligomeric peaks are formed via bimolecular termination by disproportionation. In the present calculation condition (C1), only 11.8% of polymers are formed via bimolecular termination by disproportionation, so the area of the peaks for oligomeric chains is small. The area for the oligomeric peaks increases significantly when the initiation rate is increased since a larger number of dead polymer chains are formed by termination as will be shown later. Another important point worth noting here is that these oligomeric peaks cannot be observed if the distribution is given on a weight basis since these oligomers possess negligible weight fractions. Therefore, one needs to be careful when analyzing the MWD, especially when bimolecular termination by disproportionation is important, and the usual SEC technique to determine the MWD in which the weight-based distribution is measured cannot detect the oligomeric peaks as shown in the lower figure of Figure 8. If the oligomeric molecules are not detected correctly, one cannot distinguish the difference of the termination mode.

The fact that the distribution of radicals that cause chain stoppage possesses oligomeric peaks does not mean that the chain length distribution of radicals is bimodal. Figure 9 shows the chain length distribution of radicals as well as that for dead polymers assuming the termination mode is combination. The MWD of radicals is almost the same as that for dead polymers (which is very close to the most probable distribution as will be discussed later). This is due to the fact that all polymer radicals are stopped by the interaction with small molecules, i.e., bimolecular termination with oligomeric radicals and chain transfer to monomers. Coupling with such small molecules does not change the chain length of the macroradicals significantly; therefore, the MWDs of polymer radicals and dead polymers (without the existence of disproportionation) are almost the same.

Table 2 summarizes the obtained results for the average termination rate coefficients and the average chain lengths. The number of polymer molecules simulated are 2×10^4 for each condition. The termination mode is fully by combination. In the table, $(P_n)_R$ is the number-average chain length calculated from the average termination rate coefficient determined by Russell, $(\bar{k}_t)_R$. The number-average chain lengths obtained in the present simulation P_n agree very well with $(P_n)_R$ even when $n_v = 5$. On the basis of the results shown in Table 2 and Figure 7, the simulations with $n_v \geq 5$ give satisfactory prediction in terms of the MWD. On the other hand, however, a larger number of radicals in the microreactor may be required in order to estimate the number-average termination reaction rate coefficient as shown in the values of $(\bar{k}_t)_b$, in which pseudobulk kinetics is assumed (see eq 5).

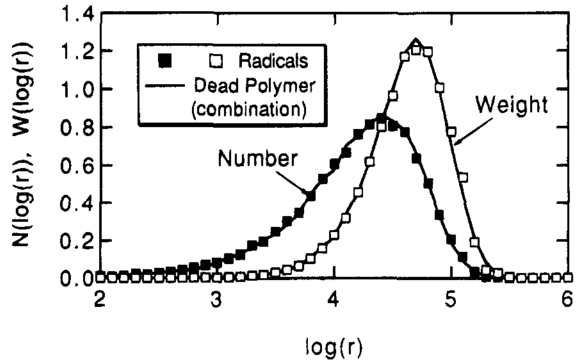

Figure 9. Instantaneous chain length distribution of the live polymer radicals (squares) and that for dead polymers. Bimolecular terminations are assumed to be fully by combination.

When pseudobulk kinetics is valid, it is expected that the number-average bimolecular termination coefficient is independent of the number of radicals within the microreactor, n_s. In such cases, the average termination rate coefficient can also be determined on the basis of the pseudoemulsion kinetics given in eq 3; i.e., the average termination rate coefficient that gives the same $\bar{n}_s$ as the simulated results $(\bar{k}_t)_e$ can be determined from eq 3. This procedure improves the results, especially for $n_v = 5$.

