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Reversible addition–fragmentation chain transfer (RAFT) polymerization of styrene in the presence of oxygen

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Abstract

Reversible addition–fragmentation chain transfer polymerization (RAFT) of styrene (St) was carried out in the presence of oxygen using 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) or benzyl (2-phenyl)-1-imidazolecarbodithioate (BPIC) as the RAFT agent. The characteristics of the "living"/controlled radical polymerization were observed at high concentration of RAFT agent and low polymerization temperature. A slight increase in the rate of polymerization was found when oxygen was added at high concentration to the polymerization system; however, the presence of oxygen incurred greater polydispersities of the polymer at the same monomer conversion compared to that obtained in the absence of oxygen. The possible mechanism of the RAFT polymerization of St in the presence of oxygen was discussed.

Keywords: Oxygen; Reversible addition–fragmentation chain transfer (RAFT); Styrene

1. Introduction

The reversible addition–fragmentation chain transfer (RAFT) polymerization has developed into an important method for generating polymeric materials with controlled molecular weights and complex macromolecular architectures under a vast variety of reaction conditions [1,2]. RAFT polymerization is usually carried out with conventional thermal initiators, e.g., 2,2′-azobisisobutyronitrile (AIBN) [3], benzoyl peroxide (BPO) [4,5] and potassium persulfate (KPS) [1]. RAFT polymerization of St can also be initiated thermally between 100 °C and 120 °C [6]. UV irradiation [7], γ-source [8] and plasma initiation [9] have also been reported in RAFT polymerization.

It has long been recognized that the presence of oxygen in the free radical polymerizations shows negative effects on the course of reaction, including causing inhibition periods and retarding the reaction rate [10–23]. As for controlled/"living" radical polymerization, the reaction solution is always thoroughly deoxygenated before polymerization, often purged with argon or nitrogen for a period of time (usually more than 10 min), or degassed by several freeze–pump–thaw cycles. However, in most industrial settings, it is difficult to attain thoroughly deoxygenated levels as in laboratory experimental conditions. And the polymerization without deoxygenated process means abridged cost in industry practice. Recently, we reported that MMA can be thermally polymerized in the presence of oxygen via the RAFT process [24]. The polymerization was well-behaved in the presence of oxygen, and it was interesting to find that the predetermined amount of oxygen could accelerate the thermal-initiated RAFT polymerization of MMA. Based on the experimental data, we concluded that the PMMA peroxide (PMMAP) formed *in situ* was likely to be responsible for the initiation behavior [24]. In comparison with MMA, the thermal-initiated polymerization of styrene (St) is more widely used in practical use for its high rates of polymerization. It will be beneficial for the RAFT polymerization of St in the presence of oxygen from the industrial standpoint. In this

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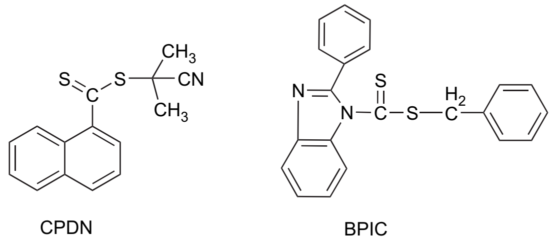
work, we investigated the RAFT polymerization of St in the presence of oxygen without additional initiator. The main emphasis was on the polymerization kinetics and the maintenance of ‘‘living’’/controlled fashions in the presence of oxygen. Two dithioesters, e.g. 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) and benzyl (2-phenyl)-1-imidazolecarbodithioate (BPIC) were used as the RAFT agents in current work, which were efficient RAFT agents for the polymerization of St [25,26]. The structures of CPDN and BPIC are shown in Scheme 1.



Scheme 1. Structures of CPDN and BPIC.

2. Experimental part

2.1. Materials

The monomer, St (99+%) was purchased from Shanghai Chemical Reagents Co. (Shanghai, China). It was washed with an aqueous solution of sodium hydroxide (5 wt%) for three times, followed by deionized water until neutralization, and then dried over anhydrous magnesium sulfate. It was distilled twice under reduced pressure and stored at −18 °C. Tetrahydrofuran (THF, analytical reagent) was obtained from Yangyuan Chemical Reagents Co. (Suzhou, China) and used as received. CPDN was synthesized according to the method reported in Ref. [25] with the purity greater than 94% (LC-6A (A), Shimadzu Co. High performance liquid chromatography (HPLC)); ^{1}H NMR ($CDCl_3$): 1.95 (s, 6H), 7.42 (m, 2H), 7.51 (m, 2H), 7.85 (m, 2H), and 8.10 (m, 1H)). BPIC was obtained according to the literature [27] as a yellow powder, and the purity was greater than 98% (HPLC). All other chemicals (reagent or analytical grade) were obtained from Shanghai Chemical Reagents Co. and used as received.

