

RAFT Polymerization of Styrene with Potassium Ethylxanthate as the Chain Transfer Agent

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Abstract: Using potassium ethylxanthate as the chain transfer agent, 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator, reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene was carried out. The influences of reaction temperature, reaction time, and the amounts of the initiator and chain transfer agent on the RAFT polymerization were investigated in terms of monomer conversion, average number molecular weight (M_n) and molecular weight distribution (\mathcal{D}) of the obtained polymer. Monomer conversion and the M_n of the obtained polystyrene (PS) improved with an increase in the reaction temperature, and the polymerization kinetics exhibited a highly linear relationship, indicating a first-order reaction. When the amounts of the initiator and chain transfer agent were increased, it led to a decreased M_n of the produced PS. Meanwhile, the \mathcal{D} of the PS was in a relatively narrow range (1.42-1.89). The chain-end functionality was further demonstrated by adding methyl methacrylate to the PS.

Keywords: Potassium ethylxanthate, Styrene, RAFT, Molecular weight, Chain-end functionality.

1. INTRODUCTION

Since Rizzardo proposed reversible addition-fragmentation chain transfer (RAFT) polymerization in 1998 [1], RAFT polymerization has attracted much attention because of its advantages of both radical and active polymerization. The polymerization conditions are mild, the application range is wide, and it has unique advantages in the preparation of narrow molecular weight polymers and the design of polymer molecular structure, such as linear [2,3], brush [4-6], block [7,8], film [9], star [10-12] and hyperbranched polymers [13-15]. Common agents for RAFT include macromonomer and thiocarbonylthio compounds (such as dithioesters, trithiocarbonates, dithiocarbamates, and xanthates) [16,17]. The efficacy of a RAFT agent [ZC(=S)S-R] is strongly affected by the properties of the radical leaving group R and group Z, which can be selected to activate or deactivate thiocarbonyl double bonds and to alter the stable free radicals of the intermediate and the monomers that are polymerized. Among them, dithioesters and trithiocarbonates are suitable for the polymerization of "more activated" monomers (MAM, such as styrene, acrylate and methacrylate), while xanthates and dithiocarbamate are suitable for the polymerization of "less active" monomers (such as vinyl acetate [18] and n-vinyl pyrrolidone). The latter tends to provide less or poorer control over the polymerization of MAMs [19]. Among the RAFT agent, xanthates showed a lower chain transfer constant during the polymerization. For instance, the chain transfer constant of styrene is in the range of 0.6~2.0 in the

presence of xanthate, whereas the exchange constant (C_{ex}) of styrene in polystyryl dithioacetate via RAFT polymerization is in the range of 4000~8000 [20,21]. Because a chain transfer constant is strongly associated with substituent Z and leaving group R of the xanthate, a proper xanthate should be selected to carry out RAFT polymerization of styrene. It is difficult to achieve copolymerization between various vinyl monomers, such as styrene and methyl methacrylate (MMA), with other methacrylates via xanthate RAFT polymerization. It has been reported that a Z group with an electron-withdrawing substituent enhanced the activity of the RAFT agent, and the substituent, which rendered the oxygen lone pair less available for delocalization with C=S, substantially improved the efficacy of xanthate [22]. Low polydispersities of approximately 1.4 and 2.0 of the produced polystyrene were obtained when using o-trifluoroethyl xanthate and o-ethyl xanthate [23] as the RAFT agent, respectively, which produced a distinct improvement in the first generation of the RAFT agent. To our knowledge, directly utilizing xanthate of metal salts as a chain transfer agent in RAFT polymerization has not been reported thus far. In this study, potassium ethylxanthate in ethanol was employed as a chain transfer agent for the bulk RAFT polymerization of styrene. We investigated the polymerization kinetics and the influences of the polymerization time, reaction temperature, and amount of initiator and chain transfer agent on the polymerization behavior in terms of monomer conversion, average number molecular weight (M_n) and molecular weight distribution ($\mathcal{D} = M_w/M_n$) of the obtained polystyrene (PS).