Besides conditions C1 and C4, we examined two other conditions. Under C2, the initiation rate is increased to be $R_I = 1.72 \times 10^{-8}$ while other parameters are the same as under C1. Since the production rate of the oligomeric radicals is increased by increasing the initiation rate, the average $\bar{k}_t$ becomes larger. Therefore, when the chain-length-dependent k_t is considered, the polymerization rate is not proportional to $(R_I)^{0.5}$ but shows a smaller power and decreases with increasing R_I as reported by Russell.[7] As a limit, the polymerization rate becomes independent of initiation rate.[35]

In C3, the chain transfer constant is increased to be $C_m = 7.06 \times 10^{-5}$, keeping other parameters same as in C1. The increase in the chain transfer constant increases the production rate of oligomeric radicals; therefore, $\bar{k}_t$ becomes larger than that under condition

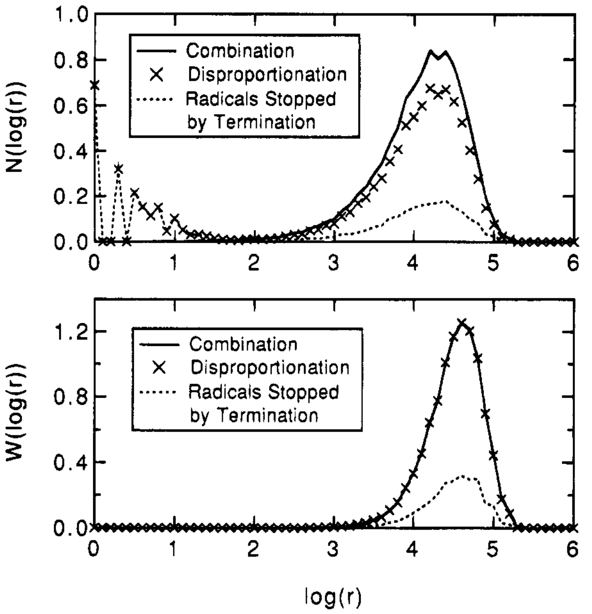

Figure 10. Instantaneous chain length distribution formed under condition C2.

C1. Incidentally, the accuracy of $\bar{k}_t$ estimated under condition C3 is a little worse than the other cases. This is simply because most polymer chains are produced by chain transfer reactions (95.6%) and the number of termination events is small even when 2×10^4 polymer molecules are generated in the microreactor.

Figure 10 shows the chain length distribution formed under condition C2. Since a larger number of polymers are formed by termination than in C1, the oligomeric peaks in the number fraction distribution becomes much larger than in C1 if the termination mode is disproportionation. As mentioned earlier, such oligomeric peaks cannot be observed in the weight fraction distribution, and the difference in the termination mode cannot be found in $W(\log(r))$ that is usually determined in a SEC measurement.

The present type of MWDs can be formed in emulsion polymerizations even with a single constant k_t.[24,27] In a typical emulsion polymerization, each polymer particle possesses only 0 or 1 radicals. When an oligomeric radical enters a polymer particle that possesses a macroradical in it, the bimolecular termination occurs before the newly entered radical grows to a sufficient chain length, resulting in producing oligomeric molecules if bimolecular termination by disproportionation is involved. In a typical emulsion polymerization, therefore, terminations between short and long polymer radicals occur due to the fact that the longer polymer radicals are isolated into polymer particles and only oligomeric radicals can be transferred into polymer particles. On the other hand, in the chain-length-dependent bimolecular termination in homogeneous polymerizations, similar behavior is caused because the mobility of large-sized macroradicals is highly suppressed while only oligomeric radicals can diffuse through the maze of a polymeric medium.