2.2. RAFT polymerization of St in the presence of oxygen

A typical polymerization procedure was as follows: a mixture of St and CPDN (or BPIC) in a prescribed molar ratio was added to a dry ampoule. In the deoxygenated system, the solution was purged with argon for 20 min; in the oxygen-added system, the addition of oxygen followed the Refs. [24,28]. The procedures were as follows: air was eliminated completely from the reaction mixture by three freeze–pump–thaw cycles (high vacuum, pressure: 3 Pa). The ampoule was sealed with a rubber septum. A predetermined amount of air (ambient temperature, 1 atm) was subsequently added to the ampoule through a syringe. For example, when 1 mL air was added to a 2 mL reaction mixture ($[St]_0 = 8.74$ mol/L), the oxygen concentration was calculated to be 0.00469 mol/L. Afterwards, the ampoule was sealed and placed in an oil bath held by a thermostat at a desired temperature. The ampoule was immersed into iced water after a preset period of time. The content was then dissolved in THF (about 2 mL) and precipitated into methanol (about 200 mL). The polymer obtained by filtration was dried under vacuum at room temperature until a constant weight is obtained. The monomer conversion was determined gravimetrically.

2.3. Chain extension of PS

A predetermined amount of PS, obtained from the RAFT polymerization in the presence of oxygen, was dissolved in St. The content was purged with argon for 20 min. The other steps were the same as described above, except that RAFT agent was replaced by the synthesized PS as a macro-RAFT agent.

2.4. Characterization

The number-average molecular weights (M_n) and polydispersity indexes (PDI) of the polymers were determined using Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), using HR 1, HR 2 and HR 4 (7.8 × 300 mm, 5 μm bead size) columns with molecular weights ranged 10^2–5×10^5 g/mol. THF was used as an eluent at a flow rate of 1.0 mL/min and 30 °C. The GPC samples were injected using a Waters 717 plus autosampler and calibrated with PS standards from Waters. ^{1}H NMR spectra of the precipitated polymers were performed on an INOVA 400 MHz nuclear magnetic resonance instrument using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. High performance liquid chromatography (HPLC) was measured in LC-6A (A) (Shimadzu Co.). An iodometric method was used to determine the concentration of peroxide in polymerization mixture with a UV spectroscopy (Lengguang 722, Shanghai Precision and Scientific Instrument Co.) [29].

3. Results and discussion

3.1. Effect of oxygen concentration on RAFT polymerization of St

Figs. 1 and 2 show the kinetic results of RAFT polymerization of St mediated with CPDN and BPIC at various concentrations of oxygen. In parallel experiments, the RAFT polymerizations in the absence of oxygen (deoxygenated system) were also conducted under the same conditions for comparison. When the concentration of oxygen increased from 0 to 0.00938 mol/L, the polymerization rates were almost unchanged. However, with the concentration of oxygen increasing from 0.00938 to 0.0563 mol/L, the polymerization rate increased slightly (Figs. 1 and 2). Similar results were found in the case of the polymerizations with different RAFT agents (CPDN or BPIC), different concentrations of RAFT agents

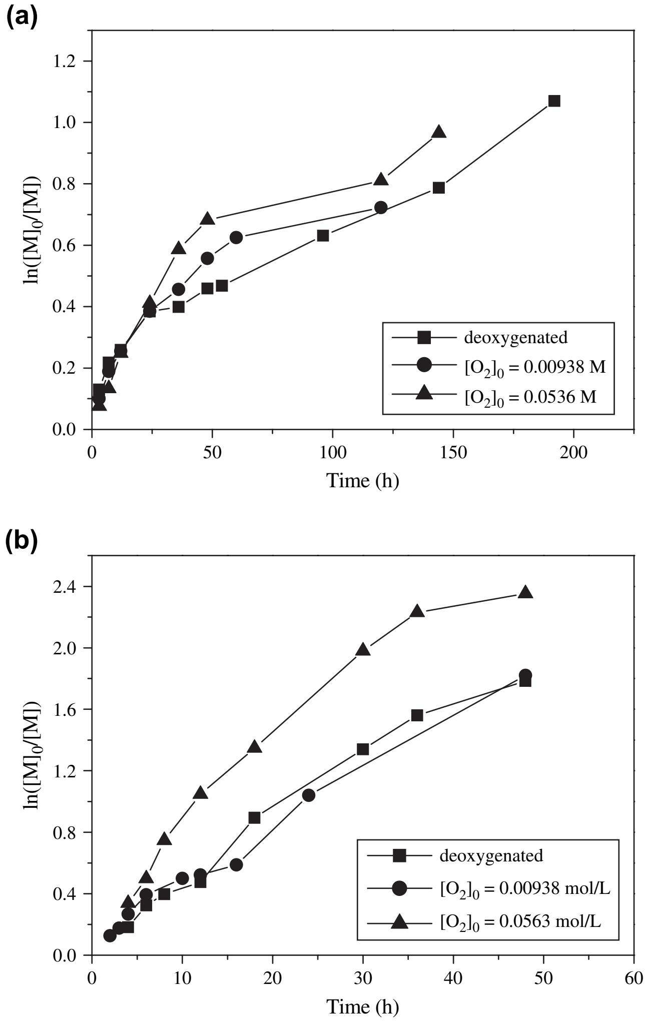


Fig. 1. ln ([M]$_0$/[M]) versus time data of the thermal-initiated RAFT polymerization of St mediated by CPDN at various oxygen concentrations: (a) $[\mathrm{CPDN}]_0 = 1.75 \times 10^{-2}$ mol/L, 80 °C; (b) $[\mathrm{CPDN}]_0 = 5.83 \times 10^{-3}$ mol/L, 110 °C. $[\mathrm{St}]_0 = 8.74$ mol/L.

