

Thioxanthene-9-thione Mediated MMA Polymerization

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Electronic Supplementary Information

Abstract In the “cycloketyl radical mediated living polymerization” (CMP) process, a cycloketyl compound, [9,9']bixanthenyl-9,9' diol (BIXAN) was utilized as initiator and mediator. The cycloketyl (CK) radical was used as the dormant radical to achieve the increase of molecular weight. Herein, a series of cycloketyl thioketones were synthesised by Lawesson's reagent by one step reaction with high yield, and we found that, when a special cycloketyl thioketone compound, thioxanthene-9-thione (TXT), was added to a routine radical polymerization system, TXT could capture chain radical, and simultaneously formed an radical analogous to CK radical in structure, which could trigger the growth of polymer chains. This simple system was efficient to initiate the polymerization of methyl methacrylate (MMA) and in all cases the molecular weights increased with the increase of conversions. By the end-group analysis with ¹H-NMR and MALDI-TOF MS, it was confirmed that the P-STXT radical was used to control the polymerization. The re-initiating reactions were achieved when PMMA was used as the macro-initiator.

Keywords Thioxanthene-9-thione; Lawesson's reagent; Methyl methacrylate; Radical polymerization

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INTRODUCTION

Living radical polymerization (LRP) is one of the most widely utilized polymerization techniques which strongly influences the fields of polymerization and material science. Many great LRP processes have been developed in the recent 30 years such as nitroxide-mediated polymerization (NMP)^[1,2], atom-transfer radical polymerization (ATRP)^[3,4], and reversible addition-fragmentation chain-transfer (RAFT) polymerization^[5]. These LRP systems could provide efficient strategies on synthesizing the well-defined polymers as well as the block polymers^[6]. The increase of molecular weight of polymer relies on the dynamic equilibrium between the propagating chain radicals and the dormant chains *via* a reversible deactivation mechanism. However, industrial-scale applications for these LRP process are still limited because there exist some inherent drawbacks for the presently available methods such as using metals, high polymerization temperature, undesired color or odor. Although significant progress for improvements of these methods in recent years has been achieved, a new polymerization system which can dodge the aforesaid disadvantages is highly required^[7].

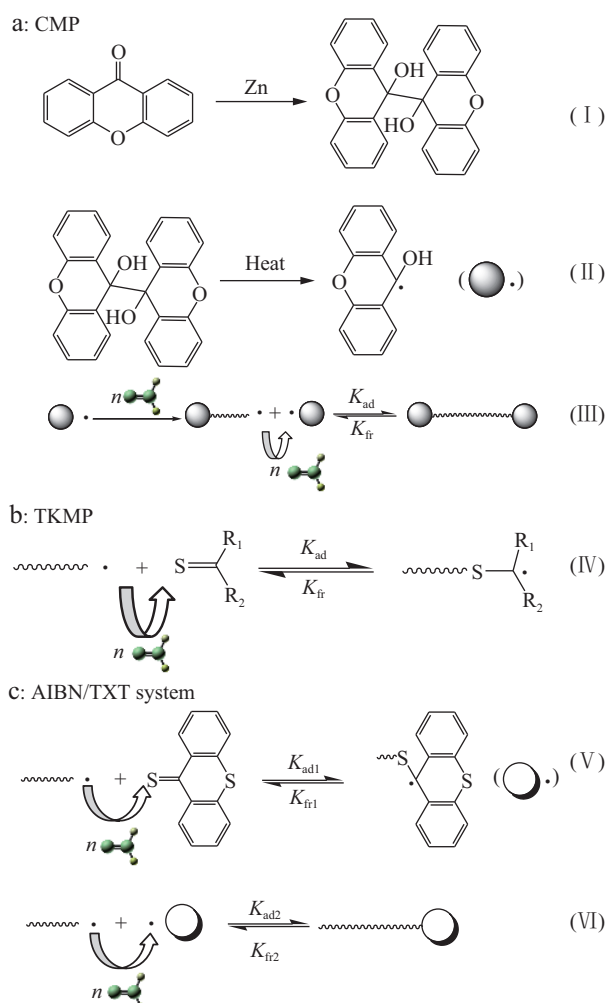
With this motivation, in 2012, a new polymerization system, cycloketyl radical mediated living polymerization

