

Research Article

RAFT Copolymerization of Styrene and Maleic Anhydride with Addition of Ascorbic Acid at Ambient Temperature

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A novel method for RAFT copolymerization of styrene (St) and maleic anhydride (MAh) at ambient temperature using ascorbic acid (Asc) as an initiator is reported. Various experimental conditions including reaction component, monomer composition, the amount of Asc, and temperature were investigated in terms of monomer conversion, molecular weight, and molecular weight distribution. In this system, the copolymer of styrene/maleic anhydride (SMA) with well-regulated molecular weight and low molecular weight distribution ($M_w/M_n = 1.30$) was obtained, and the conversion of monomer was 70.4% after 12 hours at 25°C. The NMR spectra demonstrated that the copolymer synthesized possesses a strictly alternating structure. Furthermore, the proposed mechanism adapted to the RAFT copolymerization of St and MAh initiated by Asc at ambient temperature is presented. Using this new methodology, it is possible to achieve well-defined SMA under mild conditions by RAFT copolymerization.

1. Introduction

Styrene/maleic anhydride copolymer (SMA) and its derivatives have attracted great interest in recent years because they have been widely used as a polymer blend compatibilizer [1], dispersing agent [2], metal ion adsorbent [3], drug carrier [4], and so on. It is well known that the copolymerization of styrene (St) and maleic anhydride (MAh) via conventional radical technique is capable of providing an alternating copolymer easily [5]. However, the copolymers prepared by conventional free radical methods exhibit a strong compositional drift, thus causing the copolymers to have a complicated structure [6]. So studies on the preparation of alternating copolymer of SMA with controlled molecular weight and narrow molecular weight distribution are of great significance not only in the academic fields but also in the industrial fields.

Recently, controlled radical polymerization (CRP) methods, such as nitroxide-mediated polymerization (NMP) [7, 8], atom transfer radical polymerization (ATRP)

[9, 10], and reversible addition-fragmentation chain transfer-mediated polymerization (RAFT) [11, 12], have been developed to the synthesis of well-defined polymers. The advantages of CRP lie in the fact that it would offer a better control of the molar mass and molar mass distribution over the conventional methods. And preparation of copolymer of SMA by CRP has already been employed. However, attempts in the literature [13, 14] have been fruitless to obtain the copolymer of SMA by ATRP mainly due to the poisoning of the Cu catalyst in the polymerization. When the NMP method [15] was used for the copolymerization of St and MAh, it is required to be operated at high temperature (~120°C), which is the upper limit to obtain the alternating copolymer of SMA. The RAFT method was used by Zhu and coworkers [16] in the copolymerization of St and MAh, but the structure of the resulted copolymer SMA was not strictly alternating.

A study [17] shows that St and MAh are tended to form charge-transfer-complex (CTC), and there is an equilibrium

among CTC, St, and MAh. In addition, the manner of copolymerization of St and MAh is determined by the equilibrium constant (K_c). When $K_c < 0.01 \text{ L mol}^{-1}$, the copolymerization occurs in a random rather than in an alternating manner. When $K_c > 0.1 \text{ L mol}^{-1}$, free radical alternating copolymerization can proceed easily. And K_c is related to temperature: K_c is 0.34 L mol^{-1} at the temperature of 22°C whereas K_c is 0 at the temperature of 80°C [5]. It has been discovered that copolymers of SMA with strictly alternating structure may be prepared only when the copolymerization of St and MAh is carried out at low temperature. For example, Wu et al. [18] reported that the copolymerization of St and MAh in the presence of benzyl dithiobenzoate was carried out under gamma radiation at ambient temperature, and the copolymers obtained possess a strictly alternating structure. The same group [19] also demonstrated that the strictly alternating structure of SMA was achieved by the RAFT copolymerization of St and MAh under UV irradiation at ambient temperature.