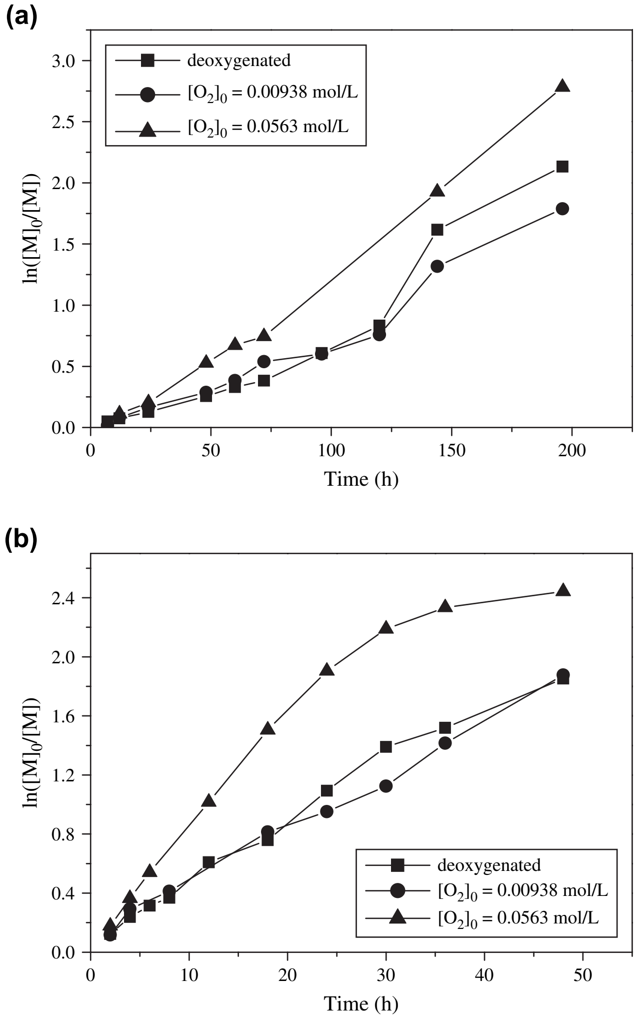


Fig. 2. ln ([M]$_0$/[M]) versus time data of the thermal-initiated RAFT polymerization of St mediated by BPIC at various oxygen concentrations: (a) $[\mathrm{BPIC}]_0 = 1.75 \times 10^{-2}$ mol/L, 80 °C; (b) $[\mathrm{BPIC}]_0 = 5.83 \times 10^{-3}$ mol/L, 110 °C. $[\mathrm{St}]_0 = 8.74$ mol/L.

(0.0175 mol/L or 0.00583 mol/L) and different polymerization temperatures (80 °C or 110 °C). It was noticeable that these results were different from the RAFT polymerization of MMA [24]. In the thermal-initiated RAFT polymerization of MMA, the presence of oxygen can accelerate the polymerization rate remarkably [24].

Figs. 3 and 4 show the evolution of number-average molecular weights measured by GPC ($M_{\mathrm{n,GPC}}$) and polydispersity indexes (PDI) of obtained polymers with monomer conversion in the presence of various amounts of oxygen. The linear relationship between $M_{\mathrm{n,GPC}}$ and conversion was obtained when the polymerization was conducted with relatively high concentration of RAFT agent (1.75×10^{-2} mol/L) and low temperature (80 °C) (Figs. 3a and 4a). The $M_{\mathrm{n,GPC}}$ of the obtained polymer were close to the theoretical values ($M_{\mathrm{n,th}}$, $M_{\mathrm{n,th}} = ([\mathrm{St}]_0/[\mathrm{RAFT\ agent}]_0) \times \mathrm{conversion} \times \mathrm{m.w.\ of\ St} + \mathrm{m.w.\ of\ RAFT\ agent}$). However, when lower concentration of RAFT agent (5.83×10^{-3} mol/L) and higher temperature (110 °C) were applied (Figs. 3b and 4b), the polymerization offered the polymers higher PDI values and lower $M_{\mathrm{n,GPC}}$ deviating negatively from the theoretical ones, indicating some loss of control over the polymerizations. Meanwhile, it can be found that the PDI values of the polymer obtained in the presence of oxygen were higher than that obtained in the absence of oxygen, which indicated that more dead polymer chains were produced in the presence of oxygen (Figs. 3 and 4). According to the RAFT mechanism [1], the fraction of dead polymer chains can be calculated by the following equation:

$$[\mathrm{Dead\ chains}] = \frac{2f\left([I]_0 - [I]_t\right)}{[\mathrm{RAFT\ agent}]_0 + 2f\left([I]_0 - [I]_t\right)}$$

where $[I]_0 - [I]_t$ is the concentration of initiator consumed, and f is the initiator efficiency, $[\mathrm{RAFT\ agent}]_0$ is the initial concentration of the RAFT agent. Therefore, the increase of the amount of the consumed initiator may be responsible for the greater PDI values in the presence of oxygen.