(CMP) system was reported by our group as shown in Scheme 1(a). Herein, a compound, [9,9']bixanthenyl-9,9' diol (BIXAN) was firstly synthesized and then combined with the monomer to construct the CMP system^[8]. In this system, BIXAN might firstly decompose into two cycloketyl (CK) radicals under heat. Then, unlike other LRP process, the CK radical itself could not only initiate the radical polymerization but also couple with the polymer chain radical as the dormant agent. Finally, the reversible activation/deactivation equilibrium was constructed with the participation of CK radical in the CMP process. Nevertheless, block polymer can be synthesized by this CMP process but the block efficiency was not that good. According to further surveys on this CMP system, we knew the fact that, there existed a side reaction in the CMP process where the CK radical could transform into xanthone again by taking off an H free radical. Therefore, it is necessary to further improve this CMP process to overcome the above obstacles.

Compounds with C=S double bond have been widely used in the LRP process. The most outstanding applications of these thio-compounds in LRP field are RAFT process, where dithioester (RAFT agent) is used as the dormant agents to control the polymerization^[5]. However, there are few publications about utilizing thioketone as the chain transfer agent to control the polymerization. In 2006, Barner-Kowollik put forward a new thioketone mediated polymerization system (TKMP) where AIBN was used as

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Scheme 1 Mechanism of (a) cycloketyl radical mediated polymerization (CMP) process, (b) thioketone mediated polymerization (TKMP) process, (c) cycloketyl thioketone mediated polymerization (T-CMP) process devised in this paper (AIBN/TXT system)

initiator and the thioketones were used as the radical capture agent. The spin trap was firstly synthesized by the addition reaction between the main chain radical and the thioketone, and then this spin trap started to control the polymerization, as shown in Scheme 1(b)^[9–12]. Though this TKMP system can make the molecular weight of polymer keep increasing with the conversion, the polydispersities ($\bar{D}$) were even close to 3.0 during the whole polymerization process. In addition, this TKMP system was not able to produce block polymer. Thus, this TKMP process was not a strict sense of livingness process.

Based on the reported addition reactions of thioketones and free radicals, in this communication, a modified cycloketyl thioketone mediated polymerization strategy (T-CMP) was devised. (1) A special cycloketyl thioketone, thioxanthene-9-thione (TXT) was synthesized by thioxanthen-9-one and Lawesson's reagent as the raw material. (2) Then an AIBN/TXT polymerization system was constructed to initiate the polymerization of methyl methacrylate (MMA). Surprisingly, we found that the

AIBN/TXT system can initiate the radical polymerization efficiently at mild temperatures such as 65 °C or 70 °C, meanwhile the molecular weight can keep growing during the whole polymerization process and the $\bar{D}$ (lower than 1.7) was significantly lower than that in the TKMP process. (3) The synthetic ability to block copolymers was also investigated. To the best of our knowledge, this is the first report to directly use AIBN/TXT system for free radical polymerization.

RESULTS AND DISCUSSION

The dormant agent, TXT, was synthesized *via* a similar procedure as the literature^[13] with a good yield (over 90%). Fig. S1 (in electronic supplementary information, ESI) shows the UV-Vis spectra of thioxanthen-9-one and TXT. When the C=O double bond in thioxanthen-9-one was transferred into C=S double bond by Lawesson's reagent, it was seen that the typical absorption of C=S in TXT was red-shifted to 460 nm, corresponding to a green colour in an organic solvent such as toluene. Advantages of this route were the simple procedure, mild reaction condition and easy separation of the product. In addition, this route could be successfully achieved in industrial process (kg levels).

Then an AIBN/TXT polymerization system was constructed and the effect of AIBN/TXT molar ratio on MMA polymerization with a constant AIBN concentration of 1.25×10^{-2} mol/L in toluene at 70 °C was investigated. The polymerization results are plotted in Figs. 1(a) and 1(b).

The conversion evolutions of MMA for various AIBN/TXT ratios are depicted in Fig. 1(a). The polymerization at a pure AIBN system as the control experiment was a rather fast process, reaching a conversion of 88.1% in 5 h. This polymerization behavior was directly related to the fast decomposition of AIBN at 70 °C. However, the conversions dropped sharply with the participation of TXT. For examples, when the molar ratios of AIBN/TXT were set to be 1/0, 1/2, 1/4 and 1/10, respectively, the conversions of MMA were 94.5%, 81.9%, 75.6% and 62.4% in 10 h. A possible explanation could be described as follows: the addition reaction between TXT and PMMA chain radicals would retard growth of PMMA chain radicals, and the higher the TXT concentration, the more significant the retardation effect.