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2. EXPERIMENTAL

2.1. Materials

Styrene [St, chemically pure (CP)], anhydrous tetrahydrofuran [THF, analytical reagent (AR)], methanol (AR), and methyl methacrylate (MMA, CP) were all purchased from the Xilong Chemical Plant in Shantou, Guangdong Province (China). THF was used as received. Potassium ethylxanthate (AR) was received from Aladdin Industrial Corporation (Shanghai, China). Anhydrous ethanol was purchased from Guanghua Scientific Co. (Guangdong Province, China). 2,2'-azobis(isobutyronitrile) (AIBN, AR) was purchased from the Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China) and recrystallized with anhydrous ethanol before use in order to remove the impurity. St was purified by passing through a column filled with potassium carbonate, silica oxide and aluminum oxide to remove hydroquinone before use. MMA was washed with 10% NaOH solution and deionized water, and vacuum distilled before use in order to remove inhibitor hydroquinone in the monomer.

2.2. RAFT Polymerization of St and MMA

Typically, potassium ethylxanthate (16.2 mg, 0.13 mmol, dissolved in anhydrous ethanol), St (4.9 g) and AIBN (8.2 mg, 0.05 mmol) were added into a 100 mL well-dried three-necked round bottom flask in a nitrogen atmosphere. After reaction at 80°C for 4h, the obtained polymer mixture was dissolved in 20 mL THF and precipitated from 150 mL methanol three times to completely remove the rest of the monomer. The precipitate was filtered and dried under vacuum at 50 °C until it reached a constant weight.

For further verification of the chain end functionality of the PS, MMA was introduced into the polymer mixture after the abovementioned experiment, and then was reacted at 80 °C for 2 h. The PS-*b*-PMMA copolymer was treated as mentioned above.

2.3. Characterization and Determination

The monomer conversions (Conv.) were calculated according to equation (1), where W_{PS} , W_{CTA} , and W_M represent the weights of the PS, the chain transfer agent of potassium ethylxanthate and the monomer, St, respectively.

$$\text{Conv.(\%)} = (W_{PS} - W_{CTA}) / W_M \times 100\% \quad (1)$$

The theoretical molecular weight ($M_{n,th}$) was calculated via equation (2). In equation (2), $[M]_0$ and $[CTA]_0$ represent the initial concentrations of the monomer and the chain transfer agent, respectively, and M_M and M_{CTA} represent the molecular weight of the monomer and the chain transfer agent, respectively.

$$M_{n,th} = [M]_0 / [CTA]_0 \times \text{Conv.} \times M_M + M_{CTA} \quad (2)$$

Chain transfer agent: $C_3H_5OS_2K$ (M_{CTA} : 160.3),
Monomer: $CH_2=CH(C_6H_5)$ (M_M : 104)

The M_n and \bar{D} of the polymers were determined using a gel permeation chromatograph (GPC, Malvern Model 270, Malvern Co. UK) equipped with a T6000 microstyragel columns, refractive detector, light scattering detector and viscosimeter detector, and THF was used as an eluent at a flow rate of 1.0 ml·min⁻¹. FT-IR spectra were obtained on a Nicolet-205 Fourier transform infrared spectrometer. Hydrogen nuclear magnetic resonance (¹H-NMR) spectra were obtained on an Avance 500 MHz spectrometer (Bruker, Switzerland) using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. The thermal decomposition of the polymers was examined by means of thermogravimetry analysis (TGA) with a heating rate of 10 K/min in nitrogen atmosphere on a TA Q500 (USA).

3. RESULTS AND DISCUSSION

3.1. FT-IR Spectrum

The structure of the obtained PS using potassium ethylxanthate as the chain transfer agent for the RAFT polymerization of St was confirmed by the FT-IR spectrum. The strong peaks at 3059 and 3025 cm⁻¹ were attributed to C-H stretching vibrations of the benzene ring on PS side chain. The strong absorption peaks at 2922 and 2848 cm⁻¹ were assigned to C-H stretching vibrations on the PS main chain. Moreover, the signals at 1601, 1493, and 1452 cm⁻¹ originated from absorption of the C-C skeleton of the benzene ring. The absorption peaks of 756 and 697 cm⁻¹ were attributed to a mono-substituted benzene ring in PS. The weak absorbance at 1068 and 905 cm⁻¹ represented the C=S and C-S stretching vibrations on the chain end, respectively.

