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Kinetics of Free-Radical Polymerization with Chain-Length-Dependent Bimolecular Termination under Unstationary Conditions

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ABSTRACT: The kinetics of chain-length-dependent bimolecular terminations in free-radical polymerization during unstationary state periods are investigated by employing Monte Carlo simulations in segregated microreactors where pseudobulk kinetics is valid. We investigate two types of unstationary conditions: (1) the pre-stationary-state period, in which the radical concentration increases from zero to the stationary-state value, and (2) the posteffect period, in which the radical concentration decreases from the stationary-state value toward zero. The simulations are made to investigate the time developments of radical concentrations and the molecular weights, and the results are compared with those for the cases where a constant termination rate coefficient that is equal to the number-average termination rate coefficient at stationary state is used. The transient periods are longer than those for the cases with constant termination rate coefficients, and the differences become larger as the chain length dependence is enhanced. On the other hand, however, the chain transfer reactions may dominate the stoppage of growing polymer radicals at the intermediate to high conversion regions due to a significant decrease in the bimolecular termination rate coefficient. In such cases, the differences from a constant bimolecular termination rate coefficient become negligible.

Introduction

The bimolecular termination in free-radical polymerization is a typical example of the diffusion-controlled reaction. Because the polymer diffusion is a function of polymer chain length, a logical consequence is that the bimolecular termination reactions are chain-length-dependent. Chain-length-dependent kinetics presents a complicated mathematical problem in which an infinite number of combinations of radical pairs whose rate coefficients are different must be considered. This problem often leads to an infinite number of simultaneous differential equations. At the stationary state, however, such differential equations reduce to an infinite number of simultaneous equations, and numerical and analytical techniques have been developed for such simplified cases.[1−8]

The stationary-state hypothesis is valid for a wide variety of free-radical polymerizations; however, this may not be the case during a significant autoacceleration period.[9] In such cases, the calculations under unstationary state are inevitable. Furthermore, consideration on the unstationary conditions would provide deeper insight into the kinetics of chain-length-dependent termination. Under unstationary conditions, however, one needs to solve an infinite number of differential equations if balance equations among various species are considered, which is much more complicated than for the stationary-state calculations.

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. O'Driscoll and Kuindersma[10] conducted a Monte Carlo simulation of pulsed laser polymerization using a segregated microreactor in which 5000 radicals are generated in a single pulse of the laser. It is known that the pseudobulk kinetics is valid if the segregated microreactor is so large as to contain more than 5−10 radicals,[11−16] at least under stationary-state conditions; therefore, the statistically valid results could be obtained by employing a large number of segregated microreactors, each of which contains only a small number of radicals.

In the conventional Monte Carlo simulations for the molecular buildup processes, monomeric units are added to each growing polymer molecule one by one; therefore, a great many random numbers and calculations are required to simulate the formation of each polymer molecule. Instead, we proposed a new concept, which is called the *competition technique*, that reduces the amount of calculation required significantly.[16−20] In this paper, we use the competition technique in the segregated microreactors and investigate the characteristics of chain-length-dependent bimolecular terminations during such unstationary conditions as the pre-stationary-state period and the posteffect period.

Competition Technique

We partition the reaction volume into segregated microreactors, each of which contains only a small number of radicals. In the competition technique, we use appropriate probability distributions to estimate the time interval for each possible event to occur and choose the event that occurs first as a real event. There are at least three types of event we need to account for in the context of the competition technique: radical generation, chain transfer reactions, and bimolecular terminations. The diffusion of radicals in and out of a microreactor could also be accounted for in the context of the competition technique. However, it was shown earlier[16] that the radical movement across the partition wall can be neglected as long as the size of the microreactor is large enough (to contain more than about 5 radicals at stationary state); therefore, such movement is not considered in the present analysis.

As an illustrative purpose, consider the case where two polymer radicals exist in a microreactor, as shown

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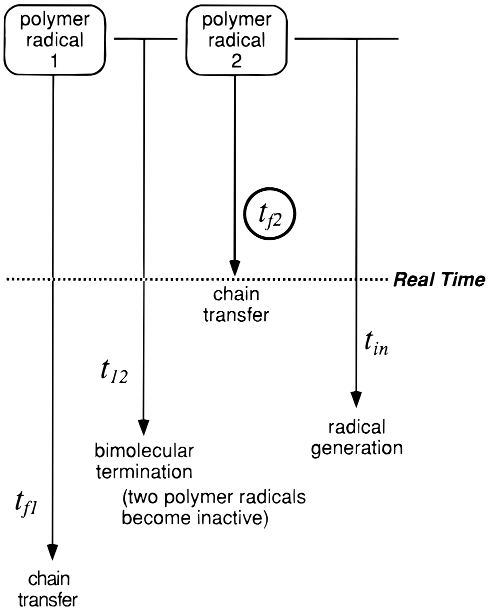

Figure 1. Schematic drawing of the competition technique.

in Figure 1. We determine the *imaginary time* for each event to occur using the Monte Carlo method and regard the event with the shortest imaginary time as a real event. In the case shown in Figure 1, we calculate the imaginary time until chain stoppage is caused by chain transfer reactions on each polymer radical (t_{f1} and t_{f2}) and by bimolecular termination between polymer radicals 1 and 2 (t_{12}) and the imaginary time for radical generation (t_{in}). At this stage, a kind of competition of events is considered, i.e., the event given by the shortest imaginary time is chosen as the real event.