The evolutions of the number-average molecular weight (M_n) and polydispersities ($\bar{D}$) of PMMA as a function of the conversions are shown in Fig. 1(b). Both the molecular weights and $\bar{D}$ had no obvious changes with a value of M_n about 1.00×10^4 and a $\bar{D}$ value over 2.0 in the pure AIBN system as the controlled experiment. The theoretical molecular weight was equated to 1.00×10^4 when the AIBN concentration was set to be 1.25×10^{-2} mol/L and MMA concentration was set to be 25 wt%. These results implied that each primary radical generated one PMMA chain with very high initiation efficiency. Meanwhile, for all three AIBN/TXT systems with different ratios (*i.e.* AIBN/TXT were set to be 1:2, 1:4 and 1:10), it could be observed that all the M_n s were promoted with conversions and the molecular weight distributions (1.7) maintained narrower than that of

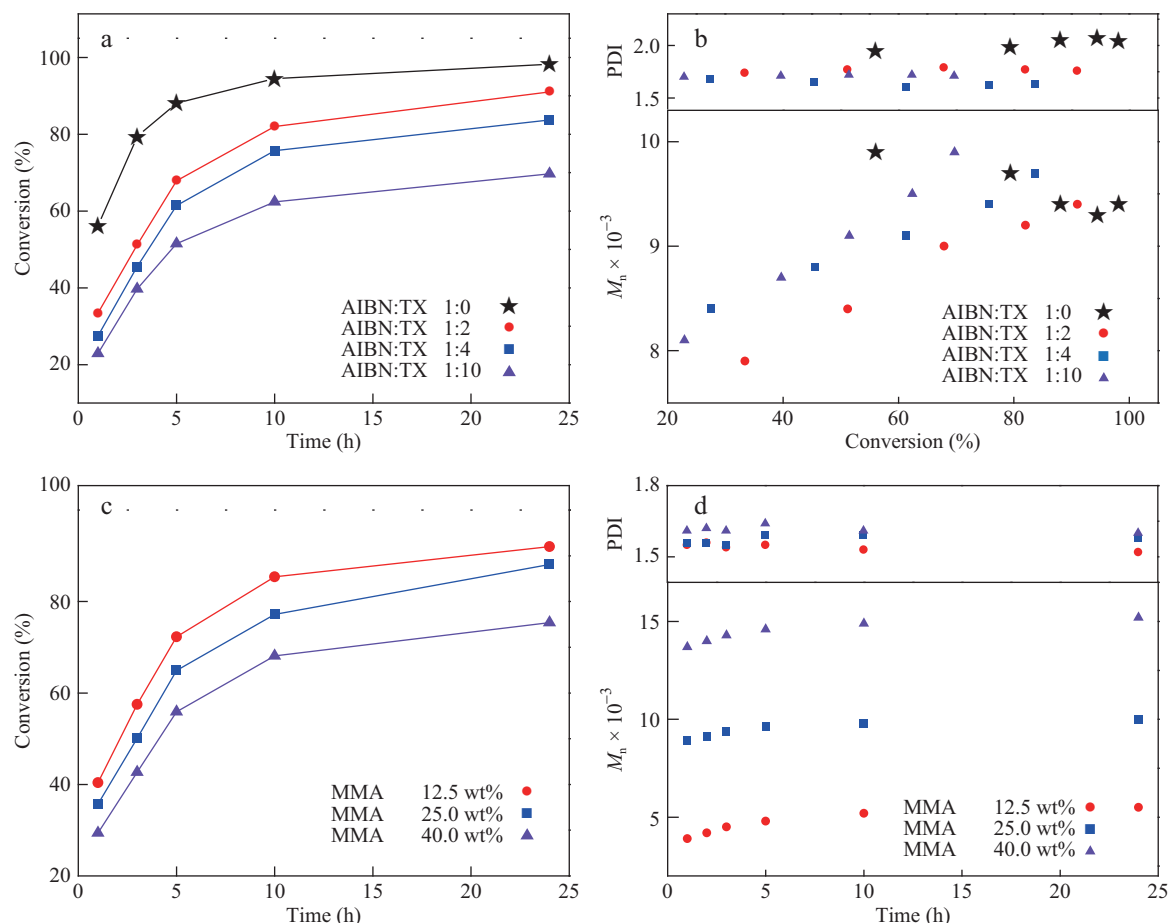


Fig. 1 (a) Conversion evolution of MMA versus time; (b) Evolution of M_n and $\bar{D}$ versus conversion; $c_{(\text{AIBN})} = 1.25 \times 10^{-2}$ mol/L, 25 wt% MMA concentration in toluene at 70 °C, and AIBN/TXT molar ratios were 1:0 (★), 1:2 (●), 1:4 (■) and 1:10 (▲); (c) Evolution of MMA conversion versus time; (d) Evolution of M_n and $\bar{D}$ with time; $c_{(\text{AIBN})} = 1.25 \times 10^{-2}$ mol/L, $c_{(\text{TXT})} = 2.50 \times 10^{-2}$ mol/L in toluene at 70 °C. The MMA concentrations were 12.5 wt% (●), 25.0 wt% (■), 40.0 wt% (▲).

pure AIBN (2.0) and TKMP process (over 2.5). This phenomenon can be explained as follows. Once the two benzene rings were conjugated through a X (O or S) atom, the free rotation of the C—C bond in the cycloketyl thioketone spin trap (P-STXT radical) had been hindered. This was believed to offer the P-STXT radical more stability through conjugated electron delocalization. According to the above, we might draw the conclusion that, the polymerizations of MMA were better controlled with the participation of the cycloketyl thioketone (TXT).

Following that, we further investigated the polymerization behaviors of MMA under different monomer concentrations at a fixed AIBN/TXT ratio of 1:2 and the results are plotted in Figs. 1(c) and 1(d).

With the same concentration of AIBN ($c_{(\text{AIBN})} = 1.25 \times 10^{-2}$ mol/L) and TXT ($c_{(\text{TXT})} = 2.50 \times 10^{-2}$ mol/L) as well as the same temperature (70 °C), the conversions of MMA with time at 3 different monomer concentrations *i.e.* 12.5 wt%, 25.0 wt% and 40.0 wt%, are shown in Fig. 1(c). It could be observed that all the polymerization behaviors were similar to that in Fig. 1(a) where all the conversions were growing with time. As for three different monomer concentrations, it was found that the higher the MMA concentration, the lower the conversion. This change tendency could be ascribed to