3.2. ¹H NMR Spectrum of the Produced PS

Figure 2 shows the ¹H NMR spectrum of the PS obtained from RAFT polymerization via the typical procedure. The peaks with chemical shifts at 6.35 ~

7.20 ppm were assigned to the protons on the benzene ring, and the peaks with chemical shifts at 0.85 ~ 1.47 and 1.60 ~ 2.20 ppm were attributed to the protons from methylene and methine on the main chain, respectively [24]. Meanwhile, the peaks with chemical shifts at 0.8 ~ 1.0 ppm were assigned to the hydrogen from methyl on the potassium ethylxanthate, and the peaks with chemical shifts between 5.0 ~ 5.25 ppm were attributed to the protons from methylene. Peaks for methyl and methylene bonding with the C(=S)-S group were present in the $^1\text{H-NMR}$ spectrum, which is consistent with the FT-IR results, indicating that the produced PS contains C(=S)-S in the chain end.

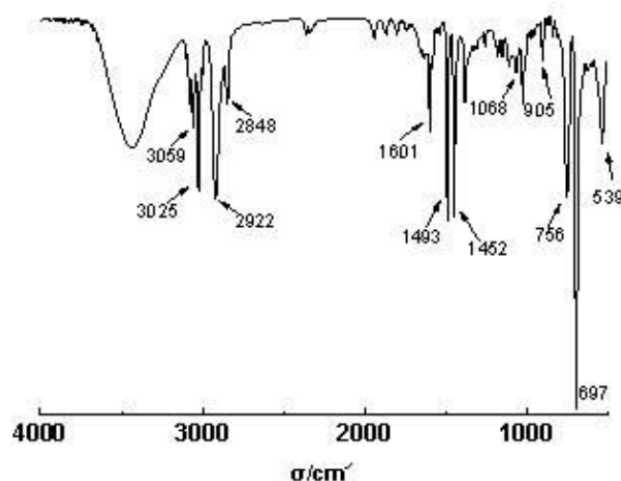


Figure 1: FT-IR spectrum of the obtained PS.

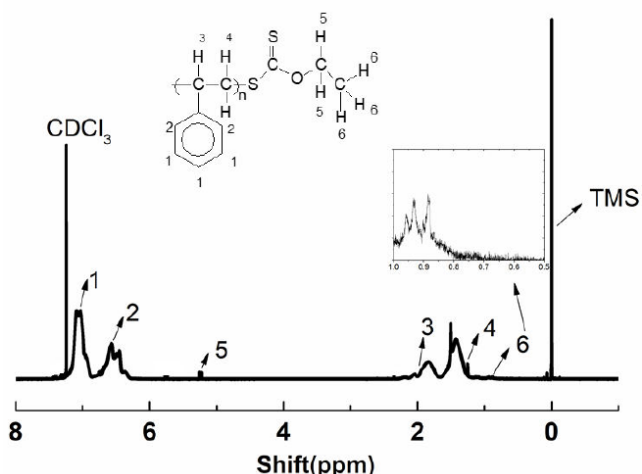


Figure 2: ^1H NMR spectrum of the obtained PS.