In the present example, the chain transfer reaction of the polymer radical 2 (t_{f2}) is chosen as a real event, which means that the events given by the other imaginary time t_{f1}, t_{12}, and t_{in}) never happened in reality and are rejected. Our "clock" has now proceeded to the time shown by the dotted line in Figure 1 (real time). The polymer radical 1 simply grows to add monomeric units during that period and still possesses an active center after the growth. The number of monomeric units (r) added to a radical center during the time interval t conforms to the following Poisson distribution:

$$p(r) = e^{-\theta}\theta^r/r! \qquad (1)$$

where θ is the expected number of monomeric units added to a radical center, given by

$$\theta = k_p[M]t \qquad (2)$$

where k_p is the propagation rate coefficient and [M] is the monomer concentration. If the number of the added monomeric units, r, is large enough, one can approximate that $r \cong \theta$. In the simulations shown later, we used $r = \theta$.

If bimolecular termination is the real event, two polymer radicals become inactive. When the radical generation wins the race, the number of radicals increases by one. By reiterating these processes, one can simulate the polymerization reactions occurring in a microreactor. If the microreactor size is large enough and the pseudobulk kinetics is valid, one can simulate bulk polymerizations.

We use the probability density function for each event to occur in order to determine the imaginary time stochastically. The appropriate probability density functions are summarized below.[16-20]

Radical Generation. Let the rate of initiation be R_{in}. The average time interval between radical generation within the microreactor is given by

$$\bar{t}_{in} = 1/(R_{in}\nu N_A) \qquad (3)$$

where ν is the volume of the microreactor and N_A is Avogadro's number. The radicals may be created in pairs, as in the case for the thermal decomposition of initiators; however, in this paper we assume that radicals are generated one by one. Because the generation of radicals is considered a random process, the time required to generate a radical is given by the following most probable distribution:

$$p_{in}(t_{in}) = (1/\bar{t}_{in})\exp(-t_{in}/\bar{t}_{in}) \qquad (4)$$

If the transformation shown in eq 2 is used, eq 4 can be rewritten as follows:

$$p_{in}(\theta_{in}) = \epsilon\exp(-\epsilon\theta_{in}) \qquad (5)$$

where $\epsilon = 1/(k_p[M]\bar{t}_{in})$. Note that the change in the monomer concentration during $\bar{t}_{in}$ can be neglected under usual polymerization conditions.

Chain Transfer Reactions. The probability density for the time interval until the chain transfer reaction occurs on a particular polymer radical is given by the following most probable distribution:

$$p_f(t_f) = (k_{fm}[M] + k_{fT}[T])\exp[-(k_{fm}[M] + k_{fT}[T])t_f] \qquad (6)$$

where k_{fm} and k_{fT} are the rate constants for chain transfer to monomer and chain transfer agents (T), respectively. The imaginary time for chain stoppage by chain transfer must be determined for all polymer radicals that exist in the microreactor.

If we use the transformation given by eq 2, eq 6 reduces to

$$p_f(\theta_f) = C_f\exp(-C_f\theta_f) \qquad (7)$$

where $C_f = C_m + k_{fT}[T]/(k_p[M])$, and C_m is the monomer transfer constant.

Bimolecular Termination. If the bimolecular termination reactions are independent of chain length, the required time for bimolecular termination between a particular radical pair is also given by the following most probable distribution:

$$p_t(\theta_t) = \xi\exp(-\xi\theta_t) \qquad (8)$$

where $\xi = k_t/(k_p[M]\nu N_A)$, and k_t is the bimolecular termination rate coefficient. The imaginary time for chain stoppage by bimolecular termination must be considered for all radical pairs that exist in the microreactor.

On the other hand, if the bimolecular termination reactions are chain-length-dependent, the parameter ξ changes with chain length. Suppose we have n radicals in the microreactor. Let the chain length of the ith radical be r_i and that for the jth radical be r_j. The probability that this radical pair causes bimolecular termination before adding one monomeric unit, $\xi(r_i,r_j)$, is given by[21]

$$\xi(r_i,r_j) = k_t(r_i,r_j)/(k_p[M]\nu N_A) \qquad (9)$$

Table 1. Parameters Used for the Present Investigation on the Basis of Eq 11

	Z3
z	0.3
$k_p[\mathrm{M}]$ (s^{-1})	5×10^{2}
R_{in} (mol L^{-1} s^{-1})	4×10^{-8}
$k_t(1,1)$ (L mol^{-1} s^{-1})	1×10^{8}

In eq 9, it is tacitly assumed that the time interval between monomer additions is $1/(k_p[\mathrm{M}])$, and the statistical deviation was neglected. Therefore, eq 9 is approximate but would be applicable for usual free-radical polymerizations where $1/(k_p[\mathrm{M}])$ is small enough.[22]

The probability that the ith radical and the jth radical continue to add more than r_{ij} monomeric units without causing bimolecular termination between them is given by

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

Therefore, r_{ij} can be determined stochastically by solving eq 10 on the basis of $P_t(r_{ij})$ that is given by a random number between 0 and 1. A method to reduce the amount of calculations when using eq 10 can be found elsewhere.[16]

Functional Form of Bimolecular Termination Rate Coefficient

In this paper, we examine two types of functional forms for the chain length dependence of the bimolecular termination reactions. The first type is an empirical relationship based on the geometric mean assumption that is given by[1-5,23,24]

$$k_t(l,m)/k_t(1,1) = (lm)^{-z} \tag{11}$$

where z is a constant usually about the order of 10^{-1} at low conversion regime and l and m are chain lengths of macroradicals. In the present paper, we examine the case with $z = 0.3$, as shown in Table 1. This condition is named Z3.

