Effects of Initiator Homolysis Rate Constant on Kinetics and Chain Length Distribution in Living Free-Radical Polymerization

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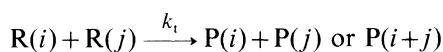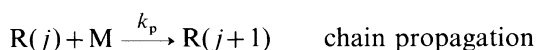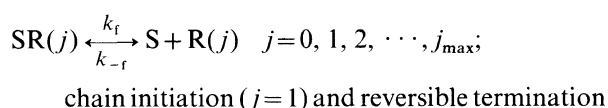
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ABSTRACT: The kinetics, chain length and distribution of living free-radical polymerization with initiators of different homolytic rate constant, k_d, were simulated by a Monte Carlo algorithm. The results show that, for the system with a lower k_d (10^{-5}—10^{-4} s^{-1}), the polymerization rate is much faster and chain length increases linearly with monomer conversion. However, for the system with higher k_d, nonlinear increase in average chain length, and lower reaction rate are found in the simulation results. Low polydispersity indices were obtained for higher and lower k_d.
    KEY WORDS   Living Free-radical Polymerization / Initiator Homolysis Rate Constant / Monte Carlo Simulation / Kinetics / Molecular Weight Distributions /

Recently, much interest in polymer chemistry is being concentrated on living free-radical polymerization (LFRP) mediated by a stable free-radical (SFR), such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). Advantageous to conventional free radical polymerization, LFRP can be applied to synthesize polymers[1−7] with narrow dispersity, block copolymers[8−11] and dendrimers.[12] There are generally two ways to conduct LFRP, *i.e.*, polymerization initiated by a pre-prepared unimolecular alkoxyamine, as well as that initiation by an initiator *in situ* in the presence of a SFR. Most theoretical derivations[13−18] and computer modeling[7,19,20] are, by including the initiator homolysis reaction, based on the following kinetic model,

$$I \xrightarrow{k_d} 2R(0) \qquad \text{initiator homolysis}$$

$$SR(j) \underset{k_{-f}}{\overset{k_f}{\rightleftharpoons}} S + R(j) \quad j=0, 1, 2, \cdots, j_{max};$$

chain initiation ($j=1$) and reversible termination

$$R(j) + M \xrightarrow{k_p} R(j+1) \qquad \text{chain propagation}$$

$$R(i) + R(j) \xrightarrow{k_t} P(i) + P(j) \text{ or } P(i+j)$$

irreversible chain termination

where I is initiator and R(0) is an initiator radical. SR(j) and R(j) are dormant chain and growing chain radicals, respectively, with chain length j; M is monomer; P(j) is "dead" polymers with chain length j and S represents stable radicals such as TEMPO. Exchange between growing and dormant chains[3−7] protects the majority of radicals throughout the polymerization, leading to increase of molecular weight with monomer conversion and low polydispersity of the resulting polymers.

In a previous work,[20] we developed a Monte Carlo algorithm very convenient for simulation of kinetics and molecular weight distribution (MWD) in LFRP. The simulation results agree very well with the results of analytical method or experiment. The results also showed

that k_d, in the range of 5×10^{-5}—5×10^{-4} s^{-1}, did not have much effect on the kinetics of LFRP when the initiator and SFR were used stoichiometrically. However, as the benzoyl peroxide (BPO)- or α,α-azobis(isobutyronitrile) (AIBN)-initiated LFRPs of styrene are always conducted at high temperature, say 130°C, in this case, k_d may be as high as 10^{-3} s^{-1}. SFR is often used less than the stoichiometrical amount to achieve a reasonable polymerization rate. The lower amount of SFR would not be enough to trap all the radicals when k_d is high. Therefore, LFRP should be sensitive to the homolysis rate constant of initiators. This is the motivation of this simulation.

