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Effect of Hydrogen Transfer Reaction on Kinetics of Nitroxide-Mediated Free-Radical Polymerization

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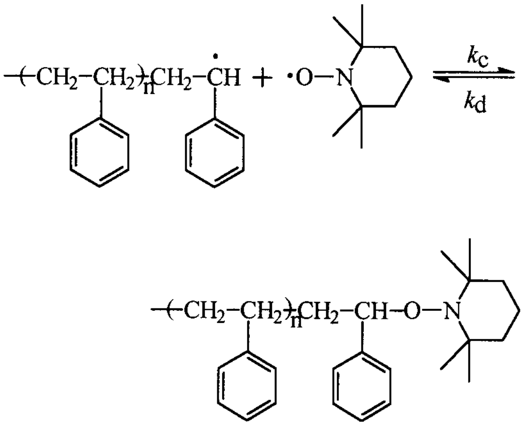
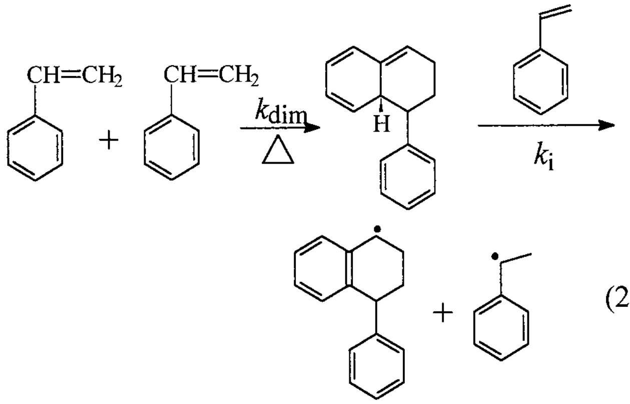
Since the first publication[1] describing the synthesis of narrow disperse resins by free-radical polymerization in the presence of a nitroxide, more and more interest has been attracted to the mechanism[2] of nitroxide-mediated free-radical polymerization and its utility to prepare well-defined polymers.[3] The living behavior of nitroxide-mediated radical polymerization is due to the reversible reaction between growing radical and nitroxyl stable radical such as 2,2,6,6-tetramethylpiperdinyl-1-oxy (TEMPO):[4]



(1)

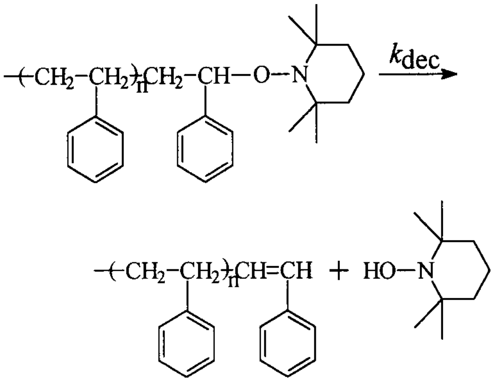
Since the equilibrium is extremely in favor of dormant chains of right hand, the concentration of growing radicals is very low, and thus biradical termination is efficiently suppressed. This leads to both stepwise growth of molecular weight and very slow polymerization rate. However, nitroxide-mediated radical polymerization is not truly a living polymerization because of some side reactions capable of killing living chains or initiating new chains. One of the side reactions is, despite low probability, biradical termination, which leads to accumulation of released stable radicals[2d,e,5] and inhibits polymerization. Another side reaction in nitroxide-mediated styrene polymerization is the thermal initiation[2c,6] of monomer following the Mayo process:[7]



(2)

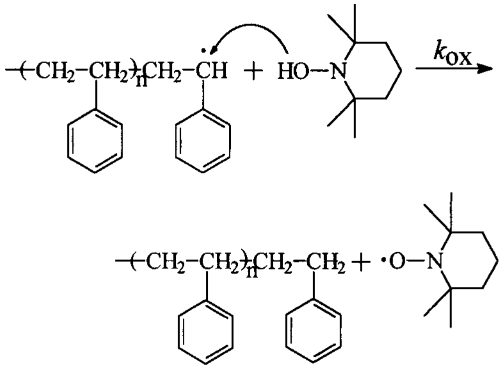
The resulting radicals are capable of initiating new chains. The rate of thermal initiation determines the polymerization rate.[2c]

Recently, it was observed[8,9] that the dormant chains in nitroxide-mediated radical polymerization can decompose to give hydroxyamines and dead polymers with unsaturated chain ends:



(3)

The resulting hydroxyamines would be successively oxidized by growing radicals:[10]



(4)

The disproportionation reactions 3 and 4, in which hydrogen transfer occurs, will undermine the livingness of nitroxide-mediated radical polymerization. The simulation result by Matyjaszewski et al. shows that reaction 3 affects slightly the polymerization kinetics but results in a broader molecular weight distribution.[2d] In this