The second type of functional form used in the present paper is the model developed by Russell et al.[6,7] The outline of their model is as follows. On the basis of the Smoluchowski equation,[25] $k_t(l,m)$ is given by

$$k_t(l,m) = 4\pi(D_l + D_m)\sigma N_{\mathrm{A}} \tag{12}$$

where D_l and D_m are the diffusion coefficients for the chain ends of macroradicals 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}:

$$D_l = D_{l,\mathrm{com}} + D_{\mathrm{rd}} \tag{13}$$

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

$$D_{l,\mathrm{com}} = \begin{cases} D_{\mathrm{mon}}/l^{a} & \text{for } l \le X_{\mathrm{c}} \\ D_{\mathrm{mon}}(X_{\mathrm{c}})^{b-a}/l^{b} & \text{for } X_{\mathrm{c}} \le l \end{cases} \tag{14}$$

$$D_{\mathrm{rd}} = k_p[\mathrm{M}]A^{2}/6 \tag{15}$$

Table 2. Parameters for Eqs 12–15 That Are Pertinent to the Bulk Polymerization of Styrene[7]

	S00	S76
condition	20 °C, $w_p = 0$[a]	50 °C, $w_p = 0.76$[a]
[M] (mol L^{-1})	8.70	2.30
σ (Å)	3	6.02
D_{mon} (cm^{2} s^{-1})	1.5×10^{-5}	7.4×10^{-8}
a	0.487	1
b	0.584	2
X_{c}	86.4	5.5
A (Å)	7.4	7.4
k_p (L mol^{-1} s^{-1})	60.3	255
C_{m}	2.92×10^{-5}	3.53×10^{-5}
R_{I} (mol L^{-1} s^{-1})	1.26×10^{-9}	8.6×10^{-10}

[a] Weight fraction of polymer.

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

The parameters used for the present investigation are shown in Table 2. These conditions are intended to fit for the bulk polymerization of styrene at 20 °C, with the polymer weight fraction $w_p = 0$ (which is called S00) and that at 50 °C with $w_p = 0.76$ (S76).[7] These conditions correspond to the conditions C4 and C1, respectively, in ref 16. It may be worth noting here that, although the parameters shown in Table 2 were determined from the experimental data for styrene polymerization, the obtained parameters as well as the functional form of k_t may need further investigation (such as the full molecular weight distribution (MWD) analysis under stationary and unstationary conditions) before it can be used extensively. Our fundamental attitude is that we expect that condition S00 shows polymerization kinetics characteristic of the low to intermediate conversion region, while condition S76 provides information on the characteristic behavior for intermediate to high conversions.

The functional forms of the chain-length-dependent bimolecular termination coefficient for the conditions Z3, S00, and S76 are shown graphically in Figure 2. The reduction of the bimolecular termination rate coefficient for large macroradical pairs compared with $k_t(1,1)$ (which is the largest k_t value within all radical pairs) is most significant under condition S76, and the decrease is the smallest for S00. From Figure 2, it would be reasonable to consider that the $k_t(l,m)$ surface decreases more rapidly for larger chain lengths as conversion increases. Note that the use of a single constant, k_t, means that $k_t(l,m)$ becomes a flat surface that is equal to $k_t(1,1)$. The simulated results for the stationary state under conditions S00 and S76 can be found elsewhere.[16] Under condition S76, most bimolecular termination reactions occur between radicals with short ($l < 10$) and long ($m < 10^{3}$) chain lengths, resulting in formation of the discrete oligomeric peaks in the number fraction distribution $\{N(\log(r))\}$ if bimolecular termination by disproportionation is significant.[16] On the other hand, under condition S00, termination reactions occur with various combinations of polymer radicals, and a smooth distribution is obtained even when the bimolecular terminations occur solely by disproportionation.[16]

Because the MWD at stationary state under conditions S00 and S76 can be found in ref 16, here we show the MWD at stationary state for Z3 (Figure 3). The Monte Carlo simulation was made to produce 2×10^{4} polymer molecules after reaching the stationary state. Under condition Z3, the obtained MWD is smooth, and

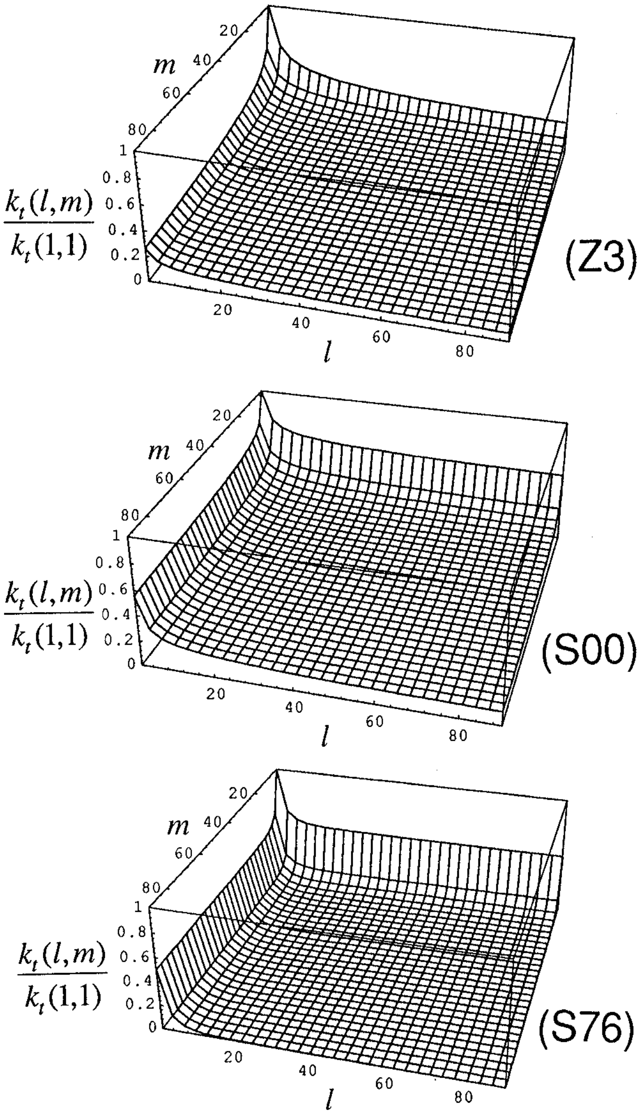

Figure 2. Graphical representation of the termination rate coefficients as a function of chain lengths, l and m, under conditions Z3, S00, and S76.