3.3. Effect of Reaction Time on the Polymerization

RAFT polymerization of St was conducted at 80 °C for different reaction times, and the monomer conversion and M_n of the obtained PS are shown in Table 1. When the reaction time was prolonged from

0.5 to 12 h, the monomer conversion and M_n linearly increased. Figure 3a shows a highly linear relationship in the plots of $\ln(M_0/M)$ versus polymerization time, indicating that the polymerization kinetics suggested a first-order reaction. Meanwhile, the molecular weight distribution (\mathcal{D}) was in the range of 1.42~2.13 as shown in Table 1. The \mathcal{D} was irregular during the first four hours, and afterwards, the \mathcal{D} increased with an increase in reaction time. Moreover, the M_n increased approximately linearly with the monomer conversion for all the polymerizations. Thus, the polymerization kinetics and the relationships between M_n and monomer conversion confirmed that our system featured a controlled polymerization. In addition, all the measured M_n were higher than the theoretical values at approximately 10 and 4 times higher at the lowest and at the highest conversions, respectively, because the efficiency of the initiator and the chain transfer agent for the RAFT polymerization in the theoretical molecular weight formula were ignored (1). Zhu *et al.* [24] performed living/controlled free radical polymerization using bis(thionaphthoyl) disulfide as a source of the RAFT agent and found that the M_n was higher than the theoretical value. Destarac *et al.* [25] reported that the M_n was four times the theoretical value when in low conversion with different substituents of Z for the RAFT polymerization of ethyl acrylate, and they also found a difference between the M_n and theoretical value when PS was synthesized in low conversion [26]. These results are consistent with our results, which displayed a higher M_n compared with the theoretical value.

Additionally, GPC traces of PS obtained for polymerization times from 1 to 12 h are shown in Figure 4. It clearly shows that prolonging the reaction time contributes to a higher M_n . Among them, formation of a shoulder at high molecular weight (samples 1, 2 and 4 h) may be due to the shorter reaction time and slightly unstable reaction, resulting in a shorter part of the polymer chain.

3.4. Effect of Reaction Temperature on the Polymerization

RAFT polymerization of St was performed at different temperatures for 4 h. The monomer conversion and M_n are listed in Table 2. With an increase in the reaction temperature, monomer conversion and the M_n of the PS increased, whereas the molecular weight distribution did not significantly change as shown in Figure 5. The activity of the system and the number of free radicals increased

Table 1: Effect of Reaction Time on the RAFT Polymerization

Reaction time h	Monomer conv. %	$M_n \times 10^4$	$M_w \times 10^4$	\bar{D}
1	11.7	5.5	7.8	1.42
2	20.6	6.0	9.6	1.60
4	35.8	7.7	11.1	1.44
8	56.0	11.0	20.4	1.85
12	74.7	13.5	28.8	2.13

Polymerization conditions: $[St]_0/[CTA]_0/[AIBN]_0 = 470/1.3/0.5$, $T = 80^\circ\text{C}$.

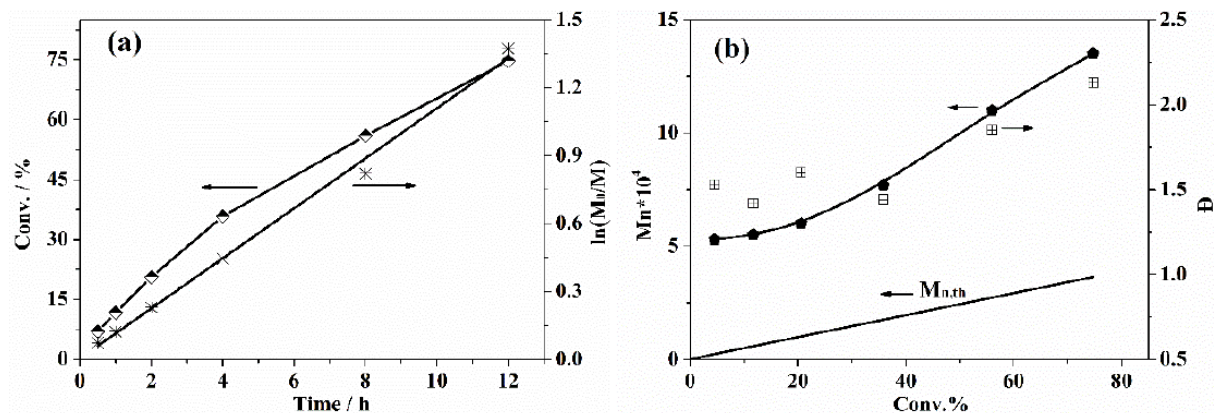


Figure 3: Correlation of reaction time with monomer conversion (a), M_n , and \bar{D} (b).

