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Rate enhancement of nitroxide-mediated living free-radical polymerization by continuous addition of initiator

Junpo He[a,b], Jingmin Chen[a,b], Li Li[a,b], Jingyun Pan[a,b], Chengming Li[a,b], Jizhuang Cao[a,b], Yuefei Tao[a,b], Fengjun Hua[a,b], Yuliang Yang[a,b,*], Graham E. McKee[c], Susanne Brinkmann[c]

[a]*Department of Macromolecular Science, Fudan University, Shanghai 200433, People's Republic of China*
[b]*Open Lab of Macromolecular Engineering, State Education Commission, People's Republic of China*
[c]*ZKT, BASF Aktiengesellschaft, D-67056 Ludwigshafen, Germany*

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Abstract

A new technique, which involves the continuous addition of a small amount of radical initiators, was developed with the assistance of computer simulation to increase the rate of nitroxide-mediated living free-radical polymerization. Using this method, the polymerization rate of styrene in the presence of 4-hydroxy-2,2,6,6-tetramethyl piperidinyl-1-oxy was increased more than 3-fold compared to that with one-batch addition of initiator, while the molecular weight and distribution remain the same, respectively, at higher monomer conversion. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Nitroxide-mediated living free-radical polymerization; Kinetics; Molecular weight distribution

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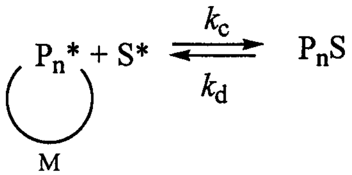
1. Introduction

Living free-radical polymerization (LFRP) is one of the recent breakthroughs in polymer synthesis [1–5]. The basic idea is to greatly reduce biradical termination, which always occurs in conventional radical polymerization, by a reversible coupling reaction between highly active carbon-centered radicals and chemical species such as nitroxide stable radical [1,2,6,7], halogen atom [3,4] or dithiocarbamate [5]. In this paper, we will concentrate on nitroxide mediated LFRP, which can be schematically written as:



where P_n^* and S^* are a chain radical and a stable radical, respectively. P_nS is a dormant chain and M represents the monomer. While P_n^* can add monomer to propagate, it is more likely to be trapped by S^* to become a dormant chain P_nS. As the equilibrium constant $K = k_c/k_d$ is as high as 10^{11} l/mol [8,9], step growth of molecular weight is achieved without much termination. To date, LFRP has been applied to synthesize narrow disperse polymers [2,10–13], block copolymers [14–16] as well as star and graft copolymers [17].

The nitroxide mediated LFRP, however, has a very slow polymerization rate due to the low concentration of growing radicals P_n^*. A typical radical polymerization in the presence of TEMPO (2,2,6,6-tetramethyl piperidinyl-1-oxy) usually needs more than 50 h to reach relatively high monomer conversion. Some approaches have been developed to increase the rate of LFRP. In 1994, Georges and coworkers [18–20] observed an unexpected rate enhancement when they used camphorsulfonic acid to suppress the styrene self-initiation that was considered harmful to LFRP. Late in 1996, they found that another chemical, namely, 2-fluoro-1-methylpyridinium *p*-toluenesulfonate, could also be used to promote the polymerization rate [21]. Recently, it was demonstrated that radical initiators with a higher decomposition rate constant, k_i, such as BHP [22] (butyl hydroperoxide) and DCPO [23] (dicumyl peroxide), were able to shorten the polymerization time as well.

We have also performed studies on LFRP mediated by a stable radical, aiming to enhance the polymerization rate. This work was aided by computer simulation, which proved

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[*] Corresponding author. Tel.: +86-21-6564-2863; fax: +86-21-6564-4642.

E-mail address: ylyang@srcap.stc.sh.cn (Y. Yang).

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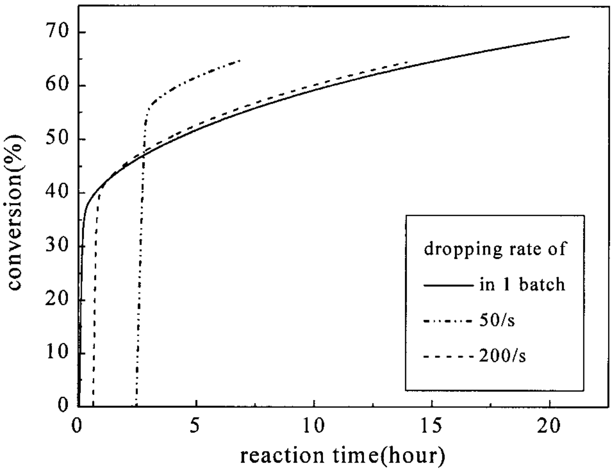

Fig. 1. Simulation results on kinetics of LFRPs with different ways of initiator addition (shown in the inset).

to be a powerful tool in the study of living radical polymerization [24]. In the following, we will present kinetic results of both simulation and experiment on systems with continuous addition of radical initiator. This technique might be one of the many choices to increase the polymerization rate of LFRP. It should be pointed out that as the homolytical rate constant of the initiator is not an adjustable parameter, this technique is advantageous in affording a desired supply rate of radicals.