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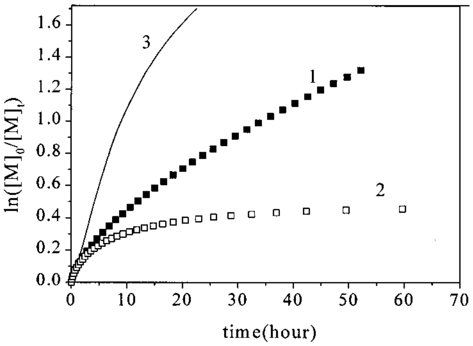

Figure 1. Kinetic plots of different systems of nitroxide-mediated radical polymerization. System 1 (■): with neither hydrogen transfer reaction nor thermal initiation. System 2 (□): with hydrogen transfer reaction and without thermal initiation. System 3 (line): with both hydrogen transfer reaction and thermal initiation. Reaction parameters: $[M]_0 = 8.7$ mol/L, $[SR]_0 = 7.6 \times 10^{-3}$mol/L, $k_p = 2000$ L/(mol s), $k_t = 10^7$ L/(mol s), $k_d = 2 \times 10^{-3}s^{-1}$, $k_c = 2.1 \times 10^8$L/(mol s), $k_{dim} = 3 \times 10^{-8}$ L/(mol s), $k_{ii} = 5 \times 10^{-8}$ L/(mol s), $k_{dec} = 1.1 \times 10^{-5}$ s^{-1}, $k_{ox} = 70$ L/(mol s).

paper, we will investigate by Monte Carlo simulation the effect of hydrogen transfer reactions 3 and 4 on kinetics and molecular weight distribution of nitroxide-mediated radical polymerization.

The simulation method was described[5] previously. In the simulation, we use alkoxyamine-initiated radical polymerization as the kinetic model. All the rate constants are assumed independent of chain length, and chain termination is presumably 100% disproportionation style. When thermal initiation of styrene is taken into account, the temperature chosen is approximately 120 °C. Thus, the parameters are set as follows: $k_p = 2000$ L/(mol s),[11] $k_t = 10^7$ L/(mol s), $k_{dim} = 3 \times 10^{-8}$ L/(mol s), $k_{ii} = 5 \times 10^{-8}$ L/(mol s).[2d] The equilibrium constant K is approximately 10^{-11} mol/L, with $k_d = 2 \times 10^{-3}s^{-1}$ and $k_c = 2.1 \times 10^8$L/(mol s). K is slightly lower than that measured by Fukuda et al. at 125 °C[2c] and almost the same as used by Matyjaszewski.[2d] The decomposition rate constant of alkoxyamine was measured by Matyjaszewski[2d] and can also be calculated from Fukuda's independent result.[9] In the simulation, we set k_{dec} nearly equal to that used in ref 2d), i.e., $k_{dec} = 1.1 \times 10^{-5}$ s^{-1}. The oxidation rate constant is set double that measured in ref 10 at 90 °C, $k_{ox} = 70$ L/(mol s), in a sense arbitrary but giving quite a good fit to the experiment. In the system corresponding to (meth)-acrylates polymerization, a value of k_{ox} as high as 2000 L/(mol s) is needed.

Three systems were examined on the basis of different kinetic models. The results are shown in Figures 1−3. System 1 is an empirical model, including the reversible reaction 1, chain propagation and termination. In Figure 1, the monomer conversion of system 1 increases steadily with time, although it exhibits a slight deviation from a straight line. System 2 includes not only the reactions in system 1 but also hydrogen transfer reactions 3 and 4. The polymerization has a much lower rate and nearly ceases after 20 h or so. System 3 includes all reactions in system 2 as well as the thermal initiation (2), giving the highest polymerization rate of the three systems.

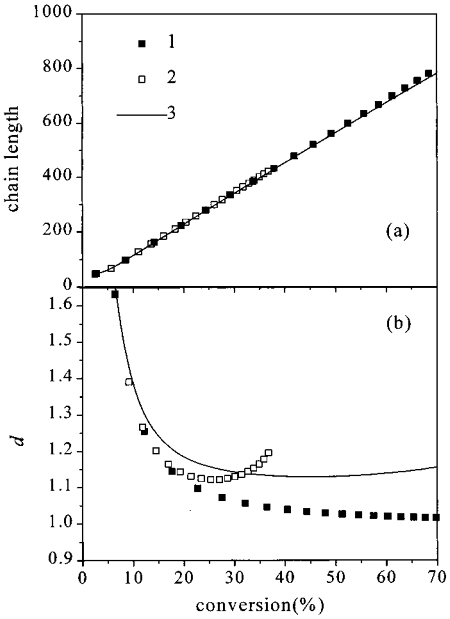

Figure 2. Chain length (a) and polydispersity index (b) as a function of monomer conversion for systems in Figure 1.