As described above, RAFT appears to be the best choice for the preparation of strictly alternating structure of SMA with well-controlled molecular weight and narrow molecular weight distribution. Because the K_c is determined by temperature, SMA with a strictly alternating structure may be obtained by performing the copolymerization of St and MAh at low temperature, such as room temperature, but it is also well known that the polymerization rate could be slow at low temperature. Although the dilemma could be solved by employing RAFT polymerization of St and MAh under gamma radiation and UV irradiation, nonetheless, the polymerization method of gamma is rarely used, and the polymerization would become less controlled for the decomposition of RAFT agent under the long exposure to the UV radiation.

Recently, redox-initiated RAFT polymerization technique [20, 21] has been of great interest to polymer chemists due to its many advantages such as low activation energies needed, facile control over the polymerization rate at low temperatures, and high elimination of the side reactions. In order to realize the quick copolymerization of St and MAh and obtain the strictly alternating structure of SMA at room temperature, the redox initiators could be used to initiate the copolymerization of St and MAh. It was reported that the RAFT polymerization could be initiated by the redox system of ascorbic acid (Asc) with peroxide [22]. Surprisingly, the experiment has shown that with the employment of reducing agent Asc only leads to the RAFT copolymerization of St and MAh. Herein, we first study the RAFT copolymerization of St and MAh initiated by Asc at ambient temperature. Subsequently, the influencing factors and the kinetics for the RAFT copolymerization of St and MAh are investigated. The strictly alternating structure of well-defined SMA will be confirmed by NMR spectra. Finally, the proposed mechanism of the RAFT copolymerization of St and MAh initiated by Asc at ambient temperature is presented.

2. Experimental Section

2.1. Materials. Styrene (St) (>99%; China) was passed through a basic alumina column. Maleic anhydride (MAh)

(>99%; China) was recrystallized from benzene. The chain transfer agent (CTA) S-1-dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (DDMAT) was synthesized according to the literature [23]. Ascorbic acid (Asc) and other reagents were of analytical grade and used as received.

2.2. RAFT Copolymerization of St and MAh. A typical procedure of copolymerization of St and MAh in 1,4-dioxane (DO) is as follows: St, MAh, DDMAT, Asc, and DO ([St]: [MAh]: [DDMAT]: [Asc] = 148/148/1/1, $w_{\text{DO}}/w_{\text{monomer}} = 1/1$) were successively added into a round-bottom flask (25 mL). The flask with a magnetic stirring was sealed with a rubber septum. And the mixture was degassed by three freeze-thaw-vacuum cycles. Then, the flask was placed in an oil bath, and the copolymerization was carried out at 25°C for a prescribed time. Finally, SMA was obtained by precipitating from methanol and dried in a vacuum oven at 60°C .

2.3. Characterizations. The monomer conversion was determined gravimetrically. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of SMA were analyzed via Waters 1515 size exclusion chromatography (SEC) equipped with a Waters 2414 refractive-index detector. Two 300×7.8 linear columns of Styragel HR3 and HR4 with a measurable molecular weight range from 5×10^2 to $6 \times 10^5 \text{ g mol}^{-1}$ were used for analysis. Tetrahydrofuran (THF) with a flow rate of 1.0 mL min^{-1} at 40°C was used as the mobile phase. ^1H and ^{13}C NMR spectra of the polymers were performed on a Bruker 500 MHz nuclear magnetic resonance (NMR) instrument using deuterated acetone as solvent and tetramethylsilane (TMS) as the internal reference.

3. Results and Discussion

3.1. Effect of Reaction Component on RAFT Copolymerization of St and MAh Initiated by Asc. Firstly, the experiment of RAFT copolymerization of St and MAh with reducing agent Asc only was carried out. Surprisingly, it was found that in this system the monomer conversion reached about 70.4% after 12 h and the molecular weight distribution of SMA was 1.30 (Entry 6 in Table S1). This indicates that the RAFT copolymerization of St and MAh at room temperature could be initiated by Asc only. The previous observation triggered further experiments to be conducted, so the reaction component in the polymerization system was varied. Without adding DDMAT and Asc, no polymer was obtained (Entry 1 in Table S1). When Asc was absent, it was found that the monomer conversion was only 10.5% after 36 h and the molecular weight distribution of SMA was 1.29 (Entry 4 in Table S1), which was in agreement with a previous report by You and coworkers [24]. The proposed mechanism for copolymerization of St with MAh in the presence of RAFT agent is that St and MAh would be tended to form CTC and then CTC comonomer generates CTC-radicals (CTC \cdot) that could initiate the RAFT polymerization of CTC comonomer [24].

