

Controlled Radical Polymerization of Styrene Mediated by Xanthene-9-thione and Its Derivatives

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Electronic Supplementary Information

Abstract In our present work, a novel controlled radical polymerization system is developed based on xanthene-9-thione (XT). It was found that the radical polymerization of styrene (St) became controlled in the presence of a small amount of XT. At the early stage of the polymerization, the polymerization rate was relatively low and the as-formed polystyrene (PS) had low number-average molecular weight (M_n) and narrow polydispersity (D). After XT was consumed, the polymerization rate increased dramatically and the M_n of PS increased gradually with polymerization proceeding. When the polymerization of St was carried out with a proper molar ratio of initiator to XT and at an appropriate temperature, shortened slow polymerization stage and good control over M_n could be achieved. To further improve the regulating ability of XT, a series of substituent groups ($-\text{CF}_3$, $-\text{CH}(\text{CH}_3)_2$, $-\text{N}(\text{CH}_3)_2$) were introduced onto the xanthene ring of XT, and the effects of these derivatives on the polymerization of St were investigated in detail. UV-Vis spectroscopy was carried out to monitor the concentration of XT during the polymerization and the chemical structure of the as-formed PS was fully characterized by ^1H -NMR and ESI-MS analysis. A possible mechanism involving the formation and evolution of the cross-termination products was proposed to interpret the observed polymerization behavior.

Keywords Controlled radical polymerization; Xanthene-9-thione; Styrene; Substituent; ESI-MS

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INTRODUCTION

Controlled/living radical polymerization (CLRP) provides an unrivalled tool for polymer chemists to synthesize polymer chains with not only well-defined molecular weight^[1–3] and narrow distribution^[4, 5] but also a rich diversity of composition, architecture and functionality^[6, 7]. Nitroxide-mediated polymerization^[8] (NMP), atom transfer radical polymerization^[9] (ATRP) and reversible addition-fragmentation chain transfer polymerization^[10, 11] (RAFT), which have been developed in the last decade of the 20th century, are three of the representative and most successful CLRP techniques. Despite the great achievements that have been made, these CLRP techniques suffer from inherent drawbacks and limitations such as toxic transition metal catalysts, odorous and expensive di- or tri-thioesters, *etc.* Therefore, the development of new CLRP methods that can overcome these disadvantages is still highly demanded.

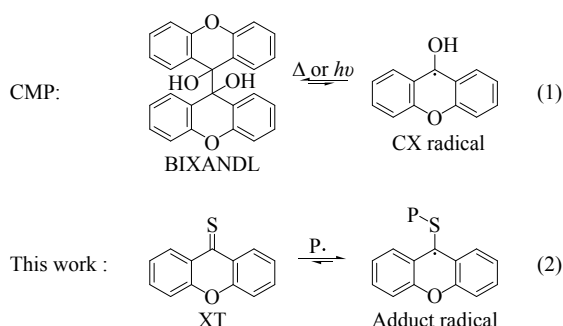
According to the mechanism of RAFT^[12–14], rapid chain transfer events based on the equilibrium of reversible addition-fragmentation dominate the polymerization to avoid unwanted radical-radical termination in the presence of chain transfer agent (CTA). However, the rate retardation of polymerization has emerged in several RAFT systems^[15–20]. Barner-Kowollik *et al.* believe that this phenomenon is consistent with the slow fragmentation model^[21], in which the adduct radical is stable enough to function as a radical sink in its own right. Subsequently, in 2005, Barner-Kowollik's group reported the radical polymerization of styrene (St) mediated by di-*tert*-butyl thioketone^[22] (DTBT) which involves the formation of highly stabilized adduct radicals. This radical contains only one C–S bond that is able to undergo β -scission and there is no possibility for chain transfer. Later, the same group investigated the polymerization behavior of butyl acrylate mediated by 4,4-bis(dimethylamino)thiobenzophenone^[23] (BDTBP). However, limited increment in M_n and broad D were obtained, demonstrating unsatisfying control over radical polymerization.

Previously, our group has developed a simple and feasible CLRP method named as cycloketyl radical mediated

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polymerization^[24] (CMP). In CMP, thermally- or photochemically-induced homolytic cleavage of 9,9'-bixanthene-9,9'-diol (BIXANDL) generates cycloketyl xanthone (CX) radicals (see Eq. 1, Scheme 1), which play dual roles of initiating and reversibly deactivating propagating radicals. Our method presents good controlled/living features in solution polymerization and has been applied for the preparation of core-shell polymeric particles^[25] and in suspension polymerization^[26]. However, CMP suffers from the occurrence of undesired side reactions such as hydrogen transfer reaction of CX radicals, which deteriorates the controllability of polymerization in some cases. Therefore, measures need to be taken to optimize the structure of dormant radicals in order to attain outstanding controlled/living characteristics.



Scheme 1 The formation reactions of deactivating radicals in CMP and this work (P· represents a chain radical.)