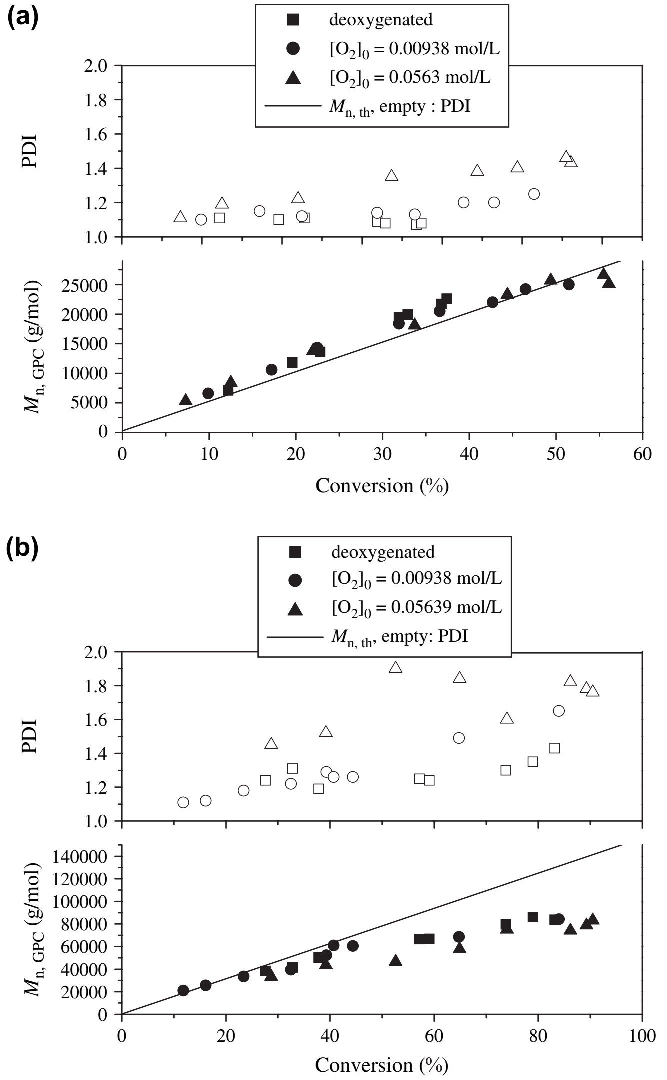


Fig. 3. $M_{n,GPC}$ and PDI values versus conversion for the thermal-initiated RAFT polymerization of St at various concentration of oxygen with CPDN as the RAFT agent: (a) and (b) are the same conditions as (a) and (b) in Fig. 1, respectively. $M_{n,th} = ([St]_0/[CPDN]_0) \times \text{conversion} \times \text{m.w. of St} + \text{m.w. of CPDN}$.

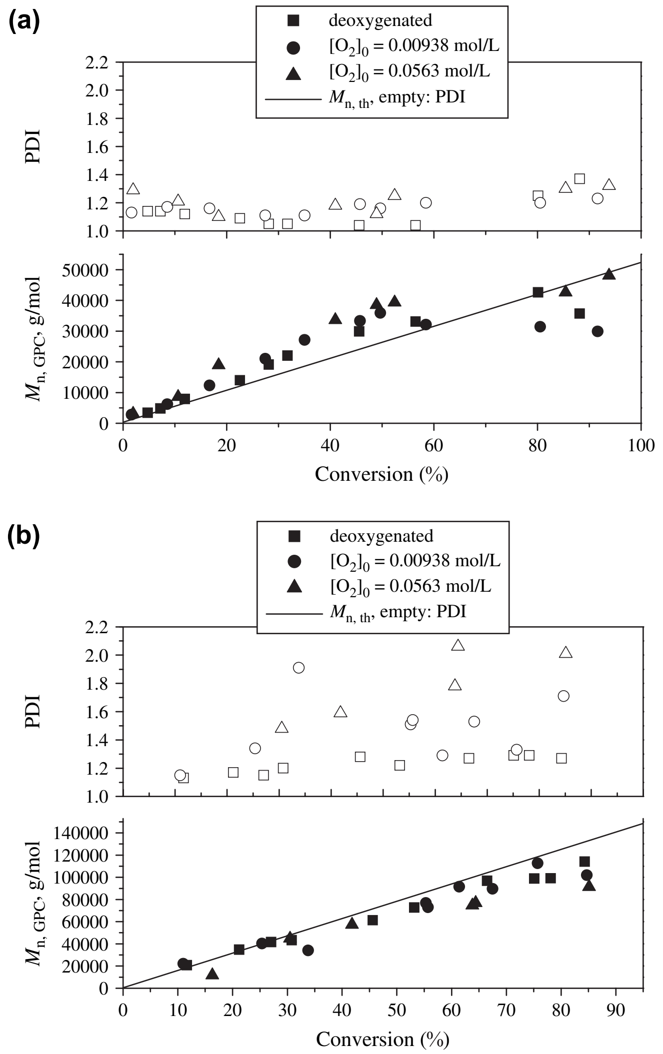


Fig. 4. $M_{n,GPC}$ and PDI values versus conversion for the thermal-initiated RAFT polymerization of St at various concentrations of oxygen with BPIC as the RAFT agent: (a) and (b) are the same conditions as (a) and (b) in Fig. 2, respectively. $M_{n,th} = ([St]_0/[BPIC]_0) \times \text{conversion} \times \text{m.w. of St} + \text{m.w. of BPIC}$.