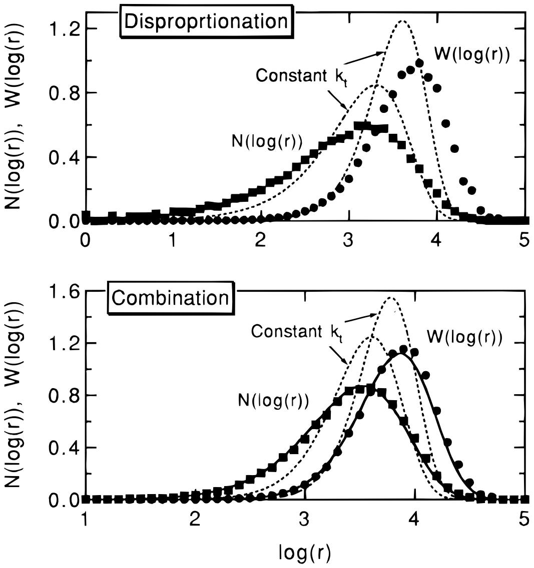

Figure 3. Number $\{N(\log(r))\}$ and weight fraction distributions $\{W(\log(r))\}$ at stationary state under condition Z3. The upper figure shows the case where all dead polymer chains are formed by disproportionation termination, while the lower figure shows the case with combination termination. The symbols show the Monte Carlo simulation results [■, $N(\log(r))$; ●, $W(\log(r))$], and the dotted curves are the theoretical MWDs formed under a constant k_t that is equal to the number-average bimolecular termination rate coefficient $\bar{k}_t$ [left curve, $N(\log(r))$; right curve, $W(\log(r))$]. The solid curve in the lower figure shows the approximate solution developed by Olaj et al.[3] [left curve, $N(\log(r))$; right curve, $W(\log(r))$].

significant discrete oligomeric peaks are not formed, even for $N(\log(r))$, with bimolecular termination solely by disproportionation (upper figure). If one uses a single constant bimolecular termination coefficient that is equal to the number-average termination rate coefficient ($\bar{k}_t$), one obtains the MWD shown by the dotted curves. Although we can determine $\bar{k}_t$ from the polymerization rate analysis experimentally, we cannot use $\bar{k}_t$ for the prediction of the MWD, as shown in the figure.

When the geometric mean assumption (eq 11) is used, an approximate solution for the MWD was obtained under conditions where dead polymer chains are formed solely via bimolecular termination by combination.[3] The calculated results are shown by the solid curves in Figure 3 (lower figure). The agreement with the simulated results is satisfactory.

Fundamental Equations for Unstationary Conditions without Chain Length Dependence

In the present paper, we compare kinetic behavior with and without chain length dependence in bimolecular termination. In this section, we show the fundamental equations for the calculations with a chain-length-independent termination rate coefficient. Let the ith moment of the polymer radical distribution be Y_i and that for the dead polymer molecules be Q_i, which are defined by

$$Y_i = \sum_{r=1}^{\infty} r^i [\mathrm{R}_r^\bullet] \qquad (16)$$

$$Q_i = \sum_{r=1}^{\infty} r^i [\mathrm{P}_r] \qquad (17)$$

where $[\mathrm{R}_r^\bullet]$ is the concentration of polymer radical with chain length r and $[\mathrm{P}_r]$ is that for the dead polymer molecule.

On the basis of the balance equations for polymer radicals and dead polymer molecules, one can readily formulate the following differential equations:[26]

$$\frac{\mathrm{d}y_i}{\mathrm{d}\theta} = \sqrt{\epsilon\xi} + C_f y_0 + \sum_{j=0}^{i-1} \binom{i}{j} y_j - (C_f + \sqrt{\epsilon\xi}\, y_0) y_i \qquad (18)$$

$$\frac{\mathrm{d}q_0}{\mathrm{d}\theta} = C_f y_0 + \sqrt{\epsilon\xi}\, {y_0}^2 (1 - \phi_c/2) \qquad (19)$$

$$\frac{\mathrm{d}q_i}{\mathrm{d}\theta} = (C_f + \sqrt{\epsilon\xi}\, y_0) y_i + \frac{\phi_c \sqrt{\epsilon\xi}}{2} \sum_{j=1}^{i-1} \binom{i}{j} y_j y_{i-j} \qquad (i \geq 1) \qquad (20)$$

where $y_i = Y_i/Y_{0,\mathrm{ss}}$, $q_i = Q_i/Y_{0,\mathrm{ss}}$, and $Y_{0,\mathrm{ss}}$ is the stationary-state value of Y_0, given by $Y_{0,\mathrm{ss}} = (R_{\mathrm{in}}/k_t)^{1/2}$.

The radical concentration development can be obtained by solving eq 18 with $i = 0$. The number- and weight-average chain lengths of the accumulated dead polymer molecules are given by $P_N = q_1/q_0$ and $P_W = q_2/q_1$, respectively.