2. Simulation

The method of Monte Carlo simulation was described previously [24]. Here we use the algorithm to simulate the polymerization process based on the reactions in the above scheme as well as the decomposition of radical initiator, I, with rate constant k_i:

$$\mathrm{I} \xrightarrow{k_i} 2\mathrm{P}_0^*,$$

and biradical irreversible termination to form dead polymers with rate constant k_t:

$$\mathrm{P}_n^* + \mathrm{P}_m^* \xrightarrow{k_t} \mathrm{P}_{n+m}.$$

For simplicity, only combination termination was considered and some side reactions, such as thermal self-initiation of styrene as well as the decomposition of TEMPO, are not included. This is reasonable because we are not trying to strictly compare the results of simulation and experiment, but to investigate the effect of continuous addition of initiator.

The reaction parameters come from styrene bulk polymerization at about 110–130°C, initiated by AIBN in the presence of TEMPO. Thereby, in the simulation, we set $[\mathrm{M}]_0 = 8.7$ M; $[\mathrm{I}]_0 = 4.4 \times 10^{-3}$ M; $[\mathrm{TEMPO}]_0 = 7.6 \times 10^{-3}$ M, i.e. $[\mathrm{TEMPO}]_0/2[\mathrm{I}]_0 = 0.864 : 1$; chain propagation rate constant $k_p = 2 \times 10^3$ l/(mols); $k_t = 10^7$ l/(mols); $k_d = 10^{-2}\ s^{-1}$ and $k_c = 10^9$ l/(mols); $k_i = 8 \times 10^{-3}\ \mathrm{s}^{-1}$. The addition rates of initiators are 50 and 200 molecules per second in the simulation.

3. Experimental

Styrene was freshly distilled under vacuum before polymerization. AIBN was recrystallized from ethanol. 4-hydroxy TEMPO (HO-TEMPO) was used as received.

3.1. Parallel polymerization: initiator was added in one batch

HO-TEMPO was dissolved in freeze-thawing degassed styrene in a three necked flask equipped with a thermometer, a gas inlet tube and a condenser. When the mixture was heated to 115°C with magnetic stirring, AIBN was added to start the polymerization. The reaction was under N_2 atmosphere. Samples were extracted from the flask at predetermined intervals, then quenched into liquid nitrogen to stop the reaction.

3.2. Rate enhancement: initiator was dropped continuously into the system

All reaction conditions are identical to the control reaction except the method of initiator addition. When the reaction mixture was heated to 115°C, 4/5 parts of AIBN was added in one batch to the flask. The rest 1/5 part of the initiator was pre-dissolved in 15 ml styrene, and the solution was dropped slowly through a capillary into the system. The dropping rate was manually controlled at 1 ± 0.1 ml per hour, usually one drop in every 40 s. The total volume of the reaction mixture, 130 ml, changed only slightly with the addition of initiator solution. This change in volume was neglected in the calculation of monomer conversion. The

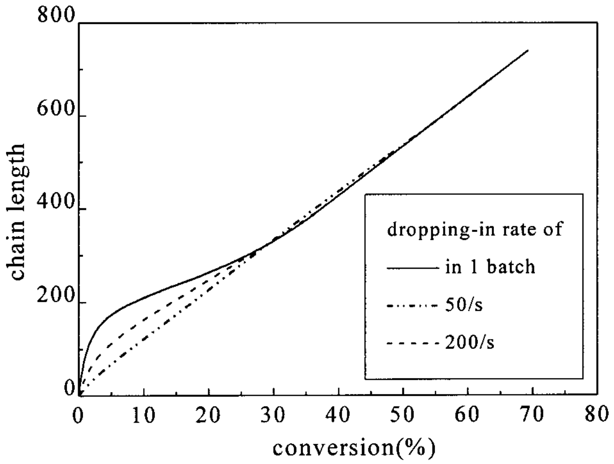

Fig. 2. Simulation results on chain length growth with monomer conversion for the same systems in Fig. 1.