In a previous experiment, no polymer was obtained when no DDMAT was added in the copolymerization system. The

probable reason is that the RAFT agent may stabilize the fewer radicals that could initiate the RAFT polymerization [25]. When adding Asc and without DDMAT, the rate of copolymerization was so quick that the gel was formed only after 1 h and the monomer conversion was 52.7%. In addition, the M_w/M_n was 3.24 (Entry 5 in Table S1). It indicates that the copolymerization was conducted through a conventional free radical polymerization. Furthermore, with both DDMAT and Asc in the system, the copolymerization was carried out successfully in a relatively slower speed than the conventional free radical polymerization. The monomer conversion reached about 70.4% after 12 h, and the M_w/M_n was 1.30 (Entry 6 in Table S1), which indicates that the reaction shows “living” nature. At the same time, experiments were conducted with St or methyl acrylate (MA) in the same polymerization conditions, but no polymer was obtained (Entries 2 and 3 in Table S1).

3.2. Effect of the Monomer Composition on RAFT Copolymerization of St and MAh Initiated by Asc. The polymerizations were conducted at 25°C at different molar ratios of [St]/[MAh], where [St]/[MAh] = 9/1, 3/1, 1/1, 1/3, and 1/9. It is demonstrated that the copolymerization proceeded quite quickly when the initial monomer composition [St]/[MAh] was 1/1 (Entry 3 in Table S2). However, when the initial molar ratio of [St]/[MAh] was raised to 3/1 or 9/1, the conversion of the copolymerization of St and MAh was 13.4% or 15.7%, respectively (Entries 1 and 2 in Table S2). It is worth noting that the homopolymerization of St could not proceed at 25°C in the RAFT copolymerization system with Asc (Entry 2, in Table S1). It may explain that the polymerization could not continue when the MAh was consumed due to consumption of the CTC comonomer while the St could not continue homopolymerization at 25°C, thus leading to the relatively low conversion of the copolymerization of St and MAh when the proportion of St in the monomer feed was high. When the initial molar ratio of [St]/[MAh] was reduced to 1/3 or 1/9, oligomer was obtained only (Entries 4 and 5 in Table S2). And the monomer conversion could not be obtained because the oligomers were soluble in methanol. Du et al. [26] used electron spin resonance (ESR) spectroscopy to study the RAFT copolymerization of St and MAh, and they pointed out that the excess of MAh in the copolymerization system would result in the formation of oligomer because of MAh at the end of propagating radical that could not polymerize in this condition.

3.3. Effect of the Amount of Asc on RAFT Copolymerization of St and MAh Initiated by Asc. The dose of initiator would affect the rate and the controllability of polymerization in thermally initiator-activated RAFT [27]. So the effect of the amount of Asc on RAFT copolymerization system was investigated. The copolymerizations were conducted at 25°C at the initial molar ratios of [St]/[MAh]/[DDMAT] = 148/148/1. In view of the low solubility of Asc in DO, the amount of Asc was varied from 0.25 to 1.0 equivalents of DDMAT. When the amount of Asc was 0.25 equivalents of DDMAT, the monomer conversion was only 17.4% after 12 h (Entry 1 in

Table S3). In contrast, when the amount of Asc was 1.0 equivalents of DDMAT, the monomer conversion reached about 69.6% after 12 h (Entry 4 in Table S3). It is demonstrated that the copolymerization rate has significantly increased with the increase of the amount of Asc. When the amount of Asc was increased from 0.25, 0.50, and 0.75 to 1.0 equivalents of DDMAT, the conversion increases gradually whereas the molecular weight distribution is still about 1.30 (Entries 2 and 3 in Table S3), indicating that the reactions are controllable.