Inspired by the radical capture reaction of thiocarbonyl groups, 9*H*-xanthene-9-thione (XT) was chosen as a precursor to generate 9-alkylsulphonyl-xanthene-9-yl adduct radicals *in situ* via the addition of propagating radicals (Eq. 2, Scheme 1). It is anticipated that this approach could overcome the hydrogen transfer problem in CMP and exert better control over radical polymerization. Therefore, the radical polymerization behavior of St in anisole in the presence of XT was investigated in the present study. Successful polymerization of St and good control over M_n could be realized under appropriate conditions. Aiming to ameliorate this method further, the effects of different substituents (see Chart 1) on the polymerization of St were investigated. Besides, a possible mechanism was proposed following a combination of UV-Vis spectroscopy, ¹H-NMR, and MS analysis.

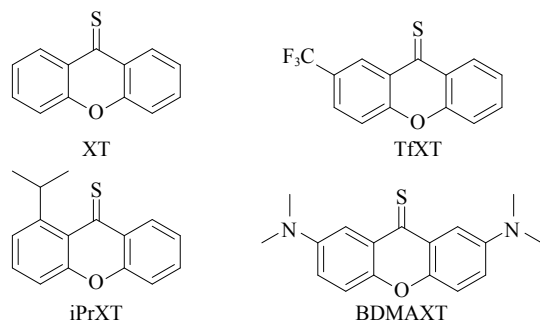


Chart 1 Thioketones used for mediating the polymerization of St

EXPERIMENTAL

Materials

All reagents and solvents were of at least analytical grade and purchased from commercial suppliers. Particularly, St and anisole were purified by distillation under reduced pressure, and azodiisobutyronitrile (AIBN) was recrystallized prior to use. 1-Isopropyl-9*H*-xanthene-9-one and 2,7-bis(dimethylamino)-9*H*-xanthene-9-one were synthesized in our lab according to previously reported procedures^[27–30].

General Thionation Procedure and Spectroscopic Data of XT and Its Derivatives

All thioketones mentioned in this work were obtained following a similar thionation procedure. Briefly, 5 mmol of ketone (xanthone, 2-(trifluoromethyl)-9*H*-xanthene-9-one, 1-isopropyl-9*H*-xanthene-9-one, and 2,7-bis(dimethylamino)-9*H*-xanthene-9-one), 1.21 g (6 mmol, 1.2 equiv.) of Lawesson's reagent and 30 mL of toluene were added into a round-bottomed flask, followed by being stirred magnetically in an oil bath at 80 °C overnight. Subsequently, the reaction mixture was distilled to dryness by rotary evaporation and the obtained solid was washed with saturated aqueous solution of NaHCO₃ repeatedly. Finally, further purification by recrystallization in toluene was conducted and pure thioketone was obtained in > 85% yields.

XT: Dark brown crystal. ¹H-NMR (acetone-*d*₆/TMS, 600 MHz, δ , ppm): 8.70 (d, 2H), 7.92 (t, 2H), 7.64 (d, 2H), 7.47 (t, 2H); ¹³C-NMR (acetone-*d*₆/TMS, 600 MHz, δ , ppm): 205.8, 151.4, 136.4, 130.2, 129.7, 125.9, 119.4; IR (KBr, cm⁻¹): 3061, 1593, 1445, 1319, 1240, 1214, 763, 744; ESI-MS: m/z = 213.0376 (M+H⁺); m/z calculated for [C₁₃H₉OS]⁺: 213.0374; UV-Vis (CHCl₃) absorption peaks: 236, 304, 406 nm (Figs. S1–S4 in electronic supplementary information, ESI).

TfXT: Dark brown crystal. ¹H-NMR (acetone-*d*₆/TMS, 600 MHz, δ , ppm): 8.89 (s, 1H), 8.59 (d, 1H), 8.16 (d, 1H), 7.95 (t, 1H), 7.81 (d, 1H), 7.63 (d, 1H), 7.49 (t, 1H); ¹³C-NMR (acetone-*d*₆/TMS, 600 MHz, δ , ppm): 204.9, 153.2, 151.2, 137.0, 131.9, 130.1, 129.7, 128.9, 127.6 (q), 127.4 (q), 125.8, 124.0, 121.3, 119.5; IR (KBr, cm⁻¹): 3033, 1604, 1455, 1298, 1211, 1178, 1146, 1117, 831, 656; ESI-MS: m/z = 281.0259 (M+H⁺); m/z calculated for [C₁₄H₈F₃OS]⁺: 281.0242; UV-Vis (CHCl₃) absorption peaks: 239, 308, 405 nm.

iPrXT: Dark green solid. ¹H-NMR (acetone-*d*₆/TMS, 600 MHz, δ , ppm): 8.43 (d, 1H), 7.80 (t, 1H), 7.74 (t, 1H), 7.55 (d, 1H), 7.51 (d, 1H), 7.41–7.38 (m, 2H), 4.90 (m, 1H), 1.32 (d, 6H); ¹³C-NMR (acetone-*d*₆/TMS, 600 MHz, δ , ppm): 210.6, 153.5, 152.2, 149.3, 135.0, 134.4, 134.1, 129.9, 129.8, 125.4, 124.5, 117.9, 116.3, 29.0, 24.8; IR (KBr, cm⁻¹): 3066, 2958, 1653, 1597, 1471, 1344, 1225, 1147, 769; ESI-MS: m/z = 255.0839 (M+H⁺); m/z calculated for [C₁₆H₁₅OS]⁺: 255.0838; UV-Vis (CHCl₃) absorption peaks: 240, 313, 412 nm.