Results and Discussion

We investigate two types of unstationary conditions assuming that the rate of radical generation can be

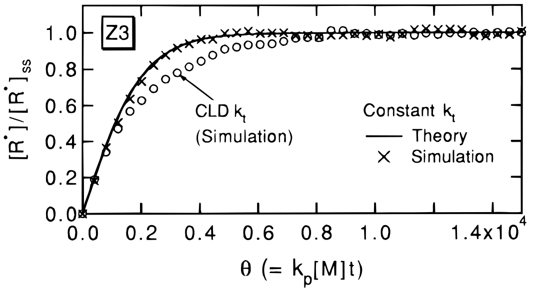

Figure 4. Radical concentration development during the start-up period under condition Z3. The solid curve is the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used (eq 18), and the symbols show the Monte Carlo simulation results (×, constant k_t; ○, chain-length-dependent k_t). In the figure, CLD k_t means the chain-length-dependent k_t.

changed instantaneously: (1) the pre-stationary-state period, in which the radical concentration increases from zero to the stationary-state value, and (2) the posteffect period, in which the radical concentration decreases from the stationary-state value toward zero.

Simulation results under the assumption that bimolecular termination is solely by disproportionation provide useful information on the chain length dependence of bimolecular termination reactions, because the chain lengths of radicals that stopped growing are preserved. In this section, however, we show the simulated results of the MWD only for the bimolecular termination reactions that occur solely by combination.

Pre-Stationary-State Period. It was shown[16] that the volume of the microreactor necessary to simulate the MWD in homogeneous polymerizations with sufficient accuracy is so small that it may contain about five radicals for the stationary-state calculations. In the present investigation of the pre-stationary-state period, we used microreactors that contains $n_\nu = 10$ radicals at stationary state, which is given by $n_\nu = \nu N_A(R_{in}/\bar{k}_{t,ss})^{1/2}$, where $\bar{k}_{t,ss}$ is the number-average bimolecular termination rate coefficient at stationary state. The Monte Carlo simulations are made for 300 microreactors in order to obtain statistically valid results.

In the calculations, we neglected change in the monomer concentration as well as in the parameters used for the calculations during the transient period. This is reasonable, because the conversion intervals (Δx) we simulated are very small, i.e., $\Delta x < 2.5 \times 10^{-4}$ for Z3, assuming the density of the reaction mixture, $\rho = 1$ g/cm^3, and the molecular weight of a monomeric unit, $M_w = 100$; $\Delta x < 1.3 \times 10^{-6}$ for S00 (bulk polymerization of styrene); and $\Delta x < 1.5 \times 10^{-2}$ for S76 (bulk polymerization of styrene).

Figure 4 shows the radical concentration development under condition Z3. In the figure, $[R^\bullet]_{ss}$ is the polymer radical concentration at stationary state. The ×'s show the Monte Carlo simulation results for a constant bimolecular termination rate coefficient that is equal to $\bar{k}_{t,ss}$, while the solid curve shows the theoretical calculation results obtained from eq 18. Excellent agreement between the ×'s and the solid curve shows that the volume of the microreactor that contains 10 radicals at stationary state is satisfactory to mimic the kinetics of bulk polymerizations, even for the unstationary conditions.

On the other hand, the ○'s in Figure 4 show the simulated results for the chain-length-dependent termination. The transient period is longer than that for the case with a constant k_t. During the start-up period, the average chain length of radicals is smaller than that at stationary state. Because the smaller radicals enhance the bimolecular termination reactions, the number-average bimolecular termination reaction rate coefficient ($\bar{k}_t$) is larger than that at the stationary state ($\bar{k}_{t,ss}$), which makes the radical concentration smaller during the transient period.

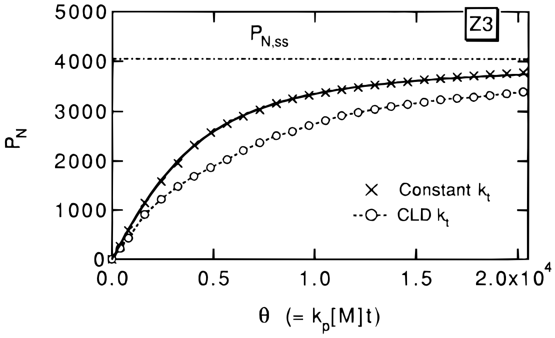

Figure 5. Number-average chain length development during the start-up period under condition Z3. The solid curve is the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used, and the symbols show the Monte Carlo simulation results. The number-average chain length at stationary state, $P_{N,ss}$ is also shown in the figure.

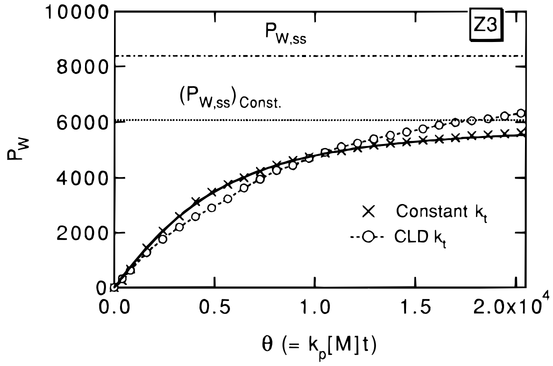

Figure 6. Weight-average chain length development during the start-up period under condition Z3. The solid curve is the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used, and the symbols show the Monte Carlo simulation results. In the figure, $P_{W,ss}$ and $(P_{W,ss})_{Const}$ are the weight-average chain length at stationary state with and without chain length dependence of k_t.

Figure 5 shows the number-average chain length development during the start-up period under condition Z3. The solid curve shows the analytical solution for a constant k_t calculated from eqs 18–20, while the symbols are the results obtained in the Monte Carlo simulations. Due to a larger termination rate coefficient, smaller chains are formed in the chain-length-dependent termination. Note that, because $\bar{k}_{t,ss}$ is used as a constant k_t value, the number-average chain length at the stationary state, $P_{N,ss}$ is the same for both with and without chain length dependence.