3.4. Effect of the Temperature on RAFT Copolymerization of St and MAh Initiated by Asc. The effect of the temperature on RAFT copolymerization system was also investigated. Copolymerizations were carried out with the initial molar ratios of [St]/[MAh]/[DDMAT]/[Asc] = 148/148/1/1, and the temperature was varied from 25, 30, and 35 to 40°C. The results are summarized in Table S4. The results show that the monomer conversion was 43.2% after 8 h at 25°C, and the monomer conversion reached about 65.5% after 8 h at 40°C (Entries 1 and 4 in Table S4). It demonstrates that the rate of polymerization enhances with the increase of temperature. Possible explanation for the rate enhancement with the temperature is that the rate coefficients of yielding radicals and propagating radicals would be enhanced with the increase of temperature [28]. The molecular weight distributions of obtained SMA are about 1.30. It indicates that the reactions are controllable in a broader range of temperature.

3.5. Polymerization Kinetics. The copolymerization kinetics of St and MAh initiated by Asc were investigated with the initial molar ratios of [St]/[MAh]/[DDMAT]/[Asc] = 148/148/1/1 in DO solution at 25°C. Figure 1(a) shows that the increase in monomer conversion over the polymerization time indicates a pseudo-first-order kinetic polymerization process after the induction period. Figure 1(b) shows the evolution of the M_n and M_w/M_n with conversion. It can be observed that the molecular weight of the polymer obtained increases linearly with monomer conversion, while the molecular weight distributions are low (<1.34). The increase in M_n with monomer conversion is in a satisfactory agreement with theory. The SEC evolutions of SMA at different time intervals during the copolymerization are displayed in Figure 2. In Figure 2, the SEC traces of SMA were less symmetrical and some tailing on the low molar mass side was observed. These features can be assigned to the decrease in the chain transfer constant of the polymeric RAFT agent, most probably due to the relatively high apparent rate constant of propagation when the proportion of MAh was 0.5. This is consistent with the results reported by Chernikova et al. [29].

3.6. Copolymer Structure. Figure 3 is the ¹H NMR spectrum of the SMA prepared by RAFT copolymerization of St and MAh initiated by Asc at room temperature. It has been reported that the methylene peak of St homopolymer appears at $\delta = 1.16$ – 1.63 [18]. In this range, there is only a relatively weak signal appearing in Figure 3, and the weak signal at $\delta = 1.3$ (d in Figure 3) is attributed to the methine protons of