BDMAXT: Dark reddish brown crystal. ¹H-NMR (acetone-*d*₆/TMS, 600 MHz, δ , ppm): 7.88 (s, 2H), 7.50 (s, 2H), 7.49 (s, 2H), 3.05 (s, 12H); ¹³C-NMR (acetone-*d*₆/TMS, 600 MHz, δ , ppm): 202.4, 148.8, 144.2, 129.7, 123.3, 119.8, 109.4, 40.9; IR (KBr, cm⁻¹): 3068, 2891, 2798, 1608, 1489, 1439, 1217, 926, 669; ESI-MS: m/z = 299.1215 (M+H⁺); m/z

calculated for $[C_{17}H_{19}N_2OS]^+$: 299.1213; UV-Vis ($CHCl_3$) absorption peaks: 251, 284, 309, 372, 452, 532 nm.

Polymerization of St Mediated by XT and Its Derivatives in Anisole

Typically, desired amounts of AIBN, thioketone, St and anisole were added into a round-bottomed flask (25 mL) with a side neck. The solution was deoxygenated by three freeze-pump-thaw cycles and backfilled with argon. Subsequently, the solution was stirred magnetically in an oil bath at a pre-set temperature. At different time intervals, aliquots were withdrawn from the solution using a syringe which was purged with nitrogen and weighed accurately (m_1). The samples were dried until constant weights (m_2) were reached. The conversion of St was estimated by gravimetry using the following equation:

$$C = \frac{m_2}{m_1 \times A}$$

where A is the weight fraction of St in the initial solution.

Characterization

NMR spectra were recorded on a Bruker AV-600 spectrometer. FTIR was conducted using a Thermo Nicolet Nexus 670 spectrometer. UV-Vis spectra were determined with a Hitachi U3900H spectrometer. HPLC-MS was carried out with a Waters HPLC/premier instrument under ESI+ mode and using acetonitrile/ H_2O as mobile phase. GPC analysis was performed with a Waters instrument equipped with a Waters 1515 HPLC pump, packing PSS columns (Styragel HT-3-4-5) and a Waters 2414 differential refractive index detector at 30 °C. The eluent was tetrahydrofuran (THF) and a flow rate of 1 mL·min⁻¹ was adopted. The packing columns were calibrated with linear PS standards supplied by PolyScience, inc.

RESULTS AND DISCUSSION

XT-mediated Polymerization of St

Anisole was chosen as solvent and AIBN was selected as thermal initiator. First, the polymerizations of St were performed at a fixed monomer concentration (30 wt%), initiator content (molar ratio of St/AIBN was 192/1, corresponding to a theoretical M_n of 1×10^4) and temperature (70 °C), while increasing the molar ratio of AIBN to XT from 0.5 (primary radical/XT = 1) to 1 (primary radical/XT = 2). The plots of conversion versus time and plots of M_n and $\bar{D}$ versus conversion are illustrated in Fig. 1. It can be seen from Fig. 1(a) that St conversion increased linearly with time, but the slope of the conversion-time curve is small. At 24 h, St conversion did not exceed 15%, indicating a rather low polymerization rate. This suggests that the incorporation of 2 equiv. of XT with respect to AIBN exerted a significant rate retardation effect on the polymerization of St. With AIBN/XT equalling 0.75, a sudden jump in conversion-time curve from 6.4% to 23.1% was observed after approximately 15 h. When AIBN and XT were added at a molar ratio of 1, the time curve exhibited a S-shaped curvature. Similarly, the polymerization accelerated at 8 h, followed by a gradual deceleration in polymerization rate after about 21 h. The final conversion at about 30 h was over 50%. The initial period was termed a slow polymerization stage. Therefore, the incorporation of XT hindered the polymerization of St obviously and the length of the slow polymerization stage was related closely to the molar ratio of AIBN to XT. These results differed from the statement of Barner-Kowollik *et al.* that severe retardation in the polymerization of St was observed and no PS was obtained within a reasonable length of time when BDTBP was introduced as mediator^[22]. Concerning the M_n and $\bar{D}$ of the polymeric products, M_n