that since the ratio of AIBN/TXT was set to be 1:2, the number of effective chain radicals in the system would have a fixed range so that the amount of MMA polymerized in unit time was completely determined by these chain radicals, and therefore the higher the MMA concentration, the lower the relative rate of the polymerized MMA in all MMA polymerization processes. The $\ln([M]_0/[M]_t)$ versus time for Figs. 1(a) and 1(c) in the first 10 h are shown in Figs. S2 and S3 (in ESI), respectively.

Fig. 1(d) shows the changes of M_n and $\bar{D}$ of PMMA with time for three initial monomer concentrations. From Fig. 1(d), the first distinctive result was that, the ratio of MMA/AIBN did directly determine the molecular weight of PMMA. With a $c_{(\text{AIBN})} = 1.25 \times 10^{-2}$ mol/L, the theoretical molecular weights of PMMA for 12.5 wt%, 25.0 wt% and 40.0 wt% MMA concentrations should be 0.50×10^4 , 1.00×10^4 and 1.60×10^4 , respectively. The calculation process is shown in ESI. The experimental molecular weights for these three concentrations were 0.55×10^4 , 1.02×10^4 and 1.50×10^4 , which were quite close to these theoretical values. In this system, the number of polymer chains was mainly related with the initiating reaction from AIBN. Thus, the molecular weights were mainly controlled by the ratio of MMA/AIBN. Moreover, the increasing in molecular weights for three

monomer concentrations had been also observed, while the most significant growth in molecular weight was seen for the highest monomer concentration (*i.e.* 40 wt% monomer concentration) where the molecular weight of PMMA raised from 1.37×10^4 to 1.50×10^4 .

From the $\bar{D}$ curves in Fig. 1(d), it is seen that MMA concentration had insignificant effect on the molecular weight distribution of PMMA in the above reaction conditions. $\bar{D}$ values for 12.5 wt%, 25.0 wt% and 40.0 wt% concentration were about 1.52, 1.58 and over 1.6, respectively, that is, the higher the MMA concentration, the broader the $\bar{D}$. This phenomenon was caused by the fact that some side reactions existed in the AIBN/TXT system, which made $\bar{D}$ broader, and the higher the molecular weight of PMMA, the stronger the effect of the side reactions on $\bar{D}$. The typical GPC traces for 40.0 wt% MMA are shown in Figs. S4 (in ESI).