Next, we consider a simple approximation for the MWD, which may be useful to rationalize the MWD in a real system. If a single constant is used for the termination rate coefficient, the dead polymer distribution follows eq 8. Obviously, eq 8 cannot be applied when bimolecular termination by disproportionation is involved since it can never give oligomeric peaks. On the other hand, if bimolecular terminations are fully by combination, oligomeric peaks are not formed even with the chain-length-dependent termination. Figure 11 shows the comparison of eq 8 (broken curve) and the simulated results. Under the present calculation conditions where only 25.8% of polymers are formed by termination by combination, the agreement with eq 8 is not so bad. However, as shown in Figure 11 (solid curve), the most probable distribution gives better agreement. This can be rationalized as follows. First of all, chain transfer reactions are not chain-length-dependent. Since the probability of chain stoppage via chain transfer is independent of chain length, chain transfer reactions result in the most probable distribution. Secondly, most bimolecular terminations are between radicals with long chain lengths ($r > 10^3$) and those with oligomeric radicals ($r < 10$) (see Figure 10). Note that the chain length of the longer polymer radicals does not change the termination rate coefficient significantly in such a radical pair. For example, $k_t(1,10^3) \approx k_t(1,10^5) = 3.37 \times 10^7$ and $k_t(10,10^3) \approx k_t(10,10^5) = 1.85 \times 10^6$. From the point of view of the longer polymer radicals, each oligomeric radical acts as a chain-stopping agent whose reactivity changes with chain length, $r = 1, 2, 3, ..., 10$. In other words, we have about 10 different types of chain-stopping agents. Therefore, the probability of chain stoppage for macroradicals ($r > 10^3$) becomes independent of the chain length, and the most probable distribution is formed for the macroradicals (except for the oligomeric chains). Since the coupling of oligomeric radicals, essentially, does not change the chain length of the macroradicals, the most probable distribution is retained for the dead polymer molecules if the termination mode is combination.

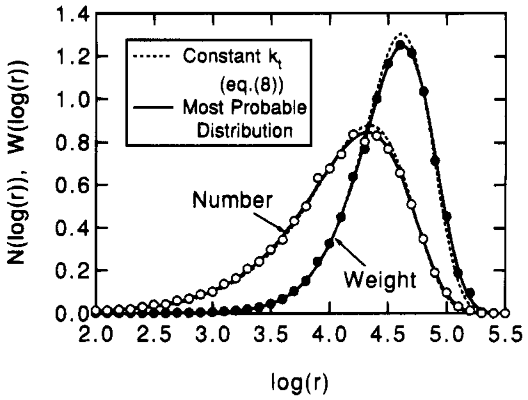

Figure 11. Approximation of the instantaneous chain length distribution formed under condition C2 with bimolecular termination by combination.

Figure 12 shows the chain length distribution formed under condition C4, i.e., in the low-conversion region. In C4, most polymer molecules (95.8% assuming combination) are formed via bimolecular termination. Termination reactions occur with various combinations of polymer radicals, and a smooth distribution is observed even when bimolecular terminations are solely by disproportionation. The situation is more complex than the intermediate conversion (C1–C3). Even when bimolecular termination reactions are solely by combination, simple approximations such as eq 8 and the most probable distribution cannot be applied as shown in Figure 13.

Assuming bimolecular termination reactions are by combination, we examined the Schulz–Zimm distribution[37,38] as an approximation of the MWD, whose functional form is given by

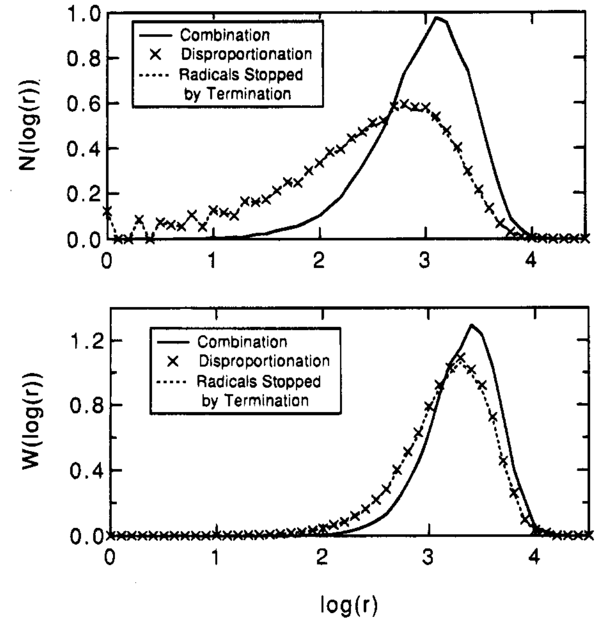

Figure 12. Instantaneous chain length distribution formed under condition C4.