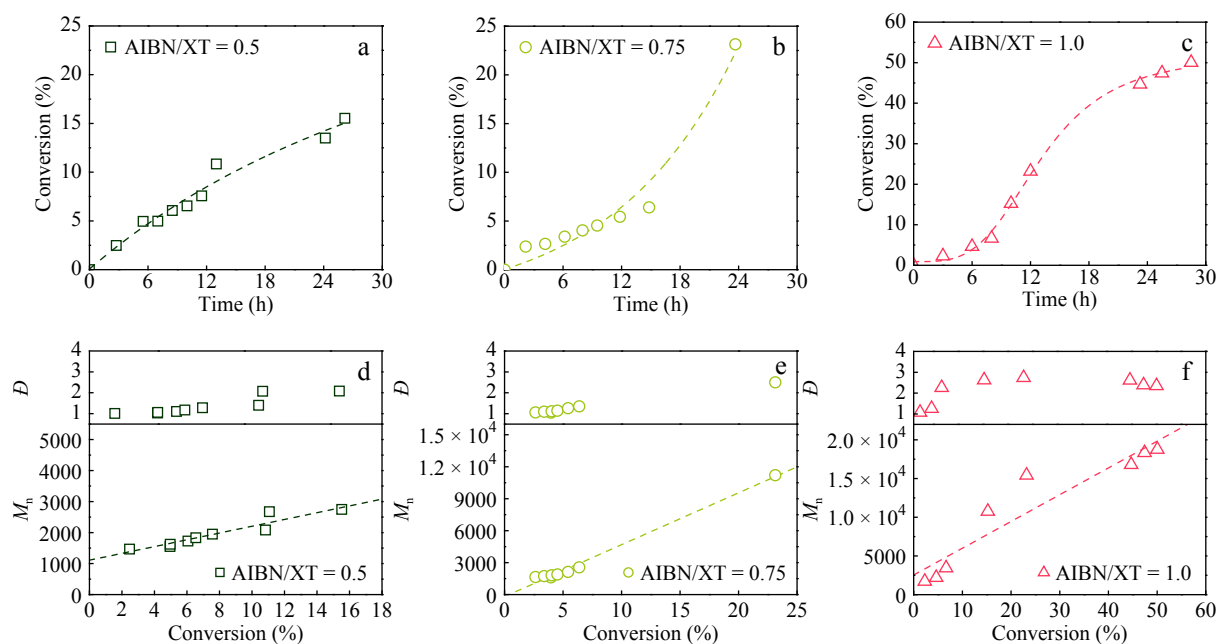


Fig. 1 Plots of conversion versus time (a–c) and plots of M_n and $\bar{D}$ versus conversion (d–f) for the polymerization of styrene in anisole with different molar ratios of AIBN to XT: 0.5 (a, d), 0.75 (b, e) and 1 (c, f). Concentration of St: 30 wt%; Molar ratio of St/AIBN: 192/1; Temperature: 70 °C

increased slightly with St conversion and was below 3000 during the course of polymerization with AIBN/XT equalling 0.5. $\bar{D}$ was below 1.2 during the initial 10 h, suggesting a rather narrow distribution. When AIBN/XT was 0.75 and 1, a rise in M_n from less than 4000 to over 1×10^4 was observed during the period corresponding to the jump in conversion. Meanwhile, $\bar{D}$ rose dramatically beyond 2.0, indicating that the distribution of PS chains widened greatly. A continuous growth in M_n was observed at the late stage when equal amounts of AIBN and XT were incorporated (the GPC curve shifted leftward with a small tailing). Thus, successful polymerization of St could be realized when the molar ratio of AIBN to XT was high enough. The polymerization demonstrated a slow polymerization stage, during which PS with low M_n and fairly low $\bar{D}$ was formed. The subsequent acceleration in polymerization rate was accompanied by a quick rise in M_n and $\bar{D}$. When AIBN/XT equalled 1, good control over M_n (though $\bar{D}$ was high) could be reached.

A change in temperature can cause changes in the rates of initiation, propagation, addition between propagating radicals and XT and possible termination. It was expected that such changes may improve the controllability of the polymerization. Hence, the influence of temperature on polymerization behavior was evaluated with AIBN/XT = 1, and the results are depicted in Fig. 2. Clearly, polymerization rate was enhanced significantly when elevating temperature from 65 °C to 80 °C. Conversion of St reached 30% after 24 h under 65 °C. However, it took only 11 and 5 h to attain such a conversion for the reaction at 75 and 80 °C, respectively. Apparently, high polymerization speed was achieved for polymerizations under high temperatures. However, elevated temperature brought about high initial M_n and limited increment in M_n during the polymerization. The M_n -conversion curve at 75 °C demonstrated the best

linearship, though a small negative deviation can still be discerned at the late stage. $\bar{D}$ at the slow polymerization stage under 65 and 75 °C was fairly low but reached beyond 2.0 once the polymerization speeded up. At 80 °C, the slow polymerization stage almost vanished, and $\bar{D}$ exceeded 2.0 from the beginning. Consequently, shortened slow polymerization stage and improved controllability of polymerization could be achieved by selecting appropriate temperature, but the improvement in $\bar{D}$ was limited.

Effects of XT's Derivatives on the Polymerization of St

In XT-mediated radical polymerization, the controllability of polymerization depends on the addition of chain radical to thioketone and the stability of the resulting adduct radical. Therefore, it is expected that the introduction of various substituents on XT's xanthene ring will bring about better control over the process of polymerization. Hence, three derivatives of XT, namely, 2-(trifluoromethyl)-9H-xanthene-9-thione (TfXT), 1-isopropyl-9H-xanthene-9-thione (iPrXT), and 2,7-bis(dimethylamino)-9H-xanthene-9-thione (BDMAXT) with different substituents ($-\text{CF}_3$: electron-withdrawing; $-\text{CH}(\text{CH}_3)_2$: weak electron-donating with steric hindrance; $-\text{N}(\text{CH}_3)_2$: strong electron-donating) were synthesized and structurally illustrated in Chart 1. The polymerization behavior of St in the presence of the three thioketones was evaluated and the results are depicted in Fig. 3. It should be noted here that for all derivatives of XT, the polymerizations were carried out under identical conditions (monomer concentration: 30 wt%; molar ratio of St/AIBN/thioketone: 192/1/1; temperature: 70 °C). Obviously, the reaction rate of the polymerization mediated by TfXT was much higher than that of the other thioketones (including XT). The conversion of St exceeded 60% after the reaction proceeded for 34 h, and the S-shaped characteristic

