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Kinetics of Controlled/Living Radical Polymerization in Emulsified Systems

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Summary: For the controlled/living radical polymerization (CLRP) in which the active period during the chain formation is extremely small, $\phi_A \ll 1$, such as the cases of usual SFRP and ATRP, the polymerization rate can be made larger by increasing the average number of monomeric units added during a single active period, $\overline{P}_{n,SA}$. The $\overline{P}_{n,SA}$-value is inversely proportional to the trapping agent concentration [X], and the polymerization rate is controlled by [X]. For small particles, even with a single trapping agent, [X] in the particle could be larger than that in corresponding bulk polymerization, and the polymerization rate decreases with D_p^3, where D_p is the particle diameter. On the other hand, for CLRPs whose ϕ_A-value is not very much smaller than unity, say $\phi_A > 0.01$, such as some of RAFT polymerization systems, the polymerization rate can be made larger by increasing the kinetic chain length for a given initiation frequency. For such reaction systems, the polymerization rate can be enhanced significantly by employing the emulsified polymerization systems.

Keywords: controlled/living radical polymerization; kinetics (polym.); miniemulsion polymerization; theory; particle size

Introduction

Recently, the controlled/living radical polymerization (CLRP) has attracted much attention as a novel method to synthesize well-defined polymers. There are several different types of CLRP systems. The time fraction of the active period during the chain formation ϕ_A, is extremely small for the stable free radical mediated polymerization (SFRP), which is often called the nitroxide-mediated polymerization (NMP), and also for the atom transfer radical polymerization (ATRP). The ϕ_A-value is much larger for the reversible addition-fragmentation chain transfer (RAFT) polymerization, and ϕ_A is close to unity in the degenerative transfer (DT) polymerization.

For the conventional emulsion polymerization in which $\phi_A = 1$, high MW polymers can be produced with a high polymerization rate, by physically isolating polymer radicals into separate polymer particles to suppress bimolecular termination reactions. For CLRP, the effects of particle size on the polymerization rate was theoretically discussed by Butte et al.[1,2], Charluex,[3] Zetterlund et al.[4–6] and Tobita et al.[7]

In this article, first, the important characteristics of different CLRP methods that control the polymerization rate are considered, and then, the reported calculation results for miniemulsion polymerization are used to clarify the effects of very small reaction locus on the kinetics of CLRPs.

Fundamental Characteristics of SFRP

The essence of CLRP resides in the following reversible reaction:

$$D \underset{k_2}{\overset{k_1}{\rightleftarrows}} R^\bullet + X \quad K \equiv \frac{k_1}{k_2}[\mathrm{mol \cdot L^{-1}}] \qquad (1)$$

where $R^\bullet$ is an active polymer radical. In SFRP, X is a stable radical such as TEMPO, and D is the dormant that is inactive toward

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polymerization. For an ATRP, the radical formation reaction is a second-order reaction, and D could be interpreted as consisting of two different molecules, dormant and transition-metal complex, or equivalently, k_1 could be considered as a pseudokinetic rate constant consisting of the product of true rate constant and the concentration of transition-metal complex. In the case of RAFT polymerization, X is the RAFT trapped dormant chain, and D represents the adduct-radical chain. The degenerative transfer could be considered as a special case of RAFT with $1/k_1 \cong 0$.

In this section, the kinetics of SFRP are considered; however, a similar argument could also be applied for ATRP. The RAFT polymerization is considered separately.

The average time interval of the dormant period for a particular dormant molecule is $\bar{t}_D^* = 1/k_1$. On the other hand, the average time interval of the active period for a particular radical is $\bar{t}_A^* = 1/(k_2[X])$. Therefore, the fraction of active period during the chain formation ϕ_A is given by:

$$\phi_A = \frac{\bar{t}_A^*}{\bar{t}_A^* + \bar{t}_D^*} = \frac{K}{K + [X]} \tag{2}$$

For a usual SFRP and ATRP, $\phi_A \ll 1$.

As shown in Figure 1, a growing chain is inactive for the most of the reaction time. For example, in the case of TEMPO-mediated styrene polymerization the K-value is as small as 2×10^{-11} mol/L, and ϕ_A is typically smaller than 1×10^{-6}. The growth time is negligibly small compared with the whole reaction time. The average number of times of the active period is simply given by $t_R/\bar{t}_D^* = k_1 t_R$.