leading to chain growth acceleration. Free radicals could form dormant intermediates with the chain transfer agents. When excess dormant intermediates are produced, the system cannot maintain a low and stable radical concentration, resulting in high monomer conversion and M_n . When the temperature rose from 65°C to 85°C , the M_n of PS increased from 5.8×10^4 to 8.9×10^4 g/mol, and the monomer conversion increased from 14% to 44.4%, respectively. The molecular weight

distributions were in the range of 1.44~1.77. This result is consistent with the literature in which Patel *et al.* [27] applied xanthate with different structures as chain transfer agents for obtaining PS with molecular weight distributions in the range of 1.05~1.90 at various temperatures (40, 60 and 80°C).

3.5. Effect of Initiator Concentration on the Polymerization

A series of RAFT polymerizations was conducted with various initiator concentrations (based on monomer weight) at 80°C for 4 h, and the results are shown in Table 3. When the monomer conversion was increased, the M_n of the PS decreased, whereas the \bar{D} did not obviously change with an increase in initiator content as shown in Figure 6. The initiator was decomposed to primary active species and then to the initiated monomer to form monomer active species. Therefore, the amount of the primary active species was increased with an increase in the initiator content, resulting in an increased collision of free radicals, formed more propagating radicals. Finally, the C=S double bond of potassium ethylxanthate reacted with the propagating radicals to produce PS, which we confirmed from FT-IR and ^1H NMR.

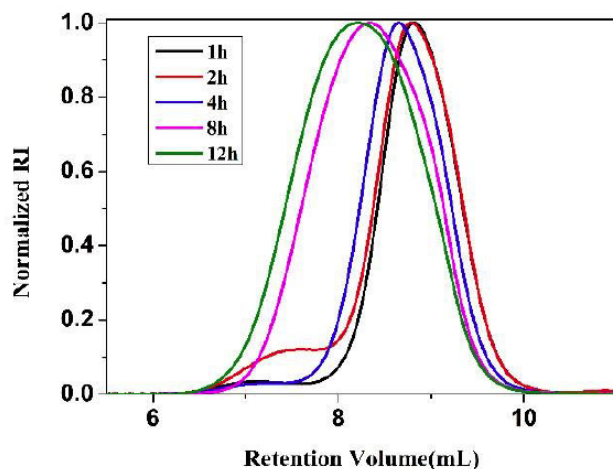


Figure 4: GPC curve of the PS for different polymerization times.

Table 2: Effect of Reaction Temperature on the RAFT Polymerization

Reaction Temp. °C	Monomer conv. %	$M_n \times 10^4$	$M_w \times 10^4$	\mathcal{D}
65	14.0	5.8	9.3	1.60
70	30.0	7.3	12.9	1.77
75	34.9	7.5	11.6	1.55
80	35.8	7.7	11.1	1.44
85	44.4	8.9	15.0	1.69

Polymerization conditions: $[St]_0/[CTA]_0/[AIBN]_0 = 470/1.3/0.5$, $t = 4$ h.

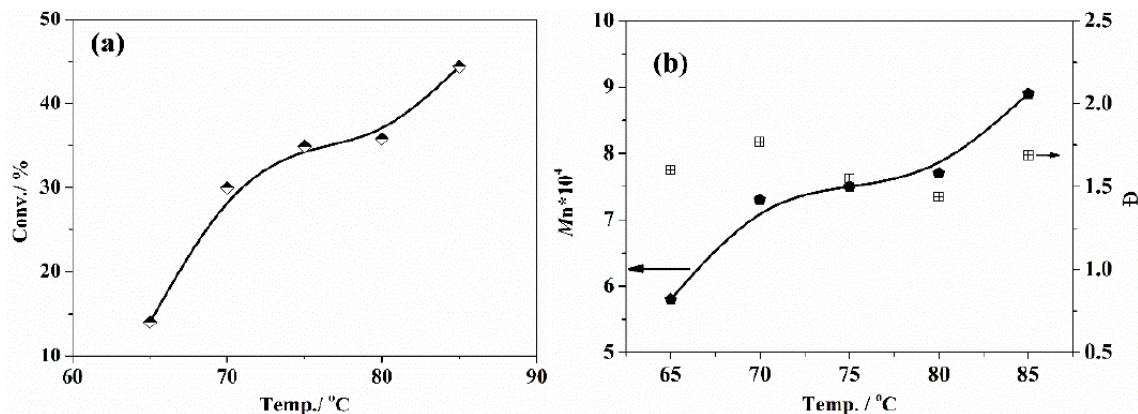
Figure 5: Correlations of reaction temperature with monomer conv. (a), M_n and \mathcal{D} (b).