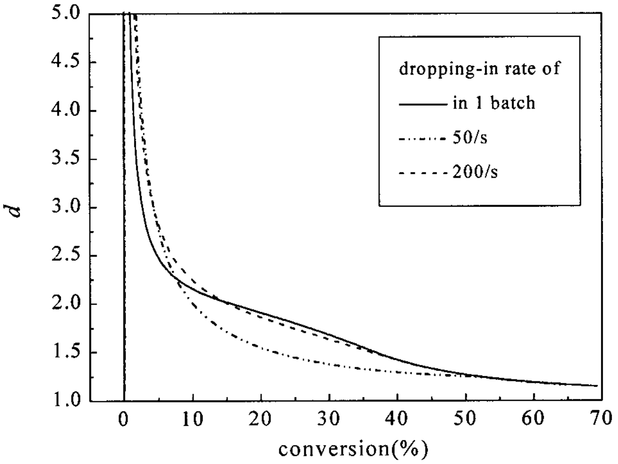

Fig. 3. Simulation results on change of polydispersities with monomer conversion for the same systems in Fig. 1.

total amount of styrene and the amount of all other chemicals are the same as in the control reaction.

3.3. Measurement

The measurement of percentage conversions was performed on a NETZSCH TG209 instrument, using Veregin's method [25]. The samples were heated in nitrogen at a rate of 20 K min^{-1} from 25°C to 510°C. Weight loss above 275°C gave the polymer content, or monomer conversion.

Molecular weights were determined by gel permeation chromatography (GPC) on samples taken directly from the reaction mixture. The analysis uses THF as eluent at 1 ml min^{-1} through three Waters Ultrastyragel columns HR4, HR3 and HR1 in series and a Waters 410 RI detector. Polystyrene was used as standard.

4. Results and discussion

Kinetics: While most kinetic studies on LFRP were conducted at early stage of the reaction and thus linear dependence on time was observed, we prefer to let the polymerization proceed to a higher conversion, both in simulation and in experiment. For example, usually after solidification of the mixture the reaction was stopped in experiment.

The simulation results show an optimistic effect of continuous addition of initiator on kinetics. From Fig. 1, it is clear that the time consumed at higher conversion for systems with continuous addition of initiator is shorter than that with one-batch addition. The chain length grows linearly in the former system while in the latter, a sharp increase in chain length appeared at the initial stage (Fig. 2). This sharp increase could be attributed to the uncontrolled polymerization resulting from excess radicals from fast homolysis of the initiator. At higher conversion, the method of initiator addition makes no difference in chain length. The reason might be that the weight percent of chains formed by uncontrolled polymerization is much smaller in the total chains in the system and therefore, the ultimate polydispersities are almost identical at higher conversion for different systems (Fig. 3).

Guided by the simulation results, a number of polymerizations were conducted with different methods of initiator addition. The results of different runs are listed in Table 1, in which St, HT, M_n and d represent styrene, 4-hydroxy-TEMPO, number averaged molecular weight and polydispersity, respectively.

A typical example is shown in Fig. 4. The overall polymerization rates for systems with continuous addition of initiators are much higher than that with one-batch addition of initiator. This agrees with the simulation results. It is interesting to note the different kinetic behavior between systems with one-batch addition and with continuous addition of initiator. For the former, there was a rapid increase in conversion at the initial stage. As mentioned before, this could be a consequence of excess AIBN with respect to HO-TEMPO in the reaction recipe. As the half-life time of AIBN at the reaction temperature is less than 1 min, it was exhausted within a very short period, then the polymerization rate leveled off till the end of the reaction. Totally, it took more than 50 h for the parallel reaction to reach about 65% conversion.

Polymerization rate was not constant either in simulation or in experiment for the system with one-batch addition of initiator, indicating that a stationary concentration of growing radicals, $[P_n^*]$, cannot be sustained. Instead, a reduction in $[P_n^*]$ with time took place due to irreversible biradical

Table 1
Experimentals with different formulas and initiator addition methods

Run no.	Formula			Hours for initiator addition	Final con. (%)	Time (min)	M_n	d
	St (g)	AIBN (g)	HT (g)					
1	120	0.7	0.8	One batch	65.4	3112	7569	1.39
2	120	0.7	0.8	16	75.9	820	12891	1.42
3	120	0.7	0.8	21	75.1	1220	14626	1.17
4	120	0.35	0.4	One batch	71.8	1444	22543	1.31
5	120	0.35	0.4	13	72.7	785	29582	1.28
6	120	0.35	0.4	15	73.5	890	31651	1.28