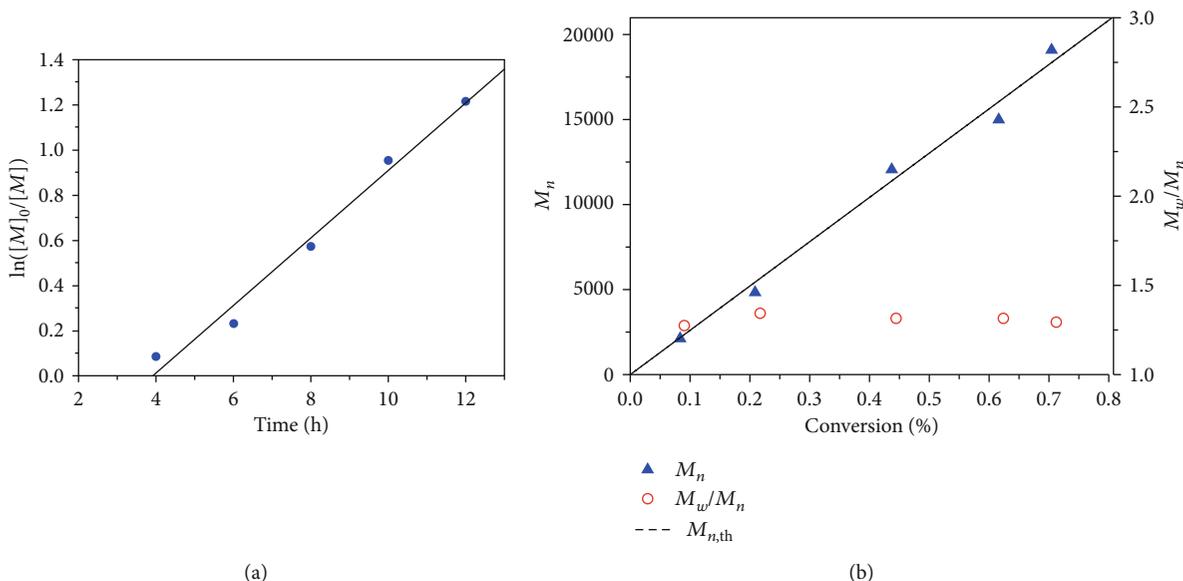


FIGURE 1: (a) $\ln([M]_0/[M])$ as a function of time for the RAFT copolymerization of St and MAh initiated by Asc. (b) Number-average molecular weight (M_n) and molecular weight distributions (M_w/M_n) versus conversion for the RAFT copolymerization of St and MAh initiated by Asc. Polymerization conditions: $[St]/[MAh]/[DDMAT]/[Asc] = 148/148/1/1$ ($[DDMAT] = 0.1$ mmol), $DO/monomer = 1/1$ (w/w), $T = 25^\circ C$.

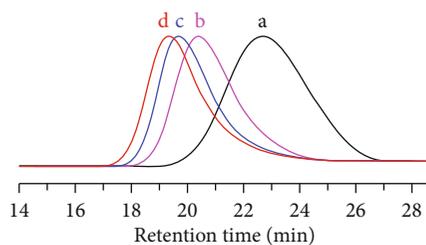


FIGURE 2: SEC traces of SMA synthesized via RAFT copolymerization of St and MAh initiated by Asc. Polymerization conditions: $[St]/[MAh]/[DDMAT]/[Asc] = 148/148/1/1$ ($[DDMAT] = 0.1$ mmol), $DO/monomer = 1/1$ (w/w), $T = 25^\circ C$. (a: 6 h, $M_n = 4900$, $M_w/M_n = 1.34$; b: 8 h, $M_n = 12100$, $M_w/M_n = 1.32$; c: 10 h, $M_n = 15000$, $M_w/M_n = 1.32$; d: 12 h, $M_n = 19100$, $M_w/M_n = 1.30$).

dodecyl CTA part. In fact, the presence of MAh in the structure of copolymer shifts the signals of St aliphatic protons to higher ppm values in comparison to the St homopolymer. So the methylene and methine protons of St unit appear at $\delta = 1.63\text{-}3.0$ (a in Figure 3). The signal at $\delta = 6.1\text{-}7.7$ (c in Figure 3) corresponds to the aromatic protons of St unit, and the peaks at $\delta = 3.1\text{-}3.8$ ppm (b in Figure 3) are ascribed to the methine protons of MAh unit. In addition, the signal at 0.88 ppm (e in Figure 3) indicates the existence of the methyl group from the CTA in the polymer chain. Figure 4 is the ^{13}C NMR spectrum of the SMA prepared by RAFT copolymerization of St and MAh initiated by Asc at room temperature. In Figure 4(a), the carbon resonances of SMA were assigned to the chemical shifts according to Butler et al. [30]. Figure 4(b) shows a local map of ^{13}C NMR spectrum of SMA, and it exhibits a main peak between 136 and 140 ppm related to the alternating MAh-St-MAh triad.