It is interesting to correspond qualitatively systems 2 and 3 to nitroxide-mediated radical polymerization of (meth)acrylates and styrene, respectively. This is reasonable in that thermal initiation[2c,6] and hydrogen transfer reaction[10] occur in the system of styrene. In the case of (meth)acrylates, there is no thermal initiation similar to that of styrene, but the hydrogen transfer is even more significant.[12,13] In actual experiments, although styrene polymerizes smoothly in the presence of TEMPO, it is difficult for (meth)acrylates to reach high monomer conversion, and the products were oligomers.[12−14] The simulation results of systems 2 and 3 agree qualitatively with the experiment. At the end of the polymerization, the molecular weight of system 2 is only approximately half of that of system 3 (Figure 2a). Further, the polydispersities for systems 1 and 3 decrease monotonically with conversion, while that for system 2 passes a minimum and then increases with conversion (Figure 2b), again qualitatively agreeing well with the experimental results in ref 15.

To explain the differences in kinetics and polydispersities between different systems, the concentration of stable radical, $[S]_t$, and the dead polymer content, $[P]_t/[SR]_0$ in which $[SR]_0$ is the initial concentration of alkoxyamines, were drawn against monomer conversion in Figure 3. The polymerization rate should be proportional to the reciprocal of $[S]_t$, and the polydispersity depends on the amount of dead polymers formed during polymerization. For system 1, $[S]_t$ increases gradually due to biradical termination, and $[P]_t/[SR]_0$ is negligible. When hydrogen transfer is considered (system 2), $[S]_t$ increases rapidly. This may be responsible for the experimental observation that the red color of TEMPO deepened in methacrylates polymerization.[16] At a conversion of 40% or so, the concentration of dead polymers is nearly equal to $[SR]_0$. This helps us to understand that the molecular weight of poly(meth)acrylates in nitroxide-mediated polymerization was always low because the polymerization came to a premature end. However, when thermal initiation is taken into account, $[S]_t$ reaches a stationary state as a consequence of dynamic balance between thermal initiation and chain deactivation. At 70% conversion, approximately 40% of living chains are deactivated, either by termination or by hydrogen transfer reaction.

Owing to the hydrogen transfer reactions 3 and 4, $[S]_t$ during the polymerization will depend on the initial

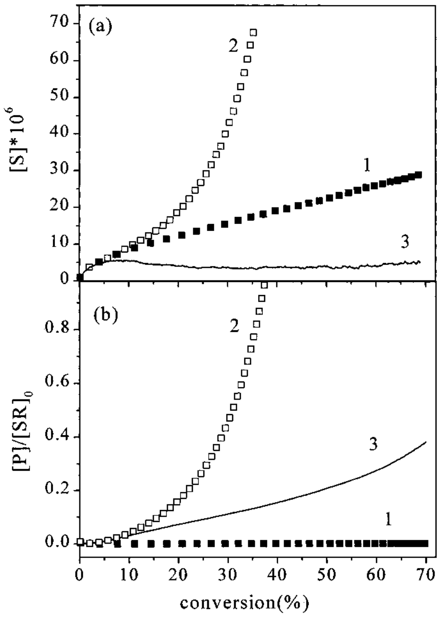

Figure 3. Concentration of stable radicals [S] (a) and dead polymer content $[P]/[SR]_0$ (b) as a funtion of monomer conversion for the systems in Figure 1.

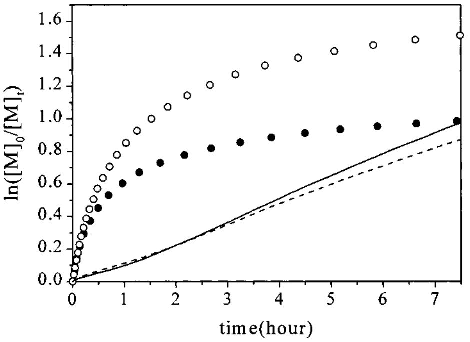

Figure 4. Dependence of polymerization rate on initial concentration of initiators, $[SR]_0$. The lines correspond to system 3 in Figure 1 with $[SR]_0$ being 7.6×10^{-3} M (dashed line) and 3.7×10^{-3}M (solid line). The dots correspond to system 2 with 1.45×10^{-3} M DCPO (homolytical rate constant[14] 3.9×10^{-5} s^{-1}), $k_p = 5000$ L/(mol s), $k_{dec} = 1.1 \times 10^{-5}$ s^{-1}, $k_{ox} = 2000$ L/(mol s), $[SR]_0$ being 7.2×10^{-2} M (●) and 3.6×10^{-2} M (○), respectively.

concentration of alkoxyamine, $[SR]_0$. This will definitely affect the polymerization rate. It was demonstrated previously that[2c,h] if $[SR]_0$ is low, the polymerization rate of styrene will be controlled by the rate of thermal initiation and independent of $[SR]_0$. The simulation shows that the polymerization rate relies strongly on $[SR]_0$ if the following conditions are satisfied: (1) $[SR]_0$ is high enough—if $[SR]_0$ is very low, the rate of hydrogen transfer is negligible as compared to thermal initiation; (2) the rate of hydrogen transfer is high; (3) there is slow initiation in the system by thermal initiation or by radical initiators with long half-life, such as dicumyl peroxide (DCPO).