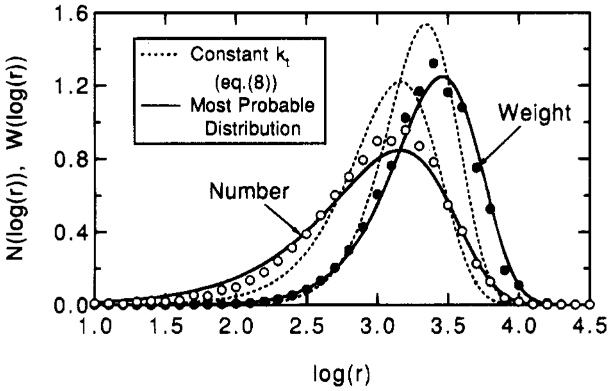

Figure 13. Approximation of the instantaneous chain length distribution formed under condition C4 with bimolecular termination by combination, using eq 8 and the most probable distribution.

$$W(r) = \frac{\sigma^{\sigma}}{u\Gamma(\sigma)}\left(\frac{r}{u}\right)^{\sigma} \exp\left(-\frac{\sigma r}{u}\right) \tag{16}$$

where u is the number-average chain length ($=P_n$), and σ is a parameter indicating the narrowness of the distribution breadth, which is given by $\sigma = P_n/(P_w - P_n)$.

Figure 14 shows the comparison of the MWDs. Satisfactory agreement is observed. Since the most probable distribution, which worked well for the intermediate conversion, belongs to the Schulz–Zimm distribution with $\sigma = 1$, it may be speculated that the instantaneous MWD may be approximated by the empirical form of the Schulz–Zimm distribution for a wide conversion range at least when the amount of polymers produced via bimolecular termination by disproportionation is negligible. While this speculation needs further examination, there is hope to represent the MWD formed with the chain-length-dependent bimolecular termination using simpler functions.

After submission of the present paper, a paper by Clay and Gilbert[39] appeared, where they discussed the effect of the chain length dependence on the instantaneous MWD formed under the stationary state by employing the same functional form of k_t as the present paper.

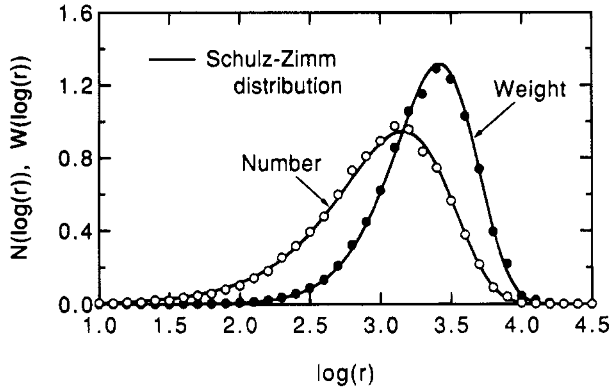

Figure 14. Approximation of the instantaneous chain length distribution formed under condition C4 using the Schulz–Zimm distribution.

They used a deterministic approach in which an infinite number of simultaneous differential equations are solved both numerically and analytically. Many of the inferences made in their paper are confirmed with the use of the Monte Carlo simulations shown in the present paper. The deterministic approach enables one to obtain exact solutions under simplified conditions. On the other hand, the Monte Carlo approach can be more widely applicable, although the solutions are always given with a finite variance as long as the sample size is finite. The two approaches are therefore nicely complementary.

Simulation for the Unsteady State. An advantage of Monte Carlo simulations is that it is straightforward to conduct simulations for the unsteady state. In order to obtain statistically valid results, the time evolution of polymerization must be reiterated many times; i.e., we need to conduct simulations for a large number of microreactors.

Suppose we stop a styrene polymerization at conversion $w_p = 0.76$ and reinitiate polymerization starting from zero concentration of radicals. Here, we make simulation for such a start up period using the parameters for condition C1. In the simulation, it is assumed that all parameters are kept constant during the start up period. This assumption would be acceptable because here we conduct simulation for the conversion interval only from $w_p = 0.76$ to $w_p = 0.77$. The simulation was reiterated 200 times; i.e., 200 microreactors were investigated.