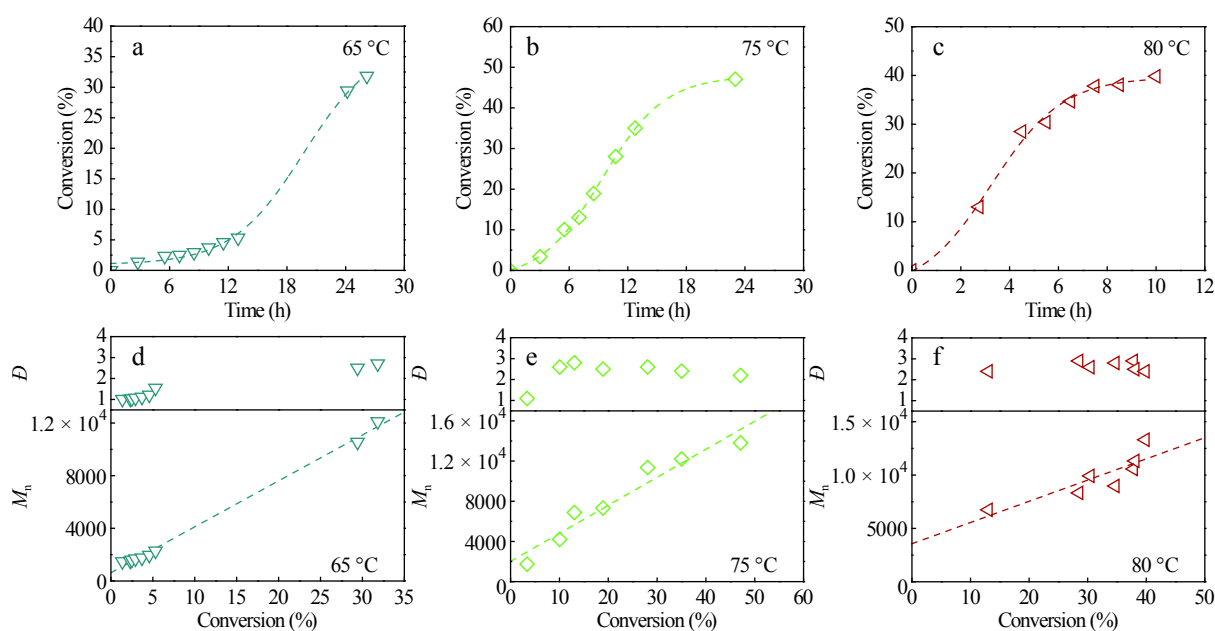


Fig. 2 Plots of conversion versus time (a–c) and plots of M_n and $\bar{D}$ versus conversion (d–f) for the polymerization of styrene in anisole with the molar ratio of St/AIBN/XT equalling 192/1/1. Concentration of St: 30 wt%; Temperature: 65 °C (a, d), 75 °C (b, e) and 80 °C (c, f)