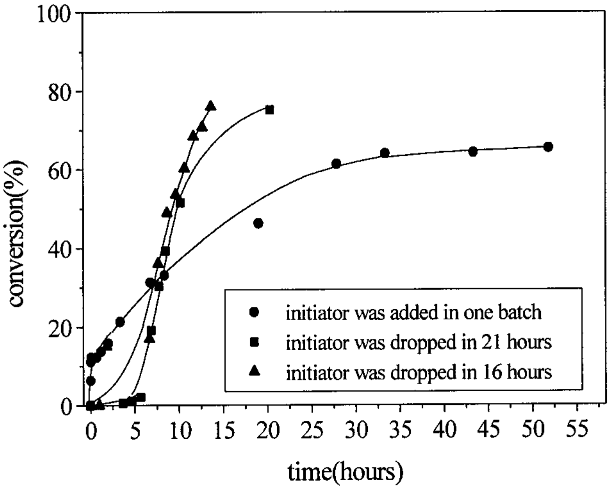

Fig. 4. Kinetic curves of styrene LFRPs (runs No. 1–3 in Table 1) using different method of initiator addition.

termination, which is known difficult to be completely eliminated (see for example Refs. [26,27]). Once termination occurs, two stable radicals are released. As polymerization proceeds, stable radicals accumulate and, in turn, suppress the concentration of growing radicals. To enhance the polymerization rate, the excess stable radicals should be "removed" or additional growing radicals be supplied. The mechanisms of rate enhancement by the addition of camphorsulfonic acid [19,20], pyridine salt [21] is actually based on the scavenging of excess TEMPO, while those using initiators with low k_i [22,23] are through the mechanism of supplying more growing radicals.

The curves for initiator continuous addition in Fig. 4 show an induction period at the initial stage of each of them, corresponding to the trapping period of the majority of initiator radicals by nitroxide. A rapid increase in monomer conversion took place after the induction period was finished. The main part of the curve is nearly a straight line, indicating a stationary concentration of growing radicals. This is even more evident in the simulation result in Fig. 2. Thus it seems that the chain radicals consumed in termination were compensated by slowly dropping the initiator into the system. As a result, a total time of about 16 h was needed to reach approx. 76% conversion, which is much faster than that using one-batch addition of initiator.

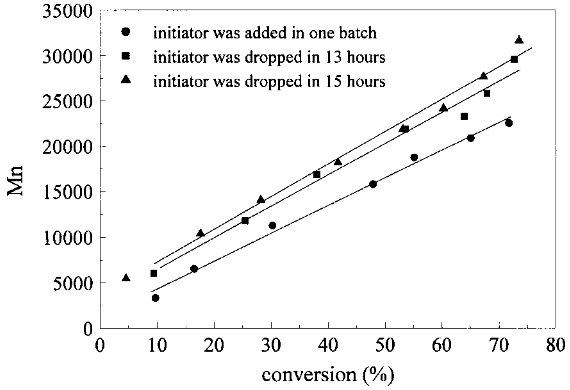

Fig. 5. The molecular weight growth with monomer conversion for runs No. 4–6 in Table 1.

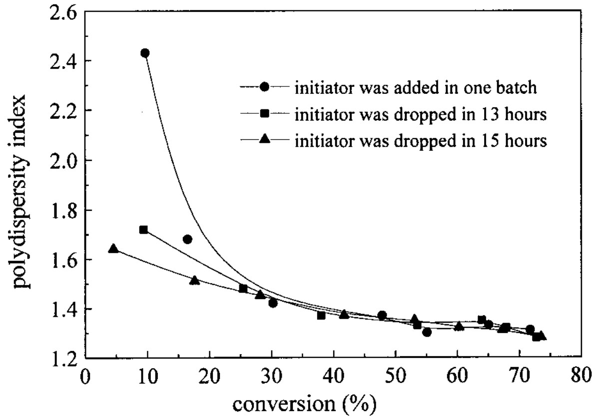

Fig. 6. Evolution of MWDs with monomer conversion for runs No. 4–6 in Table 1.

Both of these systems show linear increases in molecular weights with monomer conversions except in the initial stage, illustrating that the polymerization proceeds in a living fashion, as shown in Fig. 5. For the "initial stage" issue, it is reasonable to deduce that the molecular weight underwent a fast increase to reach a certain value, because extrapolates of the lines do not pass through the original point. This agrees qualitatively with the initial stage in the simulation. It should be mentioned that the "arch" effect at the initial stage in Fig. 2 for higher k_d is difficult to observe experimentally, owing to the very low concentration of long chains [25] and experimental uncertainties. We have discussed this issue in detail in another paper [28]. It is also noted from Table 1 that the molecular weights were relatively higher when the initiator was added for a longer time.

Probably the most important point is that the molecular weight distributions (MWDs) decreased with monomer conversion in all these systems (Fig. 6). At the later stage, there was no difference in the polydispersity indices and they were well below the theoretical limit 1.5 of conventional radical polymerization.

In conclusion, the polymerization rate was greatly enhanced without greatly broadening the dispersity of the resulting polymer using a technique of continuous feed of initiator.

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