Other impact factors such as the monomer concentration and the temperature were also investigated and the results are depicted from Fig. S5 to Fig. S8 (in ESI) where the molecular weights are increased in all cases and the $\bar{D}$ values were also limited to almost 1.6.

According to our design, the P-STXT radicals should be firstly synthesized by the addition reaction between the TXT molecule and main chain radical *via* TKMP process. Then

this P-STXT radical was used to control the polymerization. Finally, the AIBN/TXT polymerization system was constructed. In order to clear up these reactions, $^1\text{H-NMR}$ and MALDI-TOF spectra were used to characterize the structures of resultant polymers and the results are plotted in Fig. 2.

The thioxanthen-9-one (raw material), TXT molecule (dormant agent) and PMMA sample were measured by $^1\text{H-NMR}$ spectra and the results are shown in Fig. 2(a).

In Fig. 2(a), the signal of the cyclo-aromatic group (1, $\delta = 8.67$ ppm) in thioxanthen-9-one was shifted to $\delta = 9.03$ ppm (1') in TXT molecule. Both the UV-Vis and $^1\text{H-NMR}$ results strongly convinced that the C=O double bond (thioxanthen-9-one) was transferred into C=S double bond (TXT molecule) *via* the one step reaction between the thioxanthen-9-one and the Lawesson's reagent.

The bulk polymerization of MMA was done at 70 °C for 2 h with $[\text{MMA}]:[\text{AIBN}]:[\text{TXT}] = 40:1:2$. Then, after separated and purified, the PMMA sample was measured by $^1\text{H-NMR}$ spectroscopy and the result is plotted in Fig. 2(a) (black line). The chemical shifts from $\delta = 7.05$ ppm to $\delta = 7.30$ ppm in PMMA sample were assigned to the cyclo-aromatic group in P₁-STXT-P₂ adduct while the peak at $\delta = 3.62$ ppm was attributed to the protons of methyl group (—OCH₃) of PMMA. Importantly, these new signals ($\delta =$