The chain ends of PS prepared by the thermal polymerization in the presence of oxygen were analyzed by ^{1}H NMR spectroscopy. In Fig. 5, both of the polymers mediated by CPDN and BPIC showed the signals of the corresponding RAFT agent. For the polymer obtained from the polymerization mediated by CPDN, the signals at $\delta = 7.4{-}8.1$ ppm in Fig. 5(a) were attributed to the aromatic protons of the naphthalene units in CPDN. With respect to the BPIC-mediated PS, the signals at $\delta = 7.3{-}7.9$ ppm in Fig. 5(b) corresponded to the aromatic protons of BPIC units [26]. These results indicated that the moiety of the RAFT agent was attached to the end of PS.

To further demonstrate the "living" nature of the RAFT polymerization, the PS samples obtained under the oxygenated conditions were used as macro-RAFT agents for chain extension reactions. A typical chain extension reaction was carried out with the addition of fresh St monomer to PS under deoxygenated atmosphere ([St]$_0$/[macro-RAFT agent]$_0$ = 1000/1) at 115 °C for 5 h. Fig. 6 shows the GPC curves. There was an obvious peak shift from the macro-RAFT agent to the product. The molecular weights increased from 13,800 g/mol (PDI = 1.22) to 33,370 g/mol (PDI = 1.56, 26.2% conversion) with CPDN–PS as macro-RAFT agent, and from 18,900 g/mol (PDI = 1.10) to 30,300 g/mol (PDI = 1.53, 28.0% conversion) with BPIC–PS as macro-RAFT agent. However, a higher PDI value and a tail in the GPC profile of the product were observed, which may be caused by some amount of dead polymer existing in the original polymer [30,31]. These evidences revealed that most of polymers obtained under oxygen were still "living". For a comparison purpose, the polymer obtained under the deoxygenated atmosphere was used as the macro-RAFT agent under the similar conditions. The GPC profiles of the original polymer and the chain-extended polymer are presented in Fig. 7. An obvious peak shift from the macro-RAFT agent to the product could be

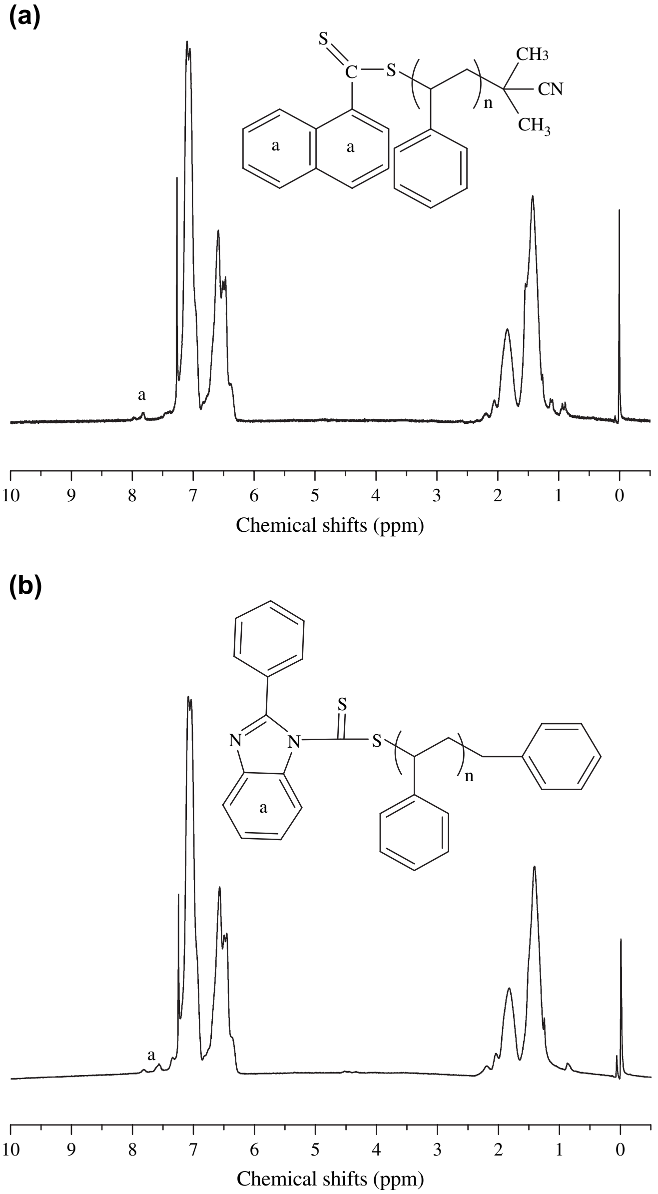


Fig. 5. ^{1}H NMR spectra of PS samples obtained from the RAFT polymerization mediated by (a) CPDN in the presence of oxygen, $M_{n,GPC} = 8400$ g/mol, PDI = 1.19; (b) BPIC in the presence of oxygen, $M_{n,GPC} = 8600$ g/mol, PDI = 1.21. Solvent: $CDCl_3$, internal standard: tetramethylsilane (TMS).