Moreover, as shown in Figure 4(a), no peak corresponding to MAh-St-St or St-St-St triads appears between 142 and 145 ppm [25]. For further verification, FTIR spectroscopy was performed. The FTIR spectra of SMA are shown in Figure S1. Based on the sum of FTIR absorption intensities for MAh (1854 , 1780 , and 1225 cm^{-1}) and St (706 , 760 , 1495 , 1450 , and 3032 cm^{-1}), it confirms the existence of the MAh group and St group at the SMA.

3.7. Proposed Polymerization Mechanism. Asc, also known as vitamin C, is a reducing agent, which widely existed in the natural plant. Asc together with peroxide acting as a redox initiator for radical polymerization has been studied for a long time [31, 32]. However, RAFT copolymerization of St and MAh was conducted only in the presence of reducing agent Asc; then, the initiating mechanism in this system may be different from the redox initiation for radical polymerization with oxidising agent/reducing agent. Misra and Gupta [33] employed the redox system $K_2S_2O_8/Asc$ as initiators for polymerization of methacrylamide under the influence of atmospheric oxygen. And they pointed that Asc could generate free radicals automatically in the presence of oxygen. The mechanism for the autoxidation of Asc is shown in Scheme 1. In this work, all experiments were carried out degassed through a three-way stopcock under nitrogen flow. Besides, the monomer of St or MA cannot be polymerized by Asc in the presence of DDMAT. So it demonstrates that the free radicals which initiated the copolymerization of St and MAh could not come from the autoxidation of Asc.

Kuramoto et al. [34] reported that the copolymerization of St with MAh could be initiated by Asc alone. And the experiment showed that no polymer was obtained when either the Asc or the MAh monomer was absent. They concluded that the initiation mechanism involved the formation

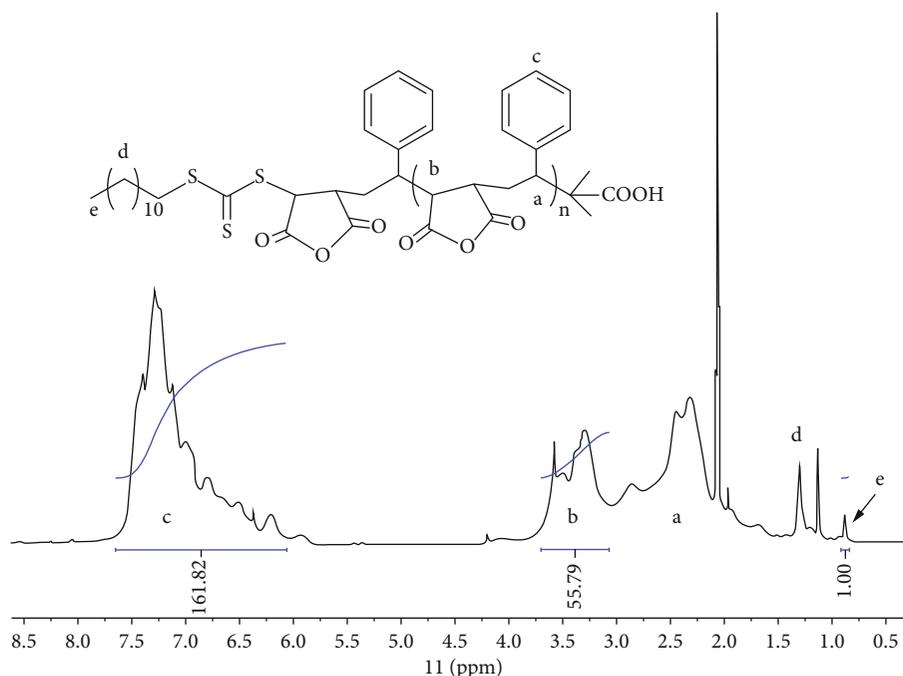


FIGURE 3: ^1H NMR spectrum of SMA ($M_n = 19100$, $M_w/M_n = 1.30$) obtained from RAFT copolymerization of St and MAh initiated by Asc. Polymerization conditions: $[\text{St}]/[\text{MAh}]/[\text{DDMAT}]/[\text{Asc}] = 148/148/1/1$ ($[\text{DDMAT}] = 0.1$ mmol), DO/monomer = 1/1 (w/w), $T = 25^\circ\text{C}$, 12 h.