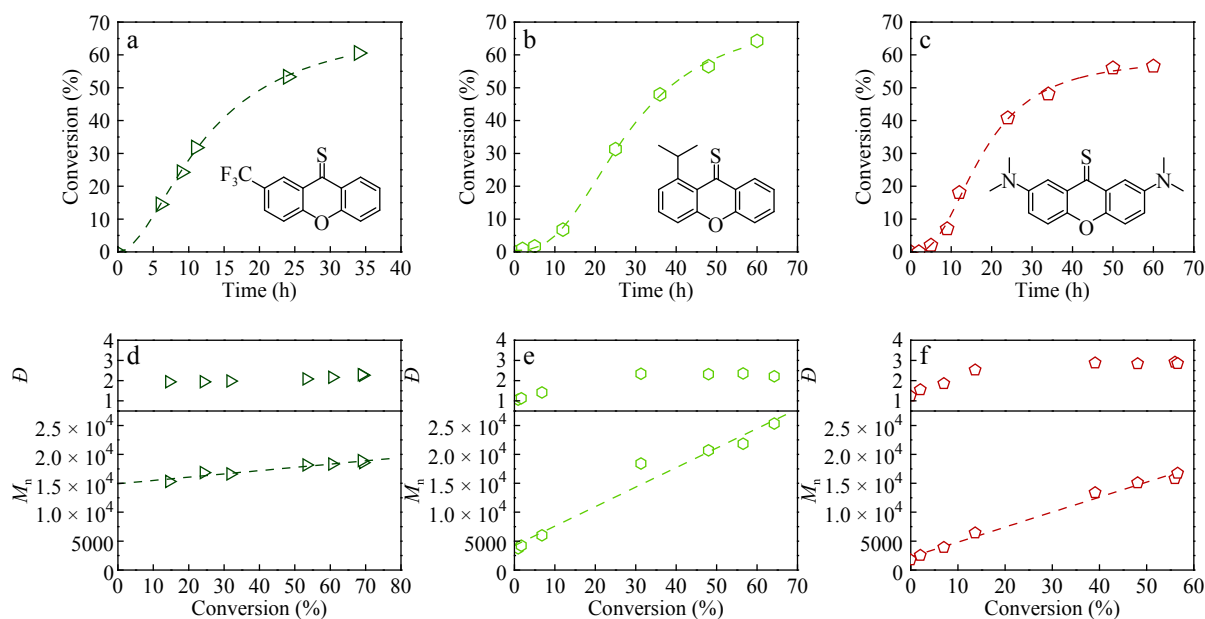


Fig. 3 Plots of conversion versus time (a–c) and plots of M_n and $\bar{D}$ versus conversion (d–f) for the polymerization of styrene in anisole with the molar ratio of St/AIBN/thioketone equalling 192/1/1: TfXT (a, d), iPrXT (b, e) and BDMAXT (c, f); Concentration of St: 30 wt%; Temperature: 70 °C

of the conversion-time curve was inconspicuous due to drastically shortened slow polymerization stage. For the polymerizations mediated by iPrXT, it took over 40 h for the conversions to achieve 60%. The conversion-time curve of the polymerization mediated by BDMAXT resembles that of iPrXT. The conversion remained below 60% at the end of the reaction period (~65 h). Concerning the controllability of the polymerizations, the polymerization mediated by TfXT demonstrated unsatisfying control over M_n , reflected by a high initial M_n and limited increment in M_n during the polymerization period. The extent of M_n growth in the polymerization mediated by BDMAXT, which was modified by the strongest electro-donating group in those of three substituents, was greater than that of TfXT, indicating an improvement in the control over molecular weight growth. Among the three thioketones, iPrXT exerted the best control over the polymerization, with the increment of M_n during the polymerization period being 2.1×10^4 . In addition, the GPC traces of the polymeric products clearly shift to the higher molecular weight direction with increasing monomer conversion (Fig. S5, in ESI). In summary, the introduction of electron-withdrawing substituent groups tends to accelerate the polymerization, while electron-donating substituent groups exert the opposite effect. Besides, steric hindrance may play an important role in ameliorating the controllability of thioketones, with iPrXT exhibiting the best control over the polymerization of St for all thioketones investigated.

Mechanism of the Polymerization of St Mediated by XT and Its Derivatives

During the slow polymerization stage, an interesting phenomenon that the color of XT and its derivatives gradually faded to light yellow drew our attention. This suggests that thioketones were consumed, and the resulting adduct radicals acted as mediating agents at the late stage of

polymerization. In order to reveal the mechanism of the present system, we first monitored the concentration of thioketone during the polymerization, taking XT as an example. UV-Vis spectroscopy was conducted on the aliquots withdrawn from the reaction solution and the result is illustrated in Fig. 4. The polymerization was conducted under identical conditions with the one corresponding to Fig. 1(c). The concentration of XT decreased rapidly at the initial stage of polymerization and then the decreasing rate dropped as the polymerization proceeded. Only about 42.3% of the initial amount of XT remained at 3 h and this continued to halve (21.2%) in the next 3 h. It took another 4 h for this value to drop to 11.3%. And a further reduction to 6.5% cost an extra time of 15.5 h. This proved directly our assumption on the consumption of XT during the polymerization.

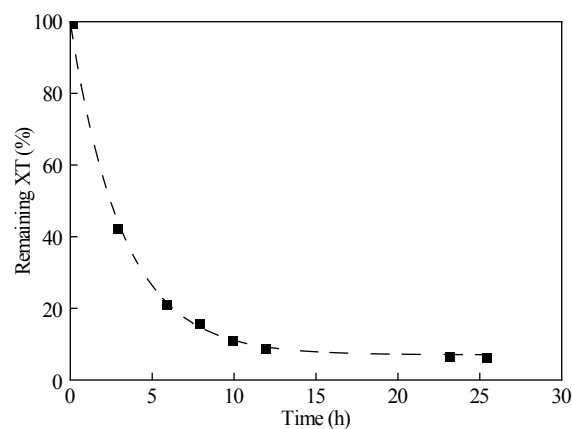


Fig. 4 Plot of remaining XT versus time for the polymerization of St in anisole with the molar ratio of St/AIBN/XT being 192/1/1, concentration of St: 30 wt%, temperature: 70 °C

Next, we aim to acquire the exact structure of the low molecular weight PS formed at the slow polymerization stage, because this provides essential information on how thioketone was consumed during polymerization. Therefore, analyses were conducted by combining multiple characterization methods including $^1\text{H-NMR}$, UV-Vis spectroscopy as well as HPLC-MS. The sample used in these characterizations was obtained by stopping the polymerization mediated by XT conducted under identical conditions with the one corresponding to Fig. 1(c) after 8 h. Then, low molecular weight PS was recovered by distillation under reduced pressure to remove anisole, followed by thin layer chromatography to remove XT that remained. NMR spectrum (Fig. S6, in ESI) shows small peaks in the range of 7.5–8.0 ppm adjacent to the characteristic peaks of PS, which can be assigned to partial protons of the xanthene rings. The absorption peak at 300 nm in UV-Vis spectrum (Fig. S7, in ESI) also points to the inclusion of the xanthene units in the low molecular weight PS. HPLC-MS is more informative because it can provide exact molecular weights of PS chains. No peaks with m/z values corresponding to the oxidized cations of the dormant adduct radicals as reported in Ref. [31] can be discerned. Peaks with m/z values being 470.2265, 574.2896, 678.3516, 782.4144, 886.4766, 990.5386 and 1094.6033 (Fig. 5) are assigned to the cross-termination products between the dormant adduct radicals and propagating PS chain radicals (No. of styrene units: 1–7), which were ionized with ammonium ions. Surprisingly, the spectrum is more abundant with peaks ($m/z = 248.1072$, 352.1696, 456.2324 and 560.2952) corresponding to cations