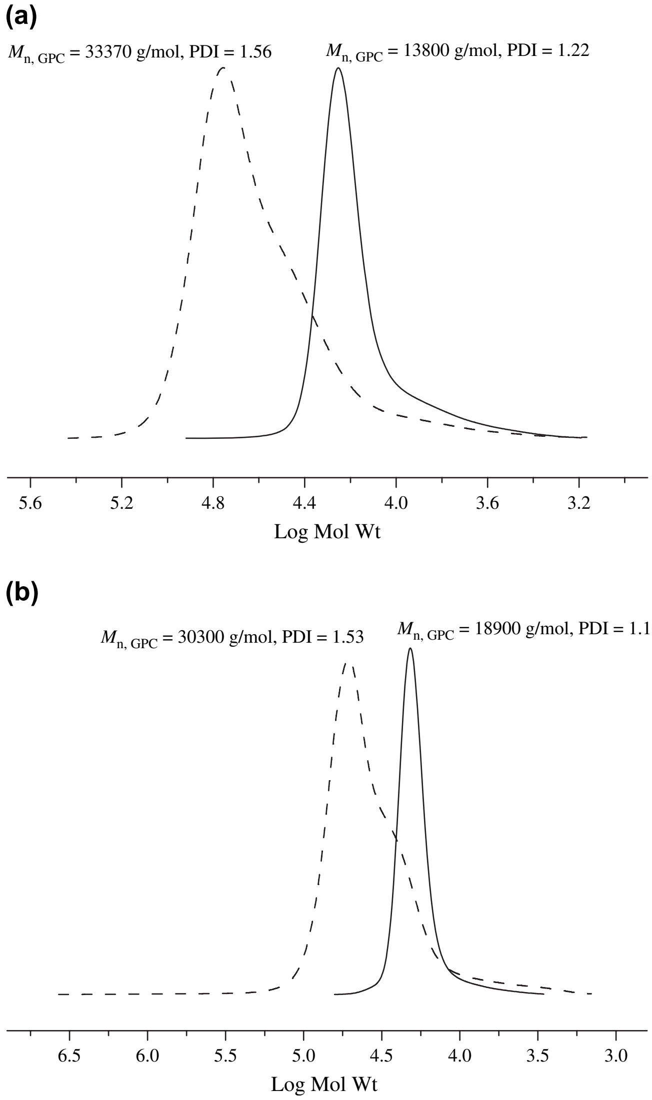


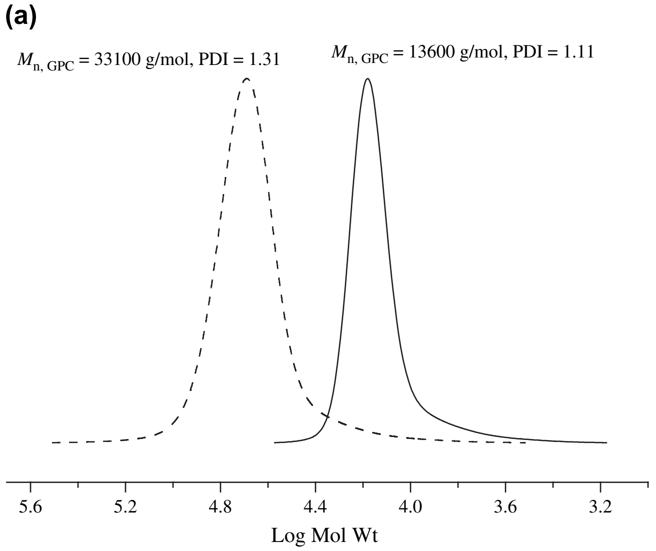
Fig. 6. GPC curves before and after chain extension with PS samples prepared by the oxygenated RAFT polymerization of St as macro-RAFT agent. (a) CPDN–PS: $[St]_0 = 8.74$ mol/L, $[St]_0/[PS]_0 = 1000/1$, 115 °C, 5 h, 26.2% conversion; (b) BPIC–PS: $[St]_0 = 8.74$ mol/L, $[St]_0/[PS]_0 = 1000/1$, 115 °C, 5 h, 28.0% conversion.

found, and there was no observable tail in the chain-extended PS, only larger PDI values of chain-extended PS were observed, which indicated that the fraction of dead polymer chains prepared in the absence of oxygen was lower than that in the presence of oxygen.

3.2. Mechanism of RAFT polymerization of St in the presence of oxygen

The results in this work demonstrated that the RAFT polymerization of St can be accelerated by adding some amount of oxygen. According to our prevenient discussion, there are two probable causes for the rate enhancement in RAFT polymerization at a constant reaction temperature [24]. One is the decrease of RAFT agent concentration, the other is the increase of initiator concentration. It had been proved that the oxygen had no obvious detrimental effects on the RAFT functionality under the experimental conditions [24]. In the present work, blank experiments were also carried out to support this viewpoint. The thermal-initiated polymerization of St at various concentrations of oxygen without RAFT agents added was conducted. The results are presented in Fig. 8.