As two typical examples, system 2 with DCPO and system 3 are compared in Figure 4. These two systems are comparable because DCPO plays the same role as thermal initiation. Obviously, in system 2 (the dots) with a small amount of DCPO, a lower $[SR]_0$ results in a faster polymerization rate. This is consistent with Fukuda's experimental results.[15] It is noted that, in order to fit better the experiment results, a hydrogen transfer rate constant k_{ox} should be much higher, being 2000 L/(mol s) in Figure 4 instead of 70 L/(mol s) in Figures 1−3. For system 3, however, if $[SR]_0$ is an order less (the lines), the polymerization rate is nearly equal to each other, with excellent linearity at early stage, as observed in experimental studies.[2c,h,4c]

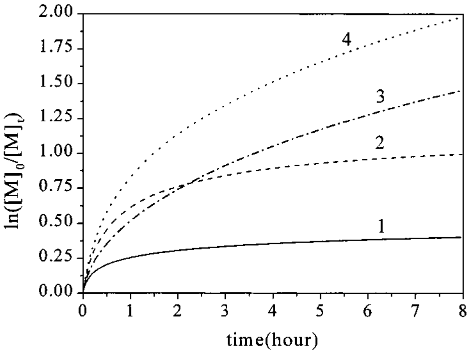

Figure 5. Rate enhancement of nitroxide-mediated radical polymerization of system 2. Reaction parameters: $[M]_0 = 8.7$ mol/L, $[SR]_0 = 7.2 \times 10^{-2}$mol/L, $k_p = 5000$ L/(mol s), $k_t = 10^7$ L/(mol s), $k_d = 2 \times 10^{-3}$ s^{-1}, $k_c = 2.1 \times 10^8$L/(mol s), $k_{dec} = 1.1 \times 10^{-5}$ s^{-1}, $k_{ox} = 2000$ L/(mol s). Curve 1: with hydrogen transfer and without thermal initiation. Curve 2: with 7.6×10^{-4} M DCPO. Curve 3: with 3.5×10^{-2} M CSA. Curve 4: with 7.6×10^{-4} M DCPO and 3.5×10^{-2} M CSA.

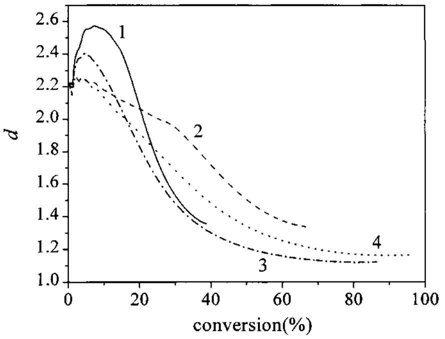

Figure 6. Polydispersity index as a function of monomer conversion for systems in Figure 5. The labels in Figures 5 and 6 correspond to each other.

It is thus demonstrated theoretically that the polymerization of system 2 can be inhibited by a concerted effect of presence of hydrogen transfer and absence of thermal initiation. To enhance the polymerization rate, one can use long half-life initiators to play the role of thermal initiation (curve 2 in Figure 5), as first proposed[2c,17] and demonstrated[18] by Fukuda and coworkers. The independent experimental result by Matyjaszewski et al. confirmed this.[19] A remarkable initiator effect on polymerization of a styrene derivative with an oligosaccharide moiety, in which thermal initiation was almost absent, can also be found in ref 20. Another approach to enhance the polymerization rate is using camphorsulfonic acid (CSA)[21] to consume the stable radicals accumulating during polymerization. In the simulation, assuming that the stable radical react with a chemical species at a rate of 0.06 L/(mol s), we found that the polymerization rate was enhanced substantially (Figure 5, curve 3) while the dispersity of the product remained narrow (Figure 6). It is more interesting that the combination of the above two methods will give the fastest polymerization rate while the polydispersity index at higher conversion is well below 1.5, the theoretical limit of free-radical polymerization.

It is concluded that hydrogen transfer reaction not only reduces the polymerization rate but also broadens the distribution of the product. The comprehensive effect of hydrogen transfer and absence of thermal initiation may be responsible for the problems in polymerization of (meth)acrylates. The simulation suggests a possibility to enhance efficiently the polymerization rate of (meth)-acrylate while keeping a narrow dispersity by addition of organic acid as well as radical initiator with long half-life.

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