THEORETICAL

The details of simulation were described previously.[20−22] The method based on the model in which each microscopic elementary reaction occurs at a certain time, and macroscopic kinetics are obtained when the reaction evolutes with time. Thus, according to Gillespie's master equation,[23] the reaction, μ, in a LFRP system shown in Scheme 1, is determined by a unit-interval, uniformly distributed random number, r_1,

$$\sum_{v=1}^{\mu-1} P_v < r_1 \le \sum_{v=1}^{\mu} P_v \tag{1}$$

where P_v is the reaction probability of initiator homolysis, chain propagation, chain end trapping and releasing (reversible termination) or bi-radical irreversible termination. P_v can generally be written as the ratio of the reaction rate, R_v, of a given reaction to the sum of all above reaction channels,

$$P_v = \frac{R_v}{\sum\limits_{v=1}^{M} R_v} \tag{2}$$

with M the total number of reaction channels. The time interval between two successive reactions, τ, is a stochastic variable determined by,

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$$\tau = \frac{1}{\sum\limits_{v=1}^{M} R_v} \ln\left(\frac{1}{r_2}\right) \qquad (3)$$

After transformation of experimentally measured macroscopic rate constants into microscopic one,[20] the kinetics and molecular weight distribution can be obtained.

The reaction parameters come from styrene bulk polymerization at about 110—130°C, initiated by initiator/TEMPO. In the simulation, we set $[M]_0 = 8.7\,M$; $[I]_0 = 4.4 \times 10^{-3}\,M$; $[TEMPO]_0 = 7.6 \times 10^{-3}\,M$, i.e., $[TEMPO]_0/2[I]_0 = 0.864{:}1$; $k_p = 2 \times 10^3\,L\,mol^{-1}\,s^{-1}$; $k_t = 10^7\,L\,mol^{-1}\,s^{-1}$; $k_f = 10^{-2}\,s^{-1}$ and $k_{-f} = 10^9\,L\,mol^{-1}\,s^{-1}$; k_d varies within the range of 10^{-5}—$10^{-2}\,s^{-1}$. To simplify the procedure, only combination termination is considered. All rate constants are assumed independent of chain length. Initiation efficiency of initiator is assumed to be 100%. We should emphasize that the SFR is lower than the stoichiometrical amount.

RESULTS AND DISCUSSION

Kinetics of LFRP with Initiators of Different k_d

In the simulation, only an empirical model is studied. Some side reactions, such as thermal self-initiation of styrene[16-19,24,25] as well as the decomposition of TEMPO,[17] are not included. For each kinetic curve in Figure 1, there is an induction period that is longer for lower k_d. It is interesting to note that, lower k_d gives higher overall reaction rate. For example, a system with $k_d = 5 \times 10^{-4}\,s^{-1}$ needs only about 5 h to reach 80% conversion, while for $k_d = 5 \times 10^{-2}\,s^{-1}$ more than 40 h is needed.

The difference in polymerization rate for higher and lower k_d may be a consequence of different yields of living chains. The ability of two-component initiating system to form living chains was described as germination efficiency,[4] f_g, defined as the number of living polymer chains, L, divided by the initial number of stable radicals, S_0,

$$f_g = \frac{L}{S_0} \qquad (4)$$

Obviously, a higher germination efficiency gives a faster polymerization rate. Initiating systems with lower k_d should thus give higher germination efficiency. However, the experimental results by Yoshida et al. demonstrate that the number of living chains is determined only by S_0 under excessive S_0, suggesting a constant f_g for a certain S_0. This weakens the possible dependence of polymerization rate on f_g even if the systems in simulation did not have excessive initial TEMPO.

There may be another reason for faster polymerization rate in system with a lower k_d, namely, the equilibrium concentration of growing radicals can be increased by homolytical decomposition of residual initiators, analogoues to styrene thermal initiation[16-19,24,25] serving as a source of growing radicals. An initiator with larger k_d, however, cannot play the above role because it is exhausted within a very short period, cf. Figure 6a.
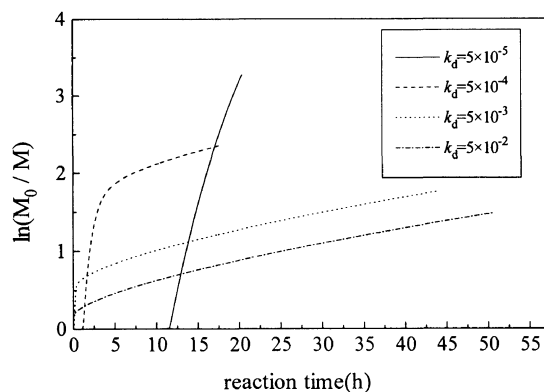
One supporting fact for this is that, in a LFRP initiated

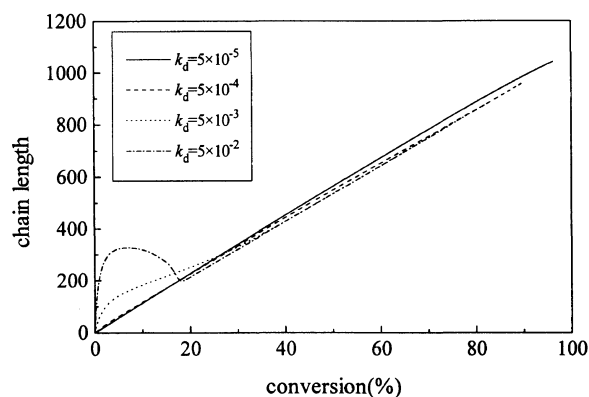**Figure 1.** Polymerization kinetics for various k_d (s^{-1}).

Figure 2. Increase of number averaged chain length with monomer conversion for various k_d.

by an alkoxyamine, or by polystyrene-TEMPO adduct, the addition of excess radical initiators, such as t-butyl hydroperoxide[26] or dicumyl peroxide,[27] gave rise to a shorter polymerization time. For this special case, the theoretical solution by Ohno et al.[28] told that the kinetic curves should have 2/3 order dependence on time t for a system without residual initiators:

$$\ln([M]_0/[M]) = (3k_p/2)(K[SR]_0/3k_t)^{1/3}t^{2/3} \qquad (5)$$

where $K = k_f/k_{-f}$. For a system with further continuous initiation, the kinetic equation reads:

$$\ln([M]_0/[M]) = (k_p/k_t^{1/2})R_i^{1/2}t \qquad (6)$$

where R_i is the initiation rate of residual initiators. Dormant species are formed in situ during the induction period in our case and thus, quantitative agreement between our simulation results and eq 5 and 6 is not expected. The simulation results agree qualitively with eq 5 and 6 as well as the experiment in ref 28. Therefore, it is reasonable to deduce that the much faster polymerization rate for a lower k_d is a consequence of continuous decomposition of residual initiators. A higher k_d results in opposite polymerization behavior.

Chain Length and Its Distribution for Different Initiator k_d

Generally, molecular weight increases linearly with monomer conversion, and a narrow dispersity should be acquired in living polymerization. A system with lower k_d obeys linearity over the whole reaction procedure (Figure 2). For higher k_d, linearity is violated and has a
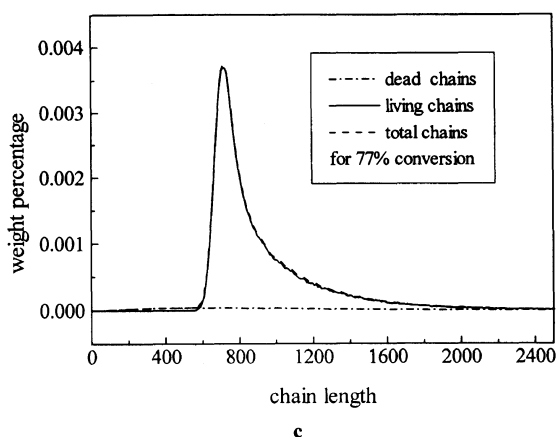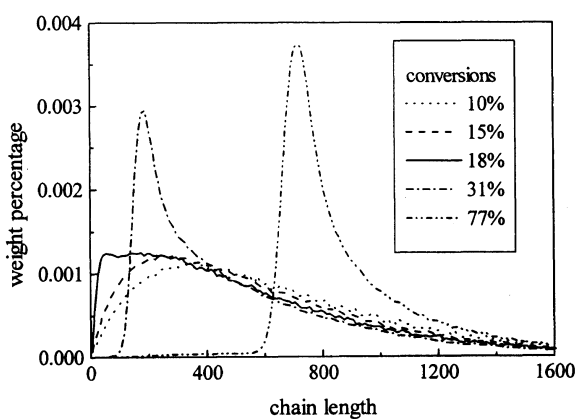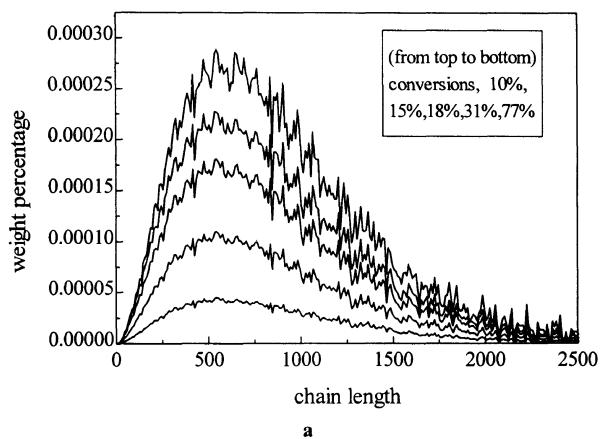
Figure 4. Variation in polydispersity index with monomer conversion for various k_d (s^{-1}).

Figure 5. GPC traces of samples from styrene bulk LFRP at 115°C with 0.012 M 4-hydroxy-TEMPO and 0.014 M AIBN, corresponding to a system with $k_d = 5 \times 10^{-2}$ s^{-1}. From bottom to top, the reaction times are 2, 4, 6, 8, 15, 90, 240, 660 min, respectively. The insert gives the relative between number averaged chain length and monomer conversion, in which the line is only for guiding the eyes.

Figure 3. Evolution of MWDs with monomer conversion (a) MWDs of dead polymer chains (unnormalized); (b) MWDs of total chains; (c) MWDs of dead, living and total chains at 77% conversion.

peak when conversion is lower than about 18% by an uncontrolled chain growth at initial stage which could result from excessive growing radicals. After some growing radicals have been irreversibly terminated, the contribution of controlled growth becomes predominant. At this time, a large population of living chains are oligomers, shorter than the chains formed at the initial stage. Therefore, the statistical average chain length in terms of total chains decreases. This can be confirmed by carefully looking at the MWD curves in Figure 3. While the MWD curves of dead polymers at different
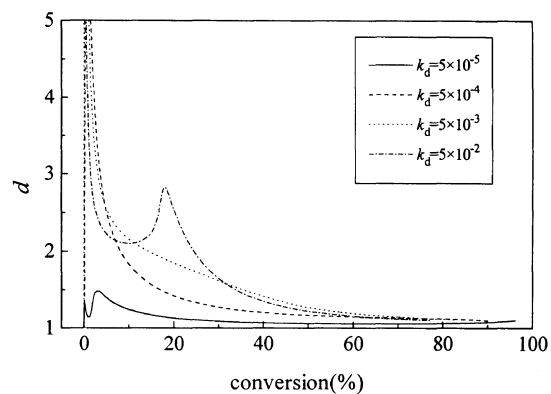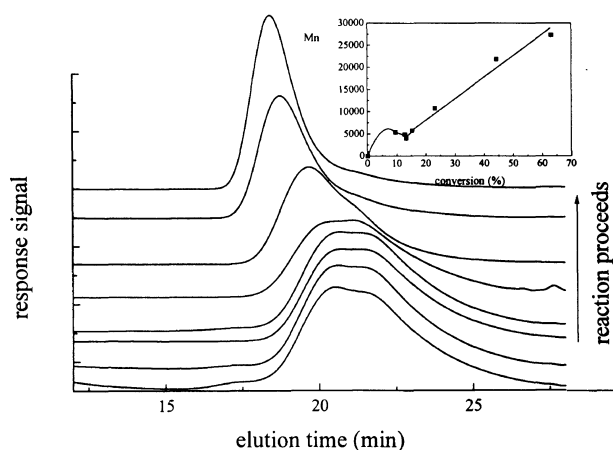
conversions remain almost unchanged (Figure 3a), a character of uncontrolled radical polymerization, the percentage of short chains in curves of living polymers weighs up with monomer conversion of about 18% (corresponding to a decrease in average molecular weight in Figure 2). When the average length of living chains is equal to or higher than that of initially formed long chains, further linear increase in average molecular weight appears as a peak shift to higher chain length in the MWD curves (Figure 3b). At higher conversion, the MWDs of living and total chains cannot be distinguished, suggesting that the percentage of dead chains can be neglected (Figure 3c).

The formation of long chains at the beginning of LFRP was predicated[4] based on two factors. First, the molar ratio of initiator to TEMPO is more than 1/2 (consider one molecule of initiator give two initiator radicals). Secondly, the homolysis rate of initiator must be high enough. By carefully condensing the reaction mixture, we got GPC traces of a number of samples taken at the very initial stage.[29] As shown clearly in Figure 5, the part corresponding to oligomers bulges with reaction time. Accordingly, the molecular weight decreases within this period.

Corresponding to the change in molecular weight, the polydispersity decreases monotonosly for a lower k_d and
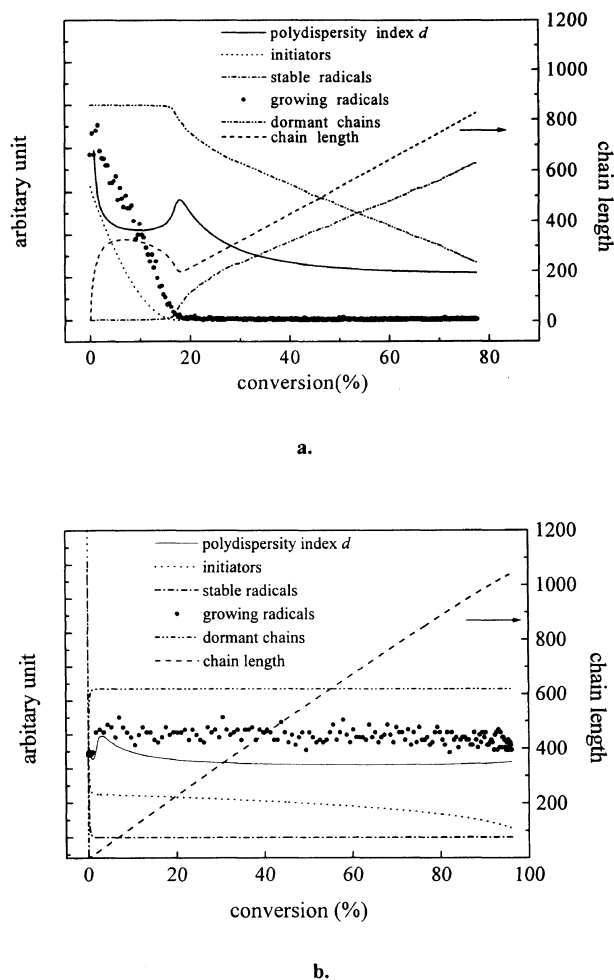
a.

b.

Figure 6. Evolution of some parameters with monomer conversion for (a) $k_d = 5 \times 10^{-2} s^{-1}$ and (b) $k_d = 5 \times 10^{-5} s^{-1}$.

shows a peak for a higher k_d. We must mention that this peak corresponds to the inflection conversion (18%) in Figure 2. This also supports the argument given above, *i.e.*, large population of short living chains are formed in this moment. It is important that, the polydispersities remain narrow at high conversions for lower and higher k_d. This is not opposite to the general concept that an instantaneous initiation is needed for narrow dispersity, because the weight of living chains by further initiation of residual initiators is much smaller than the total weight of living chains, thus making little contribution to polydispersity. Further initiation makes large contribution to polymerization rate, as the concentration of growing radicals increases substantially.

To confirm the above discussion, we show the details of polymerization in Figure 6. Substantial difference between two cases, *i.e.*, lower k_d and higher k_d, are seen. Obviously, for higher k_d, initiators were consumed at about 18% conversion, after which consequently, the concentrations of growing radicals (about $2 \times 10^{-8} M$ after 18% conversion) and dormant chains decreased, with SFRs increasing, till the end of polymerization. In Figure 6a, the inflection points on the curves correspond to each other. For lower k_d (Figure 6b), a relatively low concentration of initiators was kept from the start of chain growth. Consequently, a stationary concentrations of growing radicals (about $10^{-7} M$), dormant chains

and SFRs were sustained to the end of the reaction. This is responsible for the fast polymerization rate.

CONCLUSIONS

The effects of initiator homolysis rate constant, k_d, on kinetics, chain length and distributions of LFRP mediated by a low initial level SFR are investigated using a Monte Carlo method. The results show that, (i) k_d has large effect on polymerization kinetics, a lower k_d leading to a much faster overall polymerization rate, while keeping d of the final products almost not altered; (ii) the simulation results agree with the experimental results qualitatively; (iii) there is uncontrolled growth in molecular weight and a maximum in polydispersity at the early stage of styrene LFRP with low levels of nitroxide and higher k_d initiators.

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