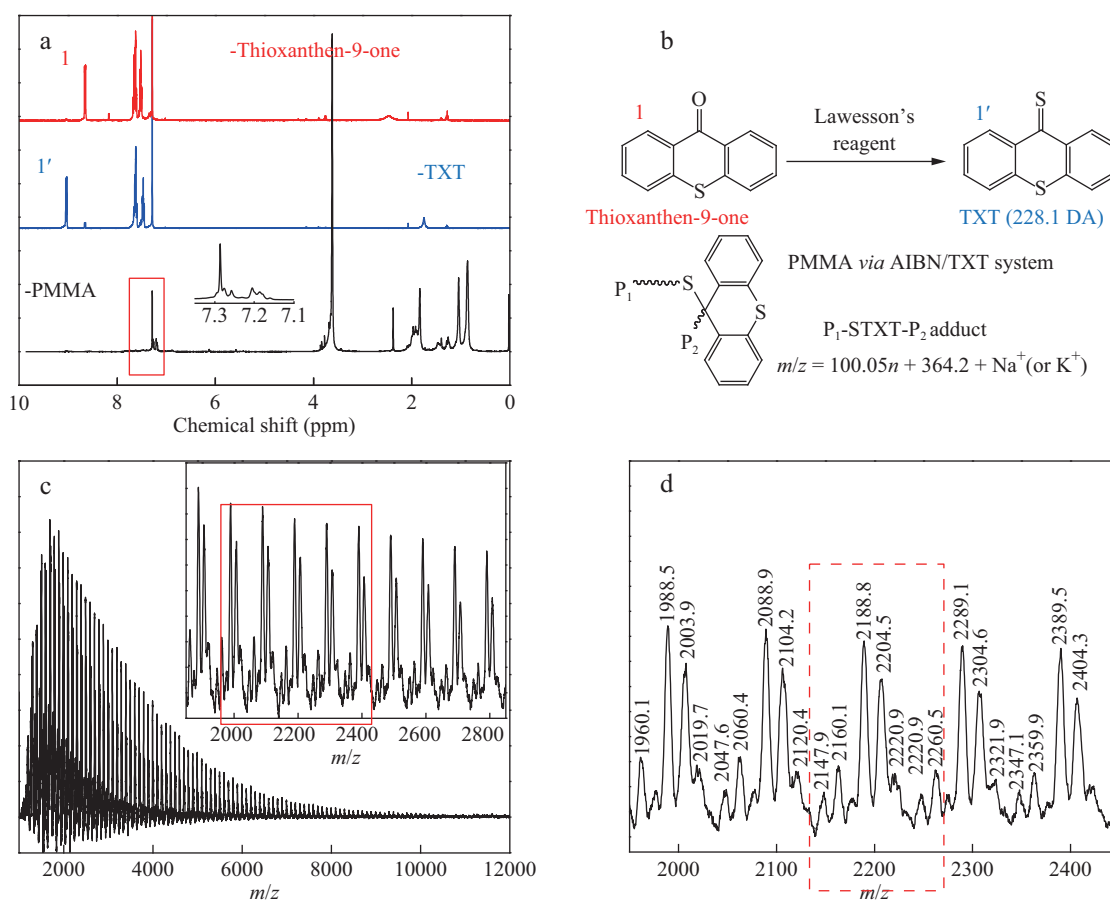


Fig. 2 (a) $^1\text{H-NMR}$ spectra for thioxanthen-9-one (red line), TXT (blue line) and PMMA *via* AIBN/TXT polymerization system (black line) in CDCl_3 ; (b) The chemical structures for thioxanthen-9-one, TXT and P-STX-P adduct; MALDI-TOF spectrum for (c) PMMA *via* AIBN/TXT system and (d) zooms into 5 MMA repeated units from m/z 1950 to 2450 in Fig. 2(c)

7.05–7.30 ppm) in PMMA samples indicated that TXT had been transferred into P₁-STXT-P₂ adduct during the polymerization process by the addition reaction between the TXT molecules and the PMMA chain radicals.

MALDI-TOF analysis was carried out to further clear up the reactions of this system and the result is plotted in Figs. 2(c) and 2(d).

The MALDI-TOF MS spectrum shown in Fig. 2(c) demonstrated that PMMA sample was a little bit complicated. According to the spectrum, all the peaks were observed with a repeating unit of 100 Da intervals, which precisely corresponds to the molar mass of the repeating unit MMA. From the values of the main peak like 1988.5 and 2088.9, and so on, after deducting the unit numbers of MMA like 16 or 17, the remained value was 364.5. After simple calculation, this value should be related to the molecular weight of the P₁-STXT-P₂ adducts. For example, the main peaks at 2088.9 and 2104.2 can be fit with the P₁-STXT-P₂ product, which contained 2 cyanisopropyl groups (68.05 DA), 1 TXT molecule (228.1 DA) and 17 MMA units with different cations (2088.9 with Na⁺; 2104.2 with K⁺), respectively. This signal might be attributed to the following steps: the decomposing of the initiator AIBN might produce the primary radical (cyanisopropyl groups) to initiate polymerization. The TXT molecule was used as the radical capture agent that could rapidly react with the main chain radical to construct addition/fragmentation equilibrium between the main chain radical and the TXT molecule as mentioned in TKMP process. The P₁-STXT radical was obtained by the above reaction at the beginning of the polymerization. Then this P₁-STXT radical might capture another main chain radical and finally constructed the P₁-STXT-P₂ adducts which had been confirmed by ¹H-NMR spectroscopy (Fig. 2a).

There were also some extra small peaks beside the main peak as shown in Fig. 2(c). For convenience, we just discussed the extra small peaks around the main peak (2188.8) as shown in Fig. 2(d). The peak at 2160.1 can be fit with the product that contained 2 cyanisopropyl groups (68.05 DA) and 20 MMA units (bearing with Na⁺ cation, $M_{n,th} = 2160.1$). This signal might be attributed to the self termination of two main chain radicals. The peak at 2220.4 can be fit with the P-STXT pieces that contained 1 cyanisopropyl group (68.05 DA), 1 TXT molecule (228.1 DA) and 19 MMA units (bearing with Na⁺ cation, $M_{n,th} = 2220.1$). The signal of the self termination reaction of P-TXT radical, however, was also observed in the MALDI-TOF MS spectrum. The peak at 2247.3 can be fit with the product that contained 2 cyanisopropyl groups (68.05 DA), 2 cyclo-aromatic group (fragment piece of TXT molecule taking off S atom, 196.1 DA) and 17 MMA units (bearing with NH₄⁺ cation, $M_{n,th} = 2247.1$). This P-TXT radical was obtained by decomposing the C—S single bond in P₁-STXT-P₂ adduct, where one P-TXT radical and one P—S radical should be produced in the AIBN/TXT polymerization system. This fragment reaction of C—S single bond was the side reaction of the AIBN/TXT system and might lead to higher