Table 3: Effect of the Initiator Content on the RAFT Polymerization

AIBN content ^a /%	Monomer conv. /%	$M_n \times 10^4$	$M_w \times 10^4$	\mathcal{D}
0.8	30.6	11.3	21.4	1.89
1.7	35.8	7.7	11.5	1.49
2.5	54.3	7.0	11.1	1.59
3.3	56.2	6.4	10.5	1.64
4.9	57.9	5.9	9.1	1.54

Polymerization conditions: $[St]_0 = 47$ mmol, $[CTA]_0 = 0.13$ mmol, $T = 80$ °C, $t = 4$ h. ^a based on monomer weight.

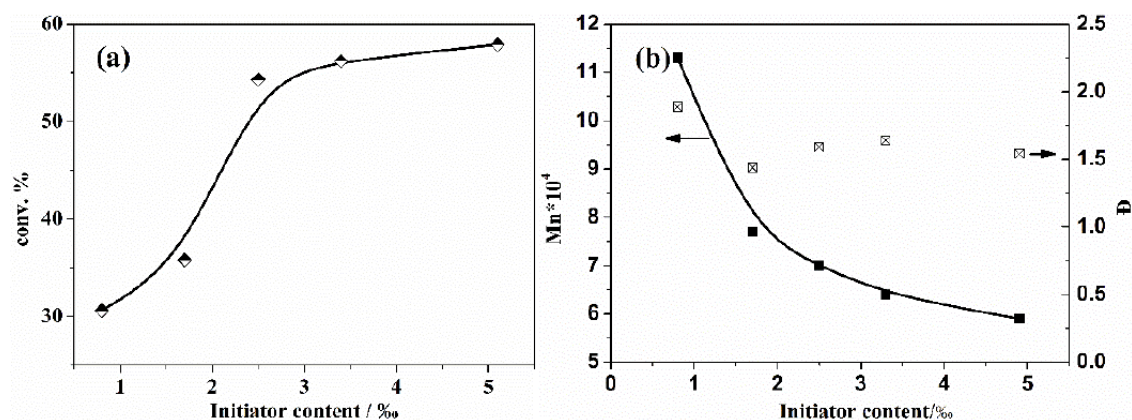
Figure 6: Correlations of initiator concentration with monomer conversion (a), M_n and \mathcal{D} (b).

Table 4: Effect of the Chain Transfer Agent Concentration on the RAFT Polymerization

Potassium ethylxanthate content ^a /%	Monomer conv./%	$M_n/\times 10^4$	$M_w/\times 10^4$	\bar{D}
0	40.1	10.4	14.8	1.42
0.08	39.5	10.0	13.0	1.30
1.7	40.7	8.8	13.2	1.50
3.3	35.8	7.7	11.1	1.44
4.9	42.3	7.4	12.8	1.73

Polymerization conditions: $[St]_0 = 47$ mmol, $[AIBN]_0 = 0.05$ mmol, $T = 80$ °C, $t = 4$ h.^a based on monomer weight.