Once the k_1 value is fixed, the only method to increase the polymerization rate is to increase the number of monomeric units added during a single active period $\overline{P}_{n,SA}$, which is given by:

$$\overline{P}_{n,SA} = k_p[M]\bar{t}_A^* = \frac{k_p[M]}{k_2[X]} \tag{3}$$

Suppose that the polymerization is started from dormant, i.e., $[X]_0 = 0$ and $[D]_0 = [D] + [X]$. The polymerization rate R_p should be proportional to:

$$R_p \propto [D]_0 \overline{P}_{n,SA} \propto \frac{[D]_0}{[X]} \tag{4}$$

Equation (4) shows that the polymerization rate can be increased by making the trapping agent concentration $[X]$ smaller.

Note that Equation (4) does not mean that the polymerization rate becomes larger by increasing the initial dormant concentration, $[D]_0$. As it is well known, the initial feed TEMPO concentration that determines $[D] + [X]$ does not change the polymerization rate in the TEMPO-mediated styrene bulk polymerization.[8,9] Equation (4) is consistent with this feed TEMPO concentration effect, as shown below.

The active radical concentration $[R^\bullet]$ and the trapping agent concentration $[X]$ is given by:

$$\frac{d[R^\bullet]}{dt} = R_I - k_t[R^\bullet]^2 + k_1[D] - k_2[R^\bullet][X] \tag{5}$$

$$\frac{d[X]}{dt} = k_1[D] - k_2[R^\bullet][X] \tag{6}$$

where R_I is the initiation rate, and k_t is the termination rate constant.

It is straightforward to show that the stationary state hypothesis (SSH) is valid for both Equation (5) and (6) as long as the initiation rate R_I is large enough, i.e., except when $R_I \ll k_1[D]$. For the TEMPO-mediated

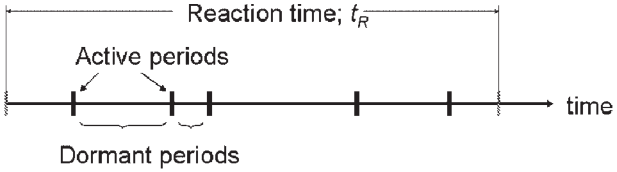

Figure 1.
Schematic representation for the chain formation process.

styrene polymerization, thermal initiation of styrene is large enough for the SSH to be valid. Therefore, one obtains the relationship:

$$[R^\bullet] = \sqrt{\frac{R_I}{k_t}} = \frac{k_1[D]}{k_2[X]} \cong \frac{k_1[D]_0}{k_2[X]} \qquad (7)$$

Note that because $[D]_0 = [D] + [X]$ and $[X] \ll [D]$, $[D]_0 \cong [D]$. The radical concentration is independent of $[D]_0$, that is, $[R^\bullet] = \sqrt{R_I/k_t}$. Even when $[D]_0$ is increased, the ratio $[D]_0/[X]$ is kept constant, and Equation (4) does not mean that R_p increases with $[D]_0$.

Equation (7) also shows that Equation (4) is consistent with the conventional radical polymerization kinetics, $R_p \propto [R^\bullet]$ when R_I is large enough. On the other hand, when R_I is very small and $R_I \ll k_1[D]$, normally when $R_I < k_1[D] \times 10^{-3}$, the SSH for Equation (6) does not hold and the relationship given by Equation (7) is not valid. Even for such cases, the SSH for the active radical $[R^\bullet]$ would be valid, and by invoking the SSH for Equation (5), one obtains:

$$[R^\bullet] = \frac{k_2[X]}{2k_t}\left\{\sqrt{1 + \frac{4k_t(R_I + k_1[D])}{k_2^2[X]^2}} - 1\right\} \cong \frac{R_I + k_1[D]}{k_2[X]} \cong \frac{k_1[D]_0}{k_2[X]} \qquad (8)$$

Note that normally, $(k_2[X])^2$ is over 100 times larger than $4k_tk_1[D]$.

Equation (7) and (8) show that Equation (4) is consistent with the conventional radical polymerization fundamental, $R_p \propto [R^\bullet]$.

For CLRP with $\phi_A \ll 1$, the polymerization rate can be increased by making the trapping agent concentration $[X]$ smaller. Cunningham et al.[10] proposed that the miniemulsion polymerization rate can be increased by the addition of ascorbic acid to reduce the excess amount of TEMPO. Equation (4) shows this is a clever method to enhance the polymerization rate.

Particle Size Effects in Miniemulsion SFRP

To simplify the discussion, the exit of small species, such as monomer radicals and trapping agents, is neglected; that is, an ideal miniemulsion polymerization in which each polymer particle is considered as a completely isolated microreactor with a uniform diameter.

Figure 2 shows the calculated conversion development for the systems with no initiation and no termination, reported in ref.[7] The kinetic parameters used are shown therein.[7] Because CLRP seeks to suppress the termination reaction as small as possible, this example may highlight the most fundamental characteristics of SFRP conducted in a dispersed medium. The

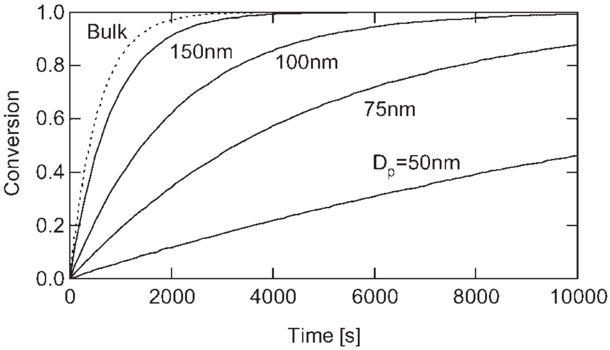

Figure 2.
Conversion developments for the systems with neither initiation nor termination. The kinetic parameters used as well as the conditions assumed are shown in ref.[7]

polymerization rate decreases by reducing the particle size, especially for $D_p < 150$ nm.

Equation (1) shows that an active radical and a trapping agent are always formed in pairs. When there exists an active radical in a particle, a trapping agent always accompanies. Equation (4) shows that the polymerization rate becomes smaller if $[X]_{particle}$ is larger than that in the corresponding bulk polymerization, $[X]_{bulk}$. If a single molecule concentration of the trapping agent exceeds $[X]_{bulk}$, the polymerization rate in the particle must always be smaller than that in bulk. The single molecule concentration in a particle is calculated from $1/(N_A v_p)$, where N_A is Avogadro's number and v_p is the particle volume $(= \pi D_p^3/6)$. In the present example, $[X]_{bulk} = 8.94 \times 10^{-7}$ mol/L, and it is expected that the polymerization rate decreases for the particles smaller than $D_{p,SMC} = 153$ nm. The subscript, SMC means the single molecule concentration is equal to the concentration in the corresponding bulk polymerization. $D_{p,SMC}$ in nm can be calculated from $[X]_{bulk}$ mol/L as follows:

$$D_{p,SMC} = \left(\frac{10}{\pi [X]_{bulk}}\right)^{1/3} \tag{9}$$

The polymerization rate shown in Figure 2 decreases significantly for $D_p < D_{p,SMC} = 153$ nm, which shows the prediction based on the present *single-molecule-concentration* (SMC) theory agrees quite well.

Figure 3 shows the calculated results for the systems with termination but without initiation, taken from ref.[7]. In this case, $[X]_{bulk}$ changes with time, however, $[X]_{bulk} \approx 4 \times 10^{-5}$mol/L at the initial stage of polymerization, which predicts that the polymerization rate must be smaller than that in bulk for $D_p < 43$ nm, which agrees reasonably well with Figure 3 that shows the polymerization rate decreases very significantly for 30 and 20 nm. The SMC theory applies also for this case.

On the other hand, for very small particles, the exit of trapping agents may not be neglected. If a single active radical is left alone after the exit of X, the polymerization rate may increase significantly as was shown in Figures 8–10 in ref.[7], because uncontrolled, conventional emulsion polymerization occurs simultaneously.

Figure 4 shows the calculated relative polymerization rate, $R_p / R_{p,bulk}$ for the TEMPO-mediated styrene miniemulsion polymerization at 10% conversion, on the basis of the data reported in ref.[6]. The kinetic parameters are slightly different from those used in ref.[7].

From Equation (7), the concentrations of radical and trapping agent in bulk

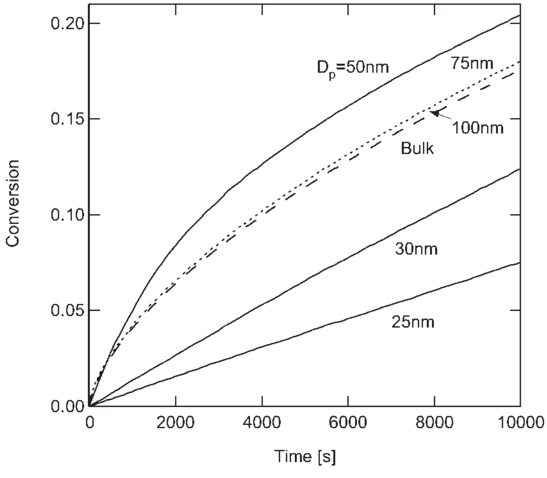

Figure 3.
Conversion developments for the systems with termination but without initiation.[7]

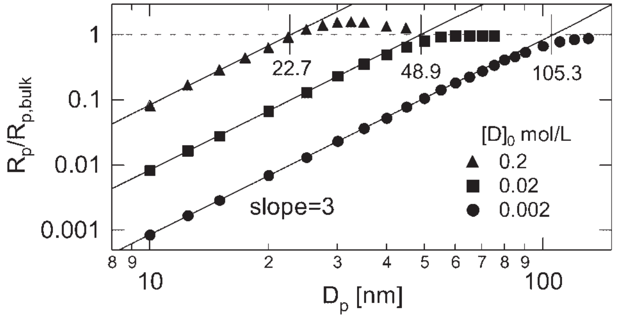

Figure 4.
Calculated relative polymerization rate $R_p/R_{p,bulk}$ for the TEMPO-mediated styrene miniemulsion polymerization at 10% conversion. The data are taken from ref.[6]

polymerization can simply be calculated without solving the differential equations as follows:

$$[R^\bullet]_{bulk} = \sqrt{\frac{R_I}{k_t}} = \sqrt{\frac{1.70 \times 10^{-10} \times (8.71 \times 0.9)^3}{3.44 \times 10^8}} = 1.543 \times 10^{-8}\ \text{mol/L} \tag{10}$$

$$[X]_{bulk} = \frac{k_1[D]_0}{k_2[R^\bullet]} = \frac{1.6 \times 10^{-3}[D]_0}{(7.6 \times 10^7)(1.543 \times 10^{-8})} = 1.364 \times 10^{-3}[D]_0\ \text{mol/L} \tag{11}$$

The diameter at which a single molecule concentration is equal to $[X]_{bulk}$ mol/L, $D_{p,SMC}$ nm can be calculated from Equation (9), and the calculated values for $[D]_0 = 0.2$, 0.02, 0.002 mol/L are 22.7, 48.9, 105.3 nm, respectively, which agree well with the data shown in Figure 4.

Equation (4) shows the polymerization rate is inversely proportional to $[X]$, $R_p \propto [X]^{-1}$.

Because the single-molecule-concentration in a particle is given by $1/(v_p N_A) \propto D_p^{-3}$, the relationship, $R_p \propto D_p^3$ holds when the kinetics is dominated by the single molecule concentration of the trapping agent. The slopes in log-log plot is 3 for the particle diameters smaller than $D_{p,SMC}$ as shown in Figure 4, which agrees with the SMC theory.

In refs.[4–7] this rate reduction effect is named as the confined space effect. It is true that the reduction is caused by the confinement of the active radical and the trapping agent. However, the number of confined trapping agents to significantly reduce the polymerization rate is unity. Therefore, I would like to propose the name of this rate reduction effect as the *single-molecule-concentration (SMC) effect* of the trapping agent. The SMC concept is very useful to predict the particle size for which the polymerization rate becomes smaller than that in bulk.

The experimental results showing the rate reduction by decreasing the particle size in the TEMPO-mediated styrene miniemulsion polymerization were reported very recently.[11]

On the other hand, Figure 3 and 4 shows that there may exist a particle size region for which the polymerization rate is larger than that in bulk. In refs.[4–7], the increase in the polymerization rate was thought to be caused by the isolation of radicals in different particles that lowers the bimolecular termination frequency.

In terms of Equation (4), the polymerization rate increases when the trapping agent concentration becomes lower. In the present reaction system, one bimolecular termination event leads to form two extra trapping agents in a particle. Therefore, reduced frequency of bimolecular termination

Table 1.
Rate constants used for RAFT polymerization.[7]

	k_1 [s^{-1}]	k_2 [$L \cdot mol^{-1} \cdot s^{-1}$]	k_p [$L \cdot mol^{-1} \cdot s^{-1}$]	k_t [$L \cdot mol^{-1} vs^{-1}$]	k_{ct} [$L \cdot mol^{-1} \cdot s^{-1}$]
Case 1	1×10^4	1×10^6	500	1×10^7	1×10^7
Case 2	0.5	1×10^6	500	1×10^7	0

leads to a decrease in the number of trapping agent molecules in a particle, leading to a lower $[X]$. On the face of the things, this seems to be a plausible explanation. However, one needs to remind that in a small polymer particle (1) an active radical does not exist in a particle for the most of reaction time, and (2) when an active radical is formed, one trapping agent molecule is added in the particle. Because the concentration of a single molecule is rather high in a small particle, $[X]$ during an active period may not be low enough to enhance the polymerization rate even when the frequency of termination is reduced.

On the other hand, it was found recently[12] that what is more important in enhancing the polymerization rate, R_p at a certain particle size range is the fluctuation of the trapping agent concentration in each particle. Even when the average number of trapping agents is the same, it is straightforward to show that the overall R_p is larger for the cases with a broader distribution of the number of trapping agents among polymer particles, compared with the cases where all polymer particles possess the same number of trapping agents. The fluctuation effect becomes significant when the average number of trapping agents in a particle is small, say smaller than about 10 trapping agents. Details of the *fluctuation effect* can be found elsewhere.[12]

Fundamental Characteristics of RAFT

In RAFT, the termination reaction is already an anticipated event, and the ''livingness'' is granted by distributing monomeric units to a large number of chains before termination. For SFRP and ATRP, the fraction of active period ϕ_A must be $\phi_A \ll 1$, but for RAFT ϕ_A does not have to be much smaller than unity.

In RAFT polymerization, it is well known that the rate retardation occurs by increasing the RAFT concentration for some RAFT polymerization systems. Monteiro and Brouwer[13] proposed a cross-termination between a propagating radical and an adduct radical, i.e., the termination reaction between D and $R^\bullet$ in Equation (1). On the other hand, Barner-Kowollik et al.[14] attributed the retardation to slow fragmentation of adduct radicals, i.e., a small k_1 value is assumed and the average time interval of adduct radical period $\bar{t}_D^*$ may take as long as a few seconds. There is an ongoing discussion on the magnitude of k_1 value.[15–17]

In ref.[7] two sets of kinetic rate constants were used as shown in Table 1. The initial concentrations used for the simulation were $[M]_0 = 8$ mol/L, $[X]_0 = 0.04$ mol/L, and $[D]_0 = 0$. The initiation rate used was $R_I = 6.366 \times 10^{-8}$ mol/(L·s). The equilibrium constant, $K = k_1/k_2$ is 1×10^{-2} mol/L for Case 1, while $K = 5 \times 10^{-7}$ mol/L for Case 2, which is 2×10^4 times of difference. On the other hand, however, in spite of a huge difference in the K-values, the conversion developments in bulk polymerization are not very much different as shown in Figure 11 of ref.[7] it would be difficult to discriminate the K-values especially when experimental errors are involved.

The fraction of active period at the start of polymerization is $\phi_A = 0.2$ for Case 1, while $\phi_A = 1.25 \times 10^{-5} \ll 1$ for Case 2.

Figure 5 shows the chain growth process of the RAFT polymerization. After adding a few monomeric units during a single active period, the growing chain becomes the adduct radical state (D in Equation 1). The adduct radical state is an intermediate

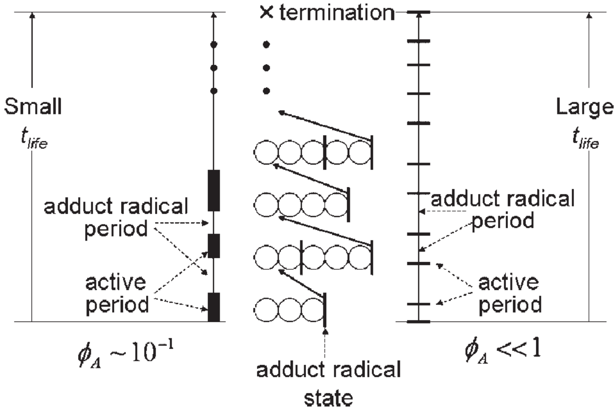

Figure 5.
Schematic drawing for the RAFT chain growth process.

stage, and is inactive toward polymerization. The adduct radical may be active for bimolecular termination with an active radical species in the elementary reactions assumed for Case 1. The adduct radical species will dissociate to form an active radical and a RAFT trapped dormant chain. With probability 1/2, chain addition occurs on another chain.

When $\phi_A \sim 10^{-1}$ as in Case 1, both the average active period $\bar{t}_A^* = 1/(k_2[X])$ and the adduct radical period $\bar{t}_D^* = 1/k_1$ have a similar order of time length. At the initial stage of Case 1, $\bar{t}_A^* = 2.5 \times 10^{-5}$ s and $\bar{t}_D^* = 1 \times 10^{-4}$ s. Both are very short but have a similar order of magnitude. When the initiation rate is fixed, the polymerization rate is faster for the system where the total number of monomeric units added until termination is large, which means that the polymerization rate can be increased by increasing the kinetic chain length.

On the other hand, consider the cases with $\phi_A \ll 1$ as in Case 2, $\bar{t}_A^* \ll \bar{t}_D^*$. At the initial stage of Case 2, $\bar{t}_A^* = 2.5 \times 10^{-5}$ s while $\bar{t}_D^* = 2$ s. The growing chain is inactive for the most of the time, similarly as in the case of SFRP represented by Figure 1. Especially, when the polymerization starts with the trapping agent and with $[D]_0 = 0$, it takes a long time before having enough number of radicals to cause bimolecular termination, because there exist too many trapping agents in the reaction system.

Figure 6 shows the kinetic behavior of Case 2, i.e., the total number of radicals

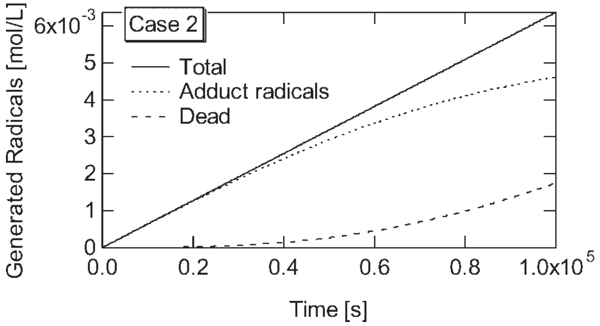

Figure 6.
Fate of generated radicals in Case 2. Up to $t = 2 \times 10^4$ s, most generated radicals stay as the adduct radicals, after experiencing a large number of chain transfer reactions.

generated up to the given reaction time (Total), the number of adduct radicals at a given time, and the sum of dead radicals (accumulated number of dead chains if termination is by disproportionation). In Case 2, the adduct radicals are piling, and dead polymer formation is negligibly small up to $t = 2 \times 10^4$ s, which shows that up to about $t_R = 2 \times 10^4$ s, $t_{life} > t_R$, where t_R is the reaction time. From the point of view of the polymerization rate, this situation is essentially the same as the case of SFRP whose growth process is shown in Figure 1.

Therefore, especially in the earlier stages of polymerization, in order to increase the polymerization rate in Case 2, the number of monomeric units added during a single active period $\overline{P}_{n,SA}$, represented by Equation (3), must be made larger, as in the case of SFRP.

Particle Size Effects in Miniemulsion RAFT Polymerization

Figure 7 shows the calculated conversion developments for Case 1 when the particle size is changed.[7] The polymerization rate, R_p increases significantly by reducing the particle size.

In Case 1, $\phi_A \sim 10^{-1}$, and therefore, R_p increases when the kinetic chain length is made larger. The isolation of radicals into different particles physically hinders bimolecular termination, resulting in increasing the kinetic chain length.

On the other hand, Figure 8 shows the conversion developments for Case 2. Note that the Monte Carlo (MC) simulation was used for the calculation, and the results are not perfectly free from errors. On sharp contrast to Case 1, the polymerization rates of miniemulsion polymerization are essentially unchanged from bulk polymerization. The curves concave upwards, which shows the accumulation of the active radicals, and termination reactions are not significant in all cases. As considered in the previous section, the polymerization rate is governed by the trapping agent concentration, at least up to about $t = 2 \times 10^4$ s.

In the present case, the initial number of trapping agent, X in a particle is as large as 1571 for $D_p = 50$ nm. Therefore, the trapping agent concentration, $[X]$ would not be different significantly, depending on the particle size. The single-molecule-concentration effects as well as the fluctuation effects are not important for this case, and the polymerization rate does not change significantly depending on the particle size, especially at the earlier stages of polymerization.

According to the MC simulation results,[7] a significant rate increase by reducing the particle size is observed only

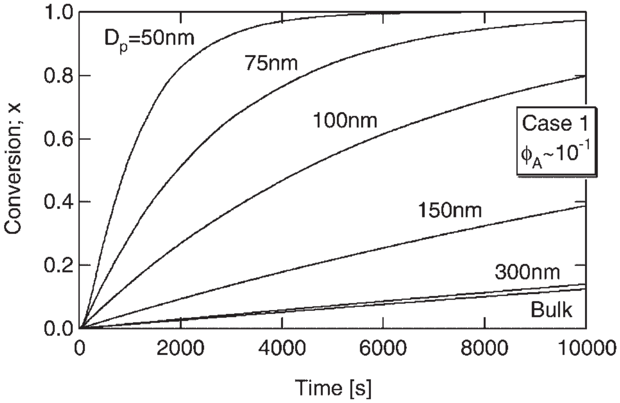

Figure 7.
Effect of particle size on the conversion development of miniemulsion RAFT polymerization for Case 1.

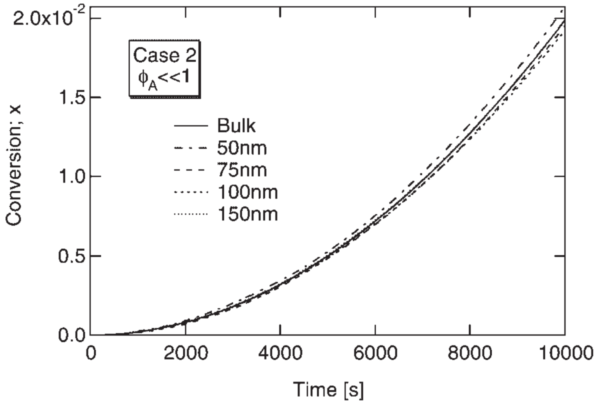

Figure 8.
Effect of particle size on the conversion development of miniemulsion RAFT polymerization for Case 2.

when $\phi_A > 0.01$. For the RAFT polymerization systems with $\phi_A > 0.01$, miniemulsion polymerization technique promises to improve the productivity. In addition, miniemulsion polymerization technique may provide a novel method to determine the K-value for the cases where it is difficult to distinguish in the bulk polymerization experiments, as also reported in ref.[18].

Conclusion

In SFRP and ATRP, the time fraction of active period is much smaller than unity, $\phi_A \ll 1$. The polymerization rate is increased by increasing the number of monomeric units added during a single active period, $\overline{P}_{n,SA}$. The polymerization rate is, therefore, inversely proportional to the trapping agent concentration $[X]$. For the particle size smaller than $D_{p,SMC}$ where the *single-molecule-concentration effects* dominate, the polymerization rate R_p decreases significantly by reducing the particle size with $R_p \propto D_p^3$. $D_{p,SMC}$ is the diameter at which the concentration of a single trapping agent molecule in a particle is equal to the concentration in corresponding bulk polymerization, $[X]_{bulk}$. On the other hand, when the number of trapping agents in a particle is less than about 10, the *fluctuation effects* may enhance the polymerization rate, and an acceleration window region of particle size could be observed, as discussed more closely in ref.[12].

For the RAFT polymerization with $\phi_A > 0.01$, the polymerization rate can be increased by making the kinetic chain length larger. By reducing the particle size, the radical isolation effects become important to reduce the frequency of bimolecular termination reactions, leading to a larger kinetic chain length. For such systems, the polymerization rate can be increased significantly by employing the miniemulsion polymerization technique.

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