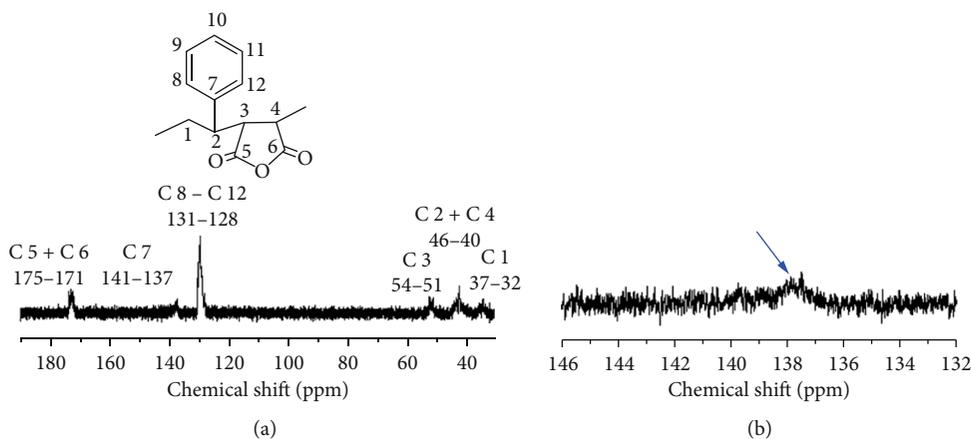


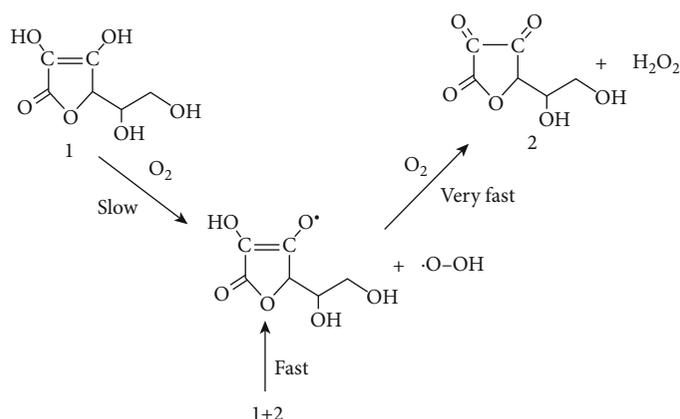
FIGURE 4: (a) ^{13}C NMR spectrum of SMA ($M_n = 19100$, $M_w/M_n = 1.30$) obtained from RAFT copolymerization of St and MAh initiated by Asc. (b) The local map of ^{13}C NMR spectrum of SMA ($M_n = 19100$, $M_w/M_n = 1.30$) obtained from RAFT copolymerization of St and MAh initiated by Asc. Polymerization conditions: $[\text{St}]/[\text{MAh}]/[\text{DDMAT}]/[\text{Asc}] = 148/148/1/1$ ($[\text{DDMAT}] = 0.1$ mmol), DO/monomer = 1/1 (w/w), $T = 25^\circ\text{C}$, 12 h.

of a CTC between Asc and MAh, which broke down to liberate the initiating radicals. Based on the report and the experiments discussed above, a proposed mechanism for the RAFT copolymerization of St and MAh is illustrated in Scheme 2. Firstly, a charge-transfer-complex (CTC_1) is generated from Asc and MAh, and another charge-transfer-complex (CTC_2) comonomer is generated from St and MAh. The initiation radicals are produced via homolytic cleavage of CTC_1 which called CTC_1^\cdot . The radical CTC_1^\cdot initiates the polymerization of CTC_2 comonomer to form a propagating radical (P_n^\cdot) (step 1). Then the propagating radical P_n^\cdot reacts with the RAFT agent 1 to form the radical adducts as intermediate 2 which can fragment to yield a