It can be found from Fig. 8 that the conversion of St at 110 °C increased with the oxygen concentration, which further proved that the slight rate enhancement by oxygen in the polymerization of St was independent of the RAFT agent. Thus, the first possibility should be ruled out from the causes for the rate enhancement [24], and the increase of initiator concentration was considered to be responsible for the rate enhancement. Coming back to Figs. 1 and 2, the presence of oxygen



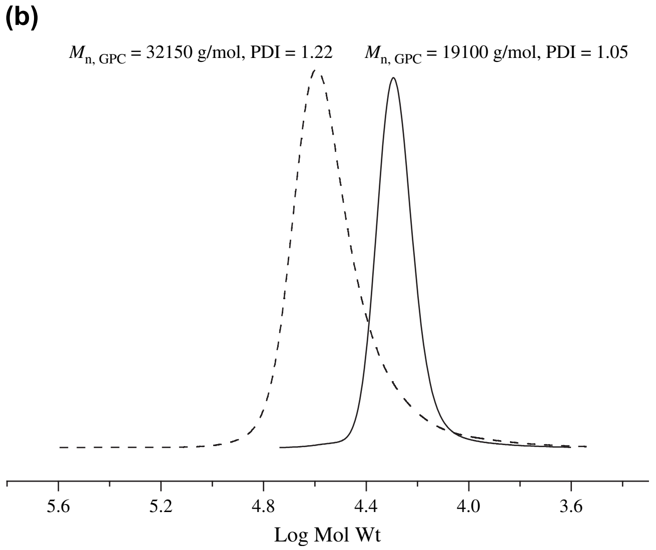


Fig. 7. GPC curves before and after chain extension with PS samples prepared by the deoxygenated RAFT polymerization of St as macro-RAFT agent. (a) CPDN–PS: $[St]_0 = 8.74$ mol/L, $[St]_0/[PS]_0 = 1000/1$, 115 °C, 5 h, 15.6% conversion; (b) BPIC–PS: $[St]_0 = 8.74$ mol/L, $[St]_0/[PS]_0 = 1000/1$, 115 °C, 5 h, 13.4% conversion.

could slightly accelerate the polymerization; it was supposed that the oxygen might be involved in the initiation process. It had been reported that the interaction of St with oxygen could yield PS peroxide (PSP) under the similar experimental conditions with this work, and the rate of absorption of oxygen by St increased with temperature [32,33]. The PSP was also reported to be used as thermal [34] or UV [35] initiator for the polymerization of MMA and St. To confirm it, an iodometric method [29] was used to measure the concentration of PSP in the polymerization. Fig. 9 shows the relationship between the concentration of PSP formed at the earlier stage of the polymerization and oxygen concentration. It was observed that the PSP concentration increased with the oxygen concentration. Therefore, it was deduced that the addition of higher concentration of oxygen produced higher PSP concentration, which joined in the initiation behavior of the polymerization and resulted in the enhanced rate just as those in Figs. 1 and 2. In the present work, the presence of oxygen slightly accelerated the RAFT polymerization of St, whereas, in the MMA polymerization, the rate enhancement by the presence of oxygen was remarkable [24]. This discrepancy between St and MMA could be attributed to the following two reasons. First, it had been revealed that the initiation efficiency of PSP was very low ($f = 0.006–0.014$) [34], which was due to the facile unzipping of the β-peroxyalkoxy radicals formed by the random scission of the peroxy bond in PSP. This unzipping process yielded non-radical products and competed with primary radical initiation, thus reduced the initiator efficiency [34]. Second, it has been well known that St can be thermally autopolymerized at elevated temperature [35]. The spontaneous generation of radicals from the Diels–Alder reaction between two molecules of St was responsible for the initiation behavior of thermal autopolymerization [36]. In the polymerization of MMA, the thermal polymerization rate was rather slow and would take several hours to produce low conversions [37].

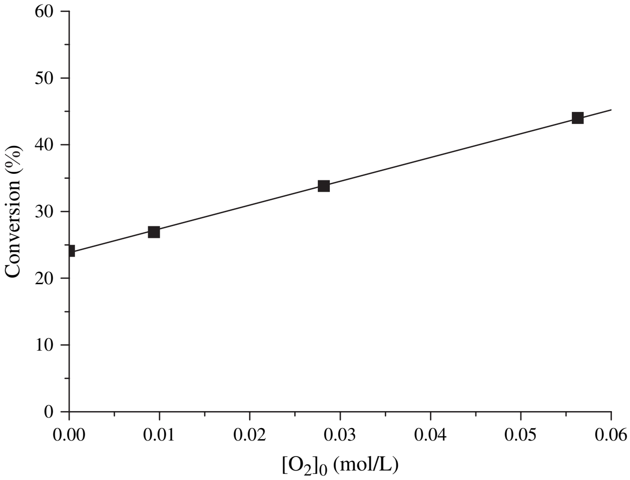


Fig. 8. Evolution of St conversion with oxygen concentration. $[\text{RAFT agent}]_0 = 0$ mol/L, temperature = 110 °C, time = 6 h.