with different lengths of PS chains (No. of styrene units: 0–3) linking to the 9-site of the xanthene rings. It is believed that these cations resulted from the fragmentation of the cross-termination products during ionization. Hence, the low molecular weight PS mainly contained the cross-termination products.

Herein, we propose a possible mechanism for XT-mediated polymerization of St involving the formation of the cross-termination products, as is demonstrated schematically in Scheme 2. It involves two equilibrium reactions: the addition reaction between propagating radicals and thioketone, and subsequent combination reaction between dormant adduct radicals and propagating radicals. At the initial stage, chain radicals are produced by the decomposition of AIBN and the addition reaction of primary radicals to St. Due to an extremely large equilibrium constant $K_1 = k_{\text{add}}/k_{\text{frag}}$ of reaction IV, the chain radicals get instantly captured by XT without propagating to a long length. Therefore, the concentration of propagating radicals maintains at a low level, which accounts for the significantly retarded polymerization. Besides, the strong spin capturing ability of XT inhibits the formation of PS with high molecular weight at the slow polymerization stage. With the consumption of XT, the capture of propagating radicals by XT weakens, accompanied by the continuous accumulation of adduct radicals. Then the adduct radicals take control of the polymerization by acting as deactivating species and establishing a new equilibrium of combination-fragmentation with chain radicals. During this stage, the concentration of propagating radicals is elevated to a higher level than the

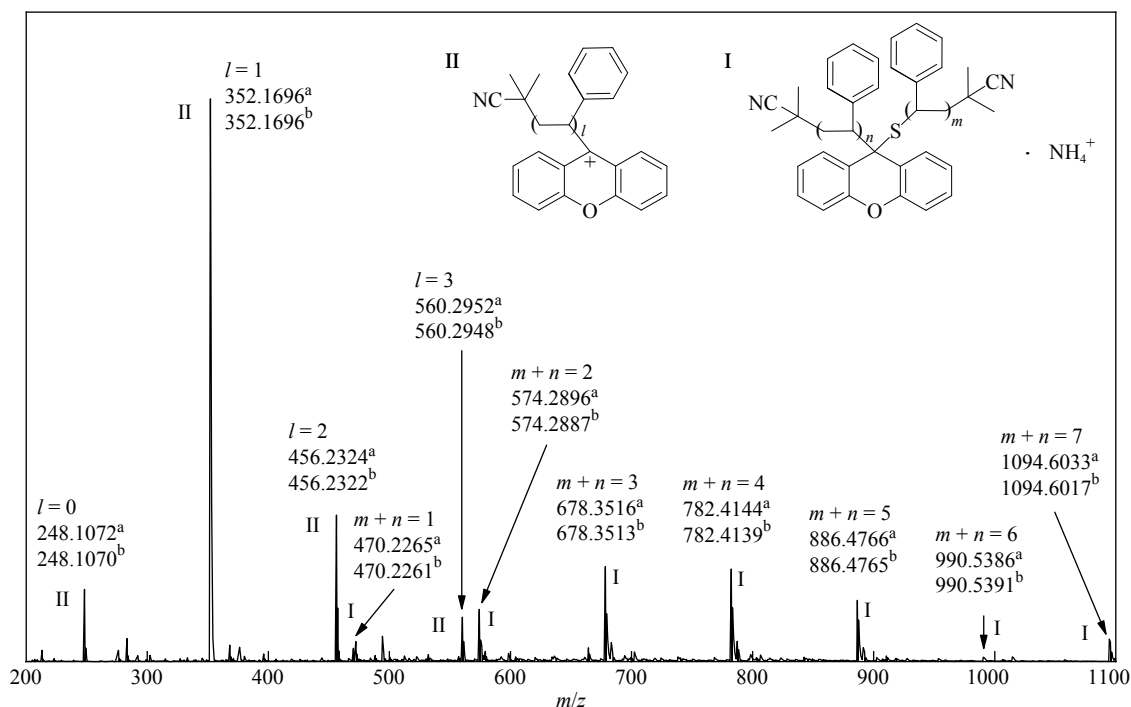
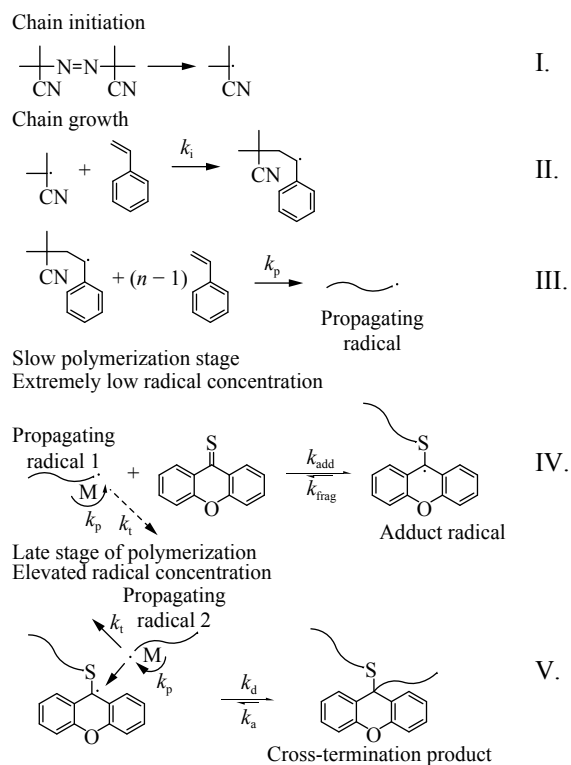