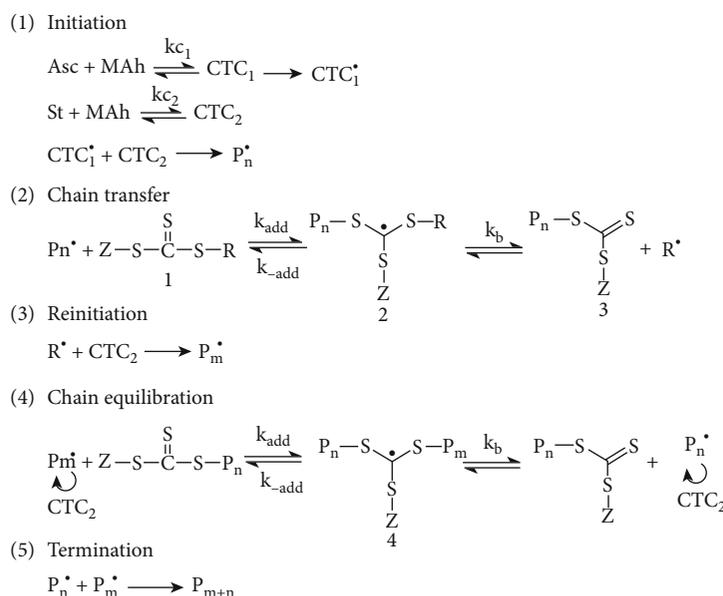
RAFT agent 3 and a reinitiating radical (R^\cdot) (step 2). Following initialization, polymer chains grow by adding a comonomer to generate a new propagating radical (P_m^\cdot) (step 3) and then rapidly exchange between the growing radicals and the thiocarbonylthio group capped species 4 (step 4). A rapid equilibrium between active and dormant chains is established, so the copolymerization of St with MAh proceeds in the RAFT process.

4. Conclusions

RAFT copolymerization of St and MAh has been successfully performed at ambient temperature initiated by the reducing



SCHEME 1: The mechanism for the autoxidation of Asc.



SCHEME 2: Proposed mechanism for the RAFT copolymerization of St and MAh initiated by Asc at room temperature.

agent only, i.e., Asc. The results show that the rate of RAFT copolymerization was significantly affected by the initial comonomer composition. Copolymerization proceeded quite quickly when the initial monomer composition [St]/[MAh] was 1/1 whereas the conversion of the copolymerization of St and MAh was lower when the molar ratio of [St]/[MAh] was 3/1 or 9/1 and only an oligomer was obtained when the molar ratio of [St]/[MAh] was 1/3 or 1/9. It was also demonstrated that the increase of either the Asc concentration (<1.0 equivalents of DDMAT) or the temperature (<40°C) would lead to an increased rate of copolymerization while maintaining molar mass control and low molar mass distributions. Kinetic studies indicate that RAFT copolymerizations proceed with an apparent “living” character, deduced from the linear increase in molar mass with monomer conversion and narrow molar mass distribution. And the NMR spectra demonstrated that the copolymers obtained possess a strictly alternating structure. We have

developed a new method for RAFT polymerization of St and MAh at ambient temperature using Asc as an initiator, which allows facile synthesis of a well-defined and strictly alternating structure of the relatively low molecular weight SMA. And the relatively low molecular weight SMA could be used as a surfactant, compatibilizer, interface modifier, adhesive, or sizing agent in paper industry [35].

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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Supplementary Materials

Table S1: effect of the reaction component on the RAFT copolymerization of St and MAh at 25°C. Table S2: effect of the monomer composition on the RAFT copolymerization of St and MAh at 25°C. Table S3: effect of the amount of Asc on the RAFT copolymerization of St and MAh at 25°C. Table S4: effect of the temperature on the RAFT copolymerization of St and MAh. Figure S1: FTIR spectrum of SMA obtained from RAFT copolymerization of St and MAh initiated by Asc. (*Supplementary Materials*)

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