Figure 6 shows the development of the weight-average chain length under condition Z3. Although a larger number of chains are formed due to a larger $\bar{k}_t$ during the start-up period with the chain-length-dependent termination, a large fraction of termination events occur by consuming smaller polymer radicals, and the weight-average chain length becomes larger than that obtained with constant k_t after a while. Note that the weight-average chain length at stationary state is larger than that for the case with a constant k_t, as proved earlier.[16]

Figure 7 shows the radical concentration development under condition S00. Condition S00 is intended to fit for the bulk polymerization of styrene at 20 °C, with

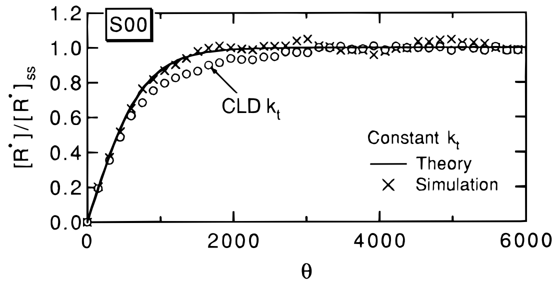

Figure 7. Radical concentration development during the start-up period under condition S00 (styrene polymerization at 20 °C, $w_p = 0$). The solid curve is the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used, and the symbols show the Monte Carlo simulation results.

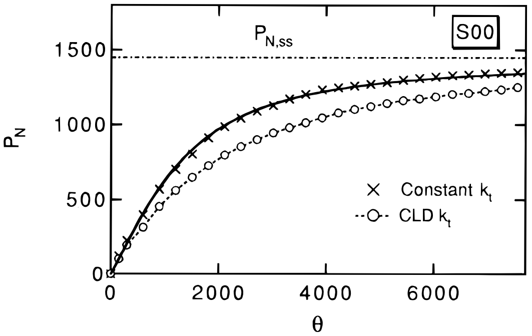

Figure 8. Number-average chain length development during the start-up period under condition S00. The solid curve shows the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used, and the symbols show the Monte Carlo simulation results.

the polymer weight fraction $w_p = 0$. The simulation results under this condition may be expected to show general characteristics of the kinetic behavior at the low to intermediate conversion level. Under the present condition, the effect of chain transfer is very small, and 95.8% of chains (on a number basis) are formed by bimolecular termination at stationary state. The difference from the result obtained a constant k_t is rather small compared with the case for Z3 (Figure 4). It would be reasonable to consider that the difference from a constant k_t becomes larger as the decrease of k_t for large polymer radicals becomes significant, i.e., the surface of $k_t(l,m)$ shown in Figure 2 drops more significantly. Because the $k_t(l,m)$ surface may decrease more significantly as conversion increases at the low to intermediate conversion region, the deviation from the estimation using a single constant k_t (solid curve) may be expected to become larger as conversion increases.

Figure 8 shows the number-average chain length development under condition S00. Even though the difference in the radical concentration development is rather small (Figure 7), there exists clear distinction from the results with a constant k_t in the average chain length developments. Figure 9 shows the weight-average chain length development for S00.

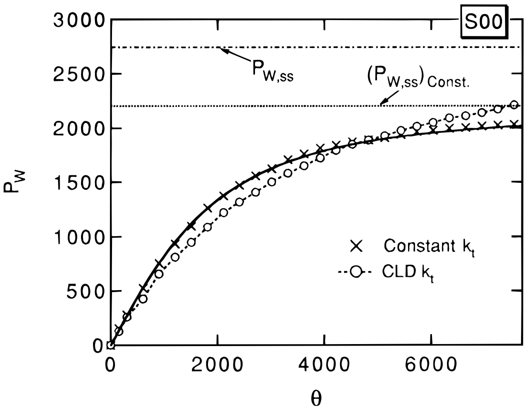

Figure 9. Weight-average chain length development during the start-up period under condition S00. The solid curve is the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used, and the symbols show the Monte Carlo simulation results. The stationary-state P_W values are different depending on chain length dependence.

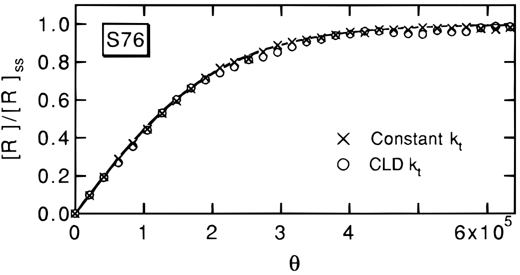

Figure 10. Radical concentration development during the start-up period under condition S76 (styrene polymerization at 50 °C, $w_p = 0.76$). The solid curve is the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used, and the symbols show the Monte Carlo simulation results.

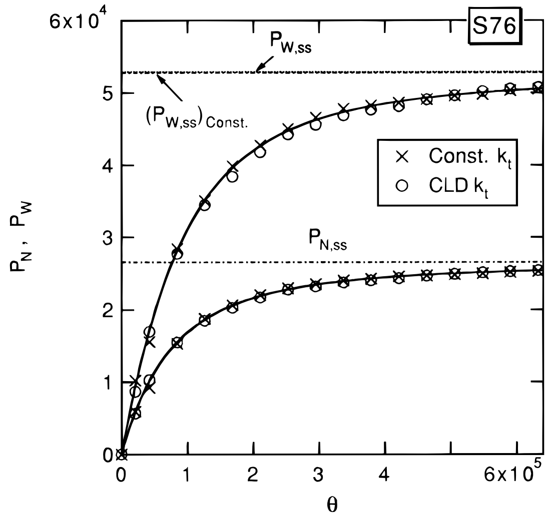

Figure 11. Average chain length development during the start-up period under condition S76. The solid curves show the analytical solution for a constant k_t ($=\bar{k}_{t,ss}$), and the symbols show the Monte Carlo simulation results. The stationary state P_W values are different depending on chain length dependence; however, they are so close under condition S76 that it is hard to distinguish the difference in the figure.