3.6. Effect of the Chain Transfer Agent Concentration on the RAFT Polymerization

RAFT polymerization of St was conducted with various concentrations of the chain transfer agent at 80 °C for 4 h, and the results are listed in Table 4. The M_n of the PS decreased with increasing chain transfer agent content, as shown in Figure 7, because the increase in the chain transfer agent content contributed to the increase in molecular chain segmentation, leading to a low M_n for the obtained PS. When the chain transfer agent content was increased from 0.1 to 4.9%, the M_n of PS decreased from 10.0×10^4 to 7.4×10^4 g/mol, whereas the molecular weight distribution was in the range of 1.30~1.73. Destarac *et al.* [26] employed eight xanthates with a general structure of R-A(C=A)- as RAFT agents and obtained a molecular weight distribution of 1.94~2.41 for the produced PS, which is a broader range than we obtained. Therefore, potassium ethylxanthate as a RAFT agent is superior to other xanthates with different Z groups. Additionally, monomer conversion was not considerably affected by changing the amount of chain transfer agent.

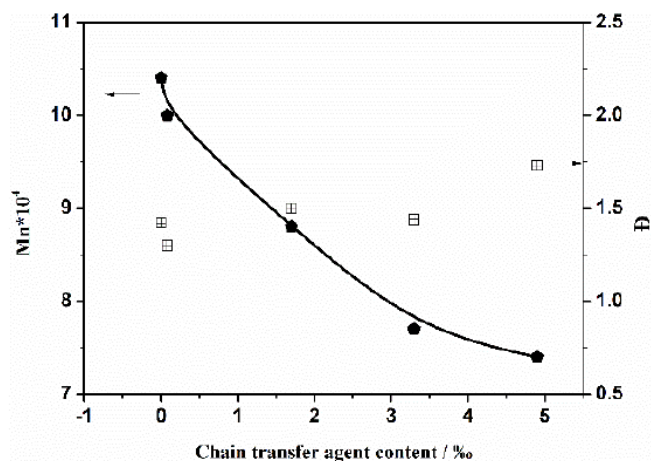


Figure 7: Correlations of the chain transfer agent content with M_n and \bar{D} .

3.7. Active Demonstration

To confirm the RAFT polymerization in our experiments was live, MMA was introduced into the polymerization system after the typical St RAFT polymerization procedure. Figure 8 shows the GPC traces of PS and PS-*b*-PMMA. The M_n of the PS-*b*-PMMA copolymer was higher than that of PS, indicating the formation of the PS-*b*-PMMA copolymer. Figure 9 shows the FT-IR spectra of the produced PS and PS-*b*-PMMA. Upon comparing the two curves, the curve for PS-*b*-PMMA was found to contain both characteristic peaks of PS and PMMA (C=O at 1730 cm^{-1}). Figure 10 shows the DSC curves for PS, PMMA and PS-*b*-PMMA. The glass transition temperatures (T_g) of PMMA, PS and PS-*b*-PMMA copolymer were 104.6, 91.1 and 100.1 °C, respectively. According to the FOX formula:

$$\frac{100}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \quad (3)$$

Where: $W_1 + W_2 = 100$

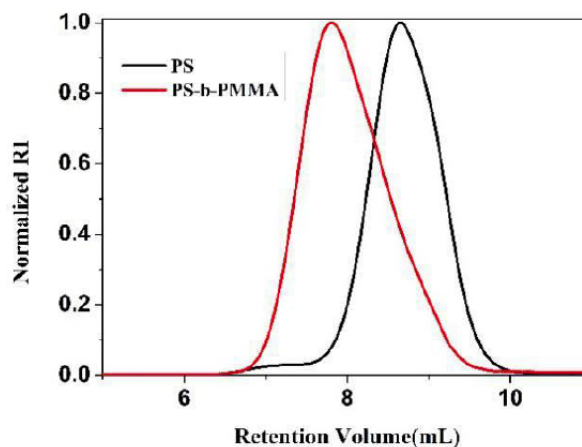


Figure 8: GPC trace of PS and PS-*b*-PMMA.