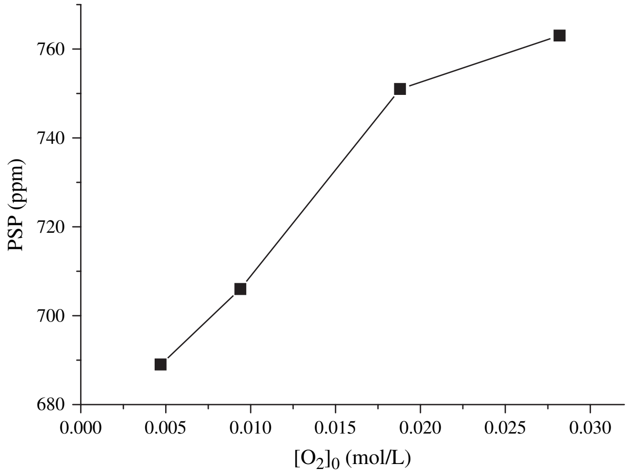
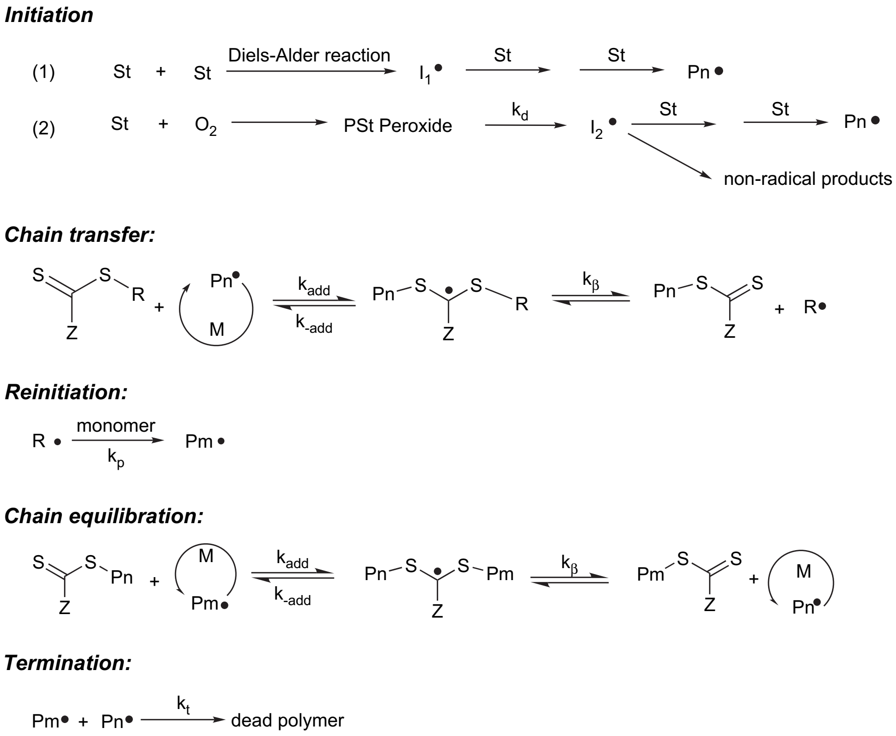


Fig. 9. Evolution of PSP concentration with oxygen concentration.



Scheme 2. Mechanism of the RAFT polymerization of St in the presence of oxygen.

Therefore, for the thermal polymerization of St in the presence of oxygen, the PSP formed *in situ* was an additional initiator besides the spontaneous initiator, the rate enhancement by the PSP was thus unobvious. In the case of MMA, the PMMAP formed *in situ* dominated the initiation behavior; its presence distinctly accelerated the polymerization.

The results of Figs. 3, 4, 6 and 7 indicated that the PDI values of the polymer obtained in the presence oxygen were larger than that obtained in the absence of oxygen. In the foregoing section, we proposed that the larger amount of the initiator consumed should be responsible for the greater PDI values under the oxygenated atmosphere. From the above discussion, the PSP formed in the presence of oxygen could act as the additional initiator. Therefore, the amount of the initiator consumed in the presence of oxygen may be greater than that in the absence of oxygen at the same monomer conversion, which then resulted in larger PDI values. The other reason for the higher PDI values may be due to some of the side reactions in the presence of oxygen, such as the St propagating radicals reacting with the oxygen to form the peroxide radicals, which then disproportionated and gave dead chains [34]. At higher temperature (110 °C), the spontaneous initiators and the formed PSP were much more than that in low temperature (80 °C), therefore, low concentration of RAFT agent (5.83×10^{-3} mol/L) led to a case where the concentration of initiator was higher than the RAFT agent concentration. Some chains in such a system were not adequately regulated through the addition–fragmentation equilibrium, and thus experienced a significant level of radical termination, and a poor control over the development of polymer molecular weight as those in Figs. 3(b) and 4(b) [24]. In conclusion, the thermal-initiated RAFT polymerization of St in the presence of oxygen was similar with the ideal RAFT polymerization except for the initiation source. In this work, the initiator was generated from two sources, one was the Diels–Alder reaction which triggered the thermal autopolymerization, and the other was the PSP formed *in situ* by St and oxygen. The PSP could also initiate the polymerization and influence the polymerization kinetics. The possible mechanism of the polymerization is shown in Scheme 2.

4. Conclusion

The RAFT polymerizations of St mediated by CPDN and BPIC with predetermined amounts of oxygen were performed. The polymerization was accelerated by the presence of oxygen but produced polymers with greater PDI values at the same conversion of monomer in comparison with that obtained in the deoxygenated polymerization. It was deduced that the PSP formed *in situ* by the interaction of St and oxygen could act as an additional initiator besides the thermal autopolymerization of St, which then accelerated the polymerization. The reasons for the higher PDI values in the presence of oxygen may be due to an increase of initiator concentration and some side reactions.

Acknowledgments

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