Next, we examine the case under condition S76 that is pertinent to the bulk polymerization of styrene at 50 °C, with the weight fraction of polymer $w_p = 0.76$. This condition may show the characteristics at the intermediate to high conversion level. As the conversion increases, the termination rate coefficient, $\bar{k}_t$, decreases due to the gel effect. With decreasing $\bar{k}_t$, the effect of chain transfer reactions forming dead polymer chains becomes increasingly significant. Under condition S76, only 6.3% of chains (on a number basis) are formed by bimolecular termination reactions at stationary state. Figure 10 shows the radical concentration development, and Figure 11 shows the developments of the average chain lengths. There is practically no difference compared with the simulation results based on a constant k_t that is equal to $\bar{k}_{t,ss}$. The difference from using a constant k_t may increase as conversion increases until a certain conversion level because the decrease of the

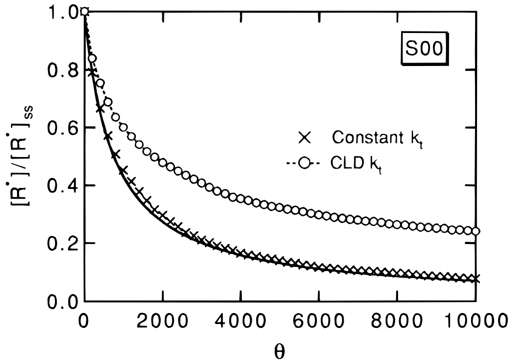

Figure 12. Radical concentration development during the posteffect period under condition S00 (styrene polymerization at 20 °C, $w_p = 0$). The solid curve is the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used, and the symbols show the Monte Carlo simulation results.

$k_t(l,m)$ surface may be enhanced; however, the differences tend to diminish after a certain conversion as the chain transfer reaction becomes the dominant chain stoppage mechanism.

Incidentally, the average chain length development under condition S76 was shown in Figure 15 of ref 16, determined using microreactors that contains $n_\nu = 20$ radicals.[27] The microreactor volume is smaller in the present paper ($n_\nu = 10$); however, there is practically no difference from the previous calculation results, which shows that the microreactor size with $n_\nu = 10$ is satisfactory for the simulation of the start-up period.

Posteffect Period. In this section, we consider the kinetic behavior in the posteffect period, where the radical generation is stopped suddenly and the radical concentration decreases from the stationary-state value, $[R^\bullet]_{ss}$, toward zero.

The pseudobulk kinetics is approximately valid as long as the microreactor contains no fewer than two radicals. On the other hand, the important features of emulsion polymerization kinetics can be observed when microreactors with fewer than two radicals are used,[11-20] i.e., the MWD is completely different from the bulk polymerizations. When using the microreactor method for the posteffect period, if the microreactors with $n_\nu = 10$ are used as in the cases for the pre-stationary-state calculations, the simulation results for $[R^\bullet]/[R^\bullet]_{ss} < 0.2$ may not be reliable. (Note that, in the cases of the pre-stationary-state calculations, the termination events seldom occur for the period with $[R^\bullet]/[R^\bullet]_{ss} < 0.2$, because the generation rate of radicals is much larger than the termination rate due to a very low polymer radical concentration. Therefore, a smaller number of radicals ($[R^\bullet]/[R^\bullet]_{ss} < 0.2$) does not present a serious problem.) For the posteffect period, we use the microreactors with $n_\nu = 20$, and the Monte Carlo simulations are made for 300 microreactors.

Figure 12 shows the radical concentration development under condition S00. The simulation results with a constant k_t (×) agree satisfactorily with the theoretical calculations based on eq 18, which shows that the microreactor size used is large enough to simulate homogeneous polymerization. The termination rate coefficient decreases significantly during the posteffect period if chain length dependence in k_t is considered, because generation of smaller polymer radicals by initiation reactions is stopped and only longer polymer radicals are left. Therefore, the decrease of the radical concentration is slower for the polymerization with chain-length-dependent k_t.

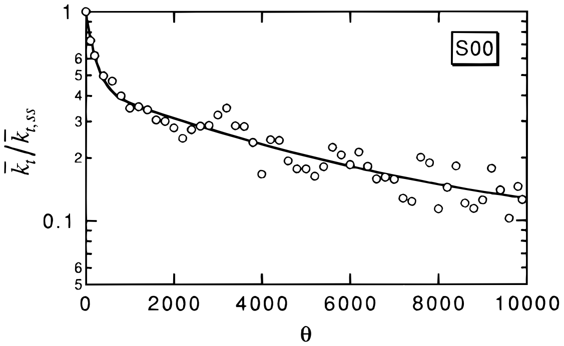

Figure 13. Change in the number-average bimolecular termination rate coefficient $\bar{k}_t$ during the posteffect period under condition S00.