The calculated composition of the copolymer is as follows: PS of 32.5% and PMMA of 67.5%. The single

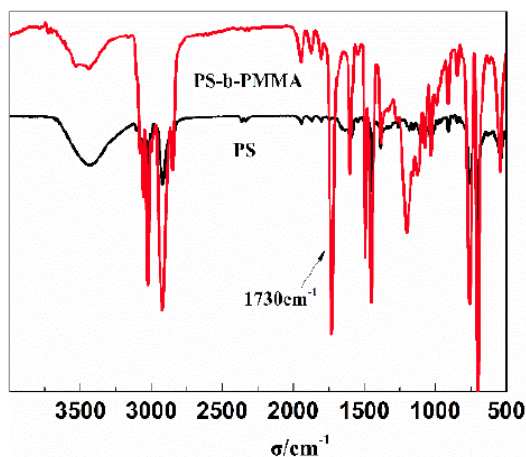


Figure 9: FT-IR spectrum of the produced PS and PS-*b*-PMMA.

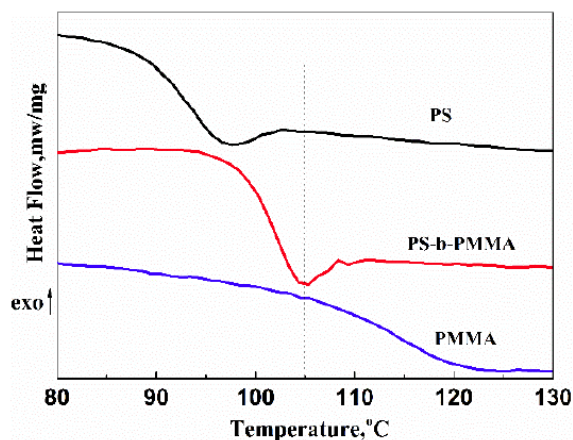


Figure 10: DSC curves of PS, PMMA and PS-*b*-PMMA.

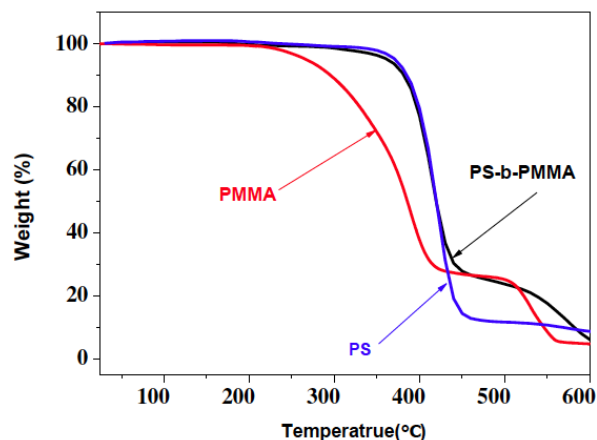


Figure 11: TGA curves of PS, PMMA and PS-*b*-PMMA.

T_g in the curve of the PS-*b*-PMMA copolymer is between the T_g values of PMMA and PS. The TGA curves of the PS, PMMA and PS-*b*-PMMA in Figure 11 shows that the thermal decomposition of PS-*b*-PMMA is between the PS and PMMA, which indicated the

formation of PS-*b*-PMMA copolymer. All these results suggested that our RAFT polymerization was living, which is also consistent with previous reported work [18].

4. CONCLUSIONS

RAFT polymerization of St was performed in the presence of potassium ethylxanthate in ethanol as a chain transfer agent. The polymerization kinetics showed a highly linear correlation and living/controlled polymerization, which was confirmed by FT-IR, DSC, TGA and GPC. The M_n of the obtained PS and monomer conversion were promoted with an increase in reaction time. Increasing reaction temperature resulted in a high M_n of the produced PS. When the amount of initiator or chain transfer agent was increased, it reasonably resulted in a low M_n product. The molecular weight distributions of the obtained PS were in the range of 1.42~1.89, which was narrower than that of the typical xanthate RAFT agent. Among the various xanthates, potassium ethylxanthate possesses a low transfer ability but a strong controlling ability for the RAFT polymerization of St, which broaden applications in the field of living polymerization.

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