If a single constant ($(\bar{k}_t)_R = 8994$) is used for the termination rate coefficient, conventional kinetics tells us that the average chain length decreases during the start up period, because termination reactions are suppressed due to a low radical concentration. However, when the chain-length-dependent bimolecular terminations are considered, the termination reactions during the start up period would be enhanced due to a higher mole fraction of oligomeric radicals in spite of a lower radical concentration. Figure 15 shows the simulated results for the average chain lengths of the dead polymer molecules (the termination mode is combination), and the average chain lengths increase with time. The molecular weight development is completely different from the predictions using a single constant termination rate coefficient. More details on the unsteady-state results will be reported separately.

Conclusions

A new Monte Carlo simulation method based on the segregated microreactor is proposed for the chain-

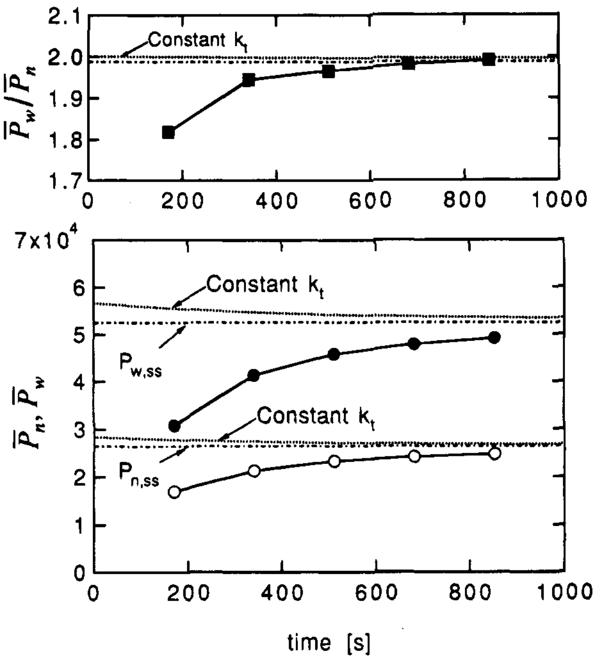

Figure 15. Average chain length development during the start up period under condition C1. Calculated results based on a single constant rate coefficient ($(\bar{k}_t)_R$ = 8994 with the stationary-state hypothesis) and the average chain lengths for the instantaneous distribution at steady state ($P_{n,ss}$ and $P_{w,ss}$) are also shown.

length-dependent kinetics in homogeneous polymerizations. This technique is deeply inspired by the kinetics of emulsion polymerization, and it is straightforward to extend the present technique to emulsion polymerization that involves chain-length-dependet kinetics, which is the topic of the second part of this series.[40]

The necessary volume of the microreactor to simulate the MWD in homogeneous polymerizations with sufficient accuracy is as small as one containing only about 5 radicals, and a large number of calculations are not required. Simulations are conducted using the parameters that are intended to be germane to the bulk polymerization of styrene. At $w_p = 0.76$, the bimolecular terminations are dominated by interactions between radicals with short ($r < 10$) and long chain lengths ($r > 10^3$). When bimolecular termination by disproportionation is significant, short oligomeric chains that are large in number but small in weight are formed, which may be difficult to determine experimentally. If bimolecular termination is solely by combination, the instantaneous MWD formed in these conversions (except for the oligomeric chains[39]) may be approximated well with the most probable distribution since all macroradicals are stopped by the interactions with small molecules. On the other hand, the MWD formed at low conversions is more complex since the probability of chain stoppage for polymer radicals changes rather gradually with chain length. The Schulz–Zimm distribution was found to be a good approximation for the conditions used in the present investigation as long as the amount of polymers formed via bimolecular termination by disproportionation is negligibly small. The molecular weight development under the unsteady state can be significantly different from the predictions based on the assumption of a single constant termination rate coefficient.

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