Fig. 5 ESI-MS spectrum of the low molecular weight PS formed in the polymerization of St in anisole with the molar ratio of St/AIBN/XT being 192/1/1 at 8 h. Concentration of St: 30 wt%; Temperature: 70 °C. The inset shows the predicted structures of the ionized polymer (I) and its fragment cation (II). Superscripts a and b represent the experimental and theoretical m/z respectively.



Scheme 2 Schematic illustration of the mechanism of XT-mediated polymerization of St

slow polymerization stage because of a smaller equilibrium constant $K_2 = k_d/k_a$ of reaction V compared with K_1 . These events cause the acceleration of the polymerization, the continuous increase of M_n as well as the widening of molecular weight distribution as conversion grows at the late stage.

Depending on the mechanism above, the polymerization behavior of St mediated by XT and its derivatives can be understood as follows. Firstly, when the molar ratio of AIBN to XT was as low as 0.5, insufficiency in chain radicals kept the reaction at the slow polymerization stage. When the molar ratio was increased to 1, an appropriate flux of propagating radicals was produced, consequently giving rise to a relatively high monomer conversion and good control over the molecular weight of PS. Secondly, elevated temperature (75 °C) could increase the rate constant k_{add} of the addition reaction between propagating radicals and thiocarbonyl groups of XT, therefore the consumption of XT speeded up and the slow polymerization stage ended in a shorter time. However, the high temperature (80 °C) could shift the second equilibrium reaction to the left direction, leading to an increase in the concentration of chain radicals. This aggravated the occurrence of irreversible chain transfer and termination reactions, which caused a reduction in the control over the polymerization. Finally, the introduction of substituents on the adjacent phenyl of thiocarbonyl groups could affect the charge distribution on the $C=S$ double bond and the stability of the adduct radicals. The effect of substituents resembles the situation of dithiocarbamates and xanthates used in RAFT system^[16, 32]. For these two RAFT agents, the interaction between N or O lone pairs and

thiocarbonyl group increases the electron density localized on the thiocarbonyl sulfur and is unfavorable for chain radical addition, while the introduction of a π -system or an electron-withdrawing group connected to the N or O atom adjacent to the thiocarbonyl group has the opposite effect. Similarly, in our work, the introduction of electron-withdrawing CF_3 group (in TfXT) enhanced the addition activity of chain radicals to thiocarbonyl groups, and therefore induced faster polymerization kinetics than the situation of BDMAXT (strong electro-donating $-N(CH_3)_2$ group) and iPrXT (weak electro-donating isopropyl group with steric hindrance). The superior control of iPrXT over the molecular weight of PS in comparison with the other XT derivatives can be ascribed to an extra contribution of the steric hindrance of the isopropyl group. It causes the cross-termination product to be overcrowded and facilitates the release of chain radicals (similar to the situation in NMP^[33–36]), therefore is beneficial to achieve higher reversibility of reaction V. Besides, it helps to stabilize the corresponding adduct radical through shielding the unpaired electron and preventing unwanted side reactions, as has been pointed out by Junkers *et al.*^[21].

CONCLUSIONS

In summary, a novel controlled radical polymerization system mediated by XT has been developed, and the experimental results indicate that the radical polymerization of St becomes controlled in the presence of a small amount of XT. There exists a slow polymerization stage, during which PS with low M_n (< 3000) and narrow D is obtained. With the consumption of XT, the polymerization rate increases dramatically and meanwhile the M_n of PS increases accordingly with polymerization time. When the conversion of St reaches a relatively high level under the present conditions, D increases, indicating reduced controllability at the end of the polymerization. To improve the regulating ability of XT further, different kinds of substituent groups ($-CF_3$, $-CH(CH_3)_2$, $-N(CH_3)_2$) have been introduced onto the xanthene ring of XT, and the influences of XT's derivatives on the polymerization behavior of St are evaluated. The experimental results demonstrate that electron-donating and sterically-hindered substituents tend to slow down the polymerization kinetics and result in better control over the polymerization of St. The ^1H -NMR and MS analyses illustrate that the low molecular weight PS with narrow D is mainly cross-termination products between the dormant adduct radicals and propagating radicals. According to the special chemical structure of the obtained PS, a possible mechanism involving the *in situ* generation of adduct radicals and their role as deactivating species has been proposed to interpret the polymerization behavior of St mediated by XT and its derivatives.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2153-4>.

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