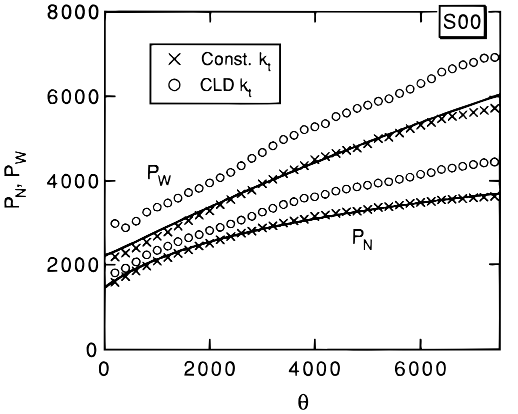

Figure 14. Average chain length development during the posteffect period under condition S00.

The change in the number-average bimolecular termination rate coefficient can be determined from the simulation data by using the following relationship:

$$\bar{k}_t = d(1/[R^\bullet])/dt \tag{21}$$

Figure 13 shows the change in $\bar{k}_t$ during the posteffect period. The value of $\bar{k}_t$ decreases significantly at the first stage, followed by a slow decrease in the second stage. Such a two-stage change in $\bar{k}_t$ during the posteffect period was observed experimentally in the free-radical polymerization of methyl methacrylate.[28]

Figure 14 shows the average chain length development during the posteffect period under condition S00. Longer chains are formed in chain-length-dependent k_t. Note that the number-average chain length (P_N) at $\theta = 0$, i.e., at stationary state, is the same for both chain-length-dependent and -independent k_t; however, the weight-average chain length (P_W) at $\theta = 0$ is larger for the case with chain-length-dependent k_t.[16]

Figures 15 and 16 show the development of the radical concentration and the average chain lengths under condition S76, respectively. When chain transfer reactions dominate the dead chain formation, both chain-length-dependent and -independent k_t give the same radical concentration and molecular weights developments. Therefore, at the intermediate to high conversion range, where the gel effect is significant and chain transfer reactions are dominant, all one needs to know to predict the reaction kinetics are the chain transfer constant and the number-average bimolecular termination rate coefficient at stationary state ($\bar{k}_{t,ss}$), which may be determined from the conversion time history data experimentally.

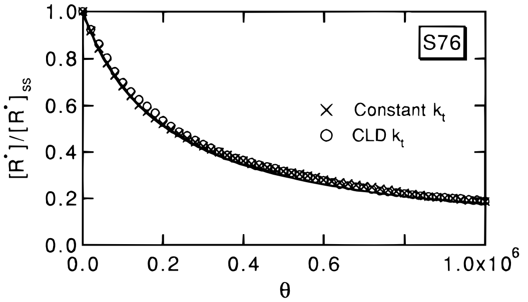

Figure 15. Radical concentration development during the posteffect period under condition S76 (styrene polymerization at 50 °C, $w_p = 0.76$). The solid curve is the analytical solution when a constant k_t ($=\bar{k}_{t,ss}$) is used, and the symbols show the Monte Carlo simulation results.

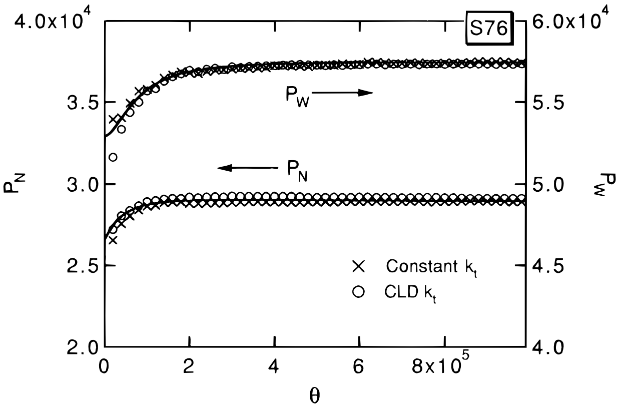

Figure 16. Average chain length development during the posteffect period under condition S76.

Conclusions

The kinetics of chain-length-dependent bimolecular terminations in free-radical polymerization during unstationary-state periods are investigated by using the microreactor method. In both the pre- and post-stationary-state periods, the number-average bimolecular termination rate coefficient, $\bar{k}_t$, decreases, because the chain lengths of polymer radicals increase during the transient periods. The comparison was made with the cases for a constant k_t value that is equal to $\bar{k}_{t,ss}$. In the chain-length-dependent termination reactions, $\bar{k}_t$ changes with the development of the MWD of polymer radicals. As a consequence, the transient periods are longer than those in the cases with a constant k_t for both pre- and post-stationary-state conditions, and the differences may become larger as conversion increases until a certain conversion level. On the other hand, however, when the bimolecular termination rates decrease significantly at the intermediate to high conversion region due to the gel effect, the chain transfer reactions tend to dominate the chain stoppage of growing polymer radicals. In such cases, the differences from the predictions based on a constant k_t become negligible.

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(21) We need to determine the imaginary time for the termination event to happen, assuming other events do not occur. Therefore, the rate terms for the other events, such as chain transfer and bimolecular termination of another radical pair, are not involved in eq 9. Note that eq 1 in ref 19 and the Appendix therein need correction.
(22) Strictly, the competition of events between monomer addition by propagation and bimolecular termination for a particular radical pair must be considered at each chain length. However, such exact treatment is required only when the magnitude of $k_t(r_i,r_j)/(\nu N_A)$ is comparable to k_p[M], such as in the case of the emulsion polymerization, where the probability of possessing more than one radical in the polymer particle is quite small. Even for such emulsion polymerizations, however, the error introduced by using eq 9 may become significant only for the prediction of the chain lengths of oligomeric chains formed via bimolecular termination by disproportionation.
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(26) See, for example: Tobita, H.; Hamielec, A. E. *Macromolecules* **1989**, *22*, 3098.
(27) Because the stationary-state hypothesis is not valid in the start-up period, the calculation results based on a constant k_t shown in Figure 15 of ref 16 must be replaced by Figure 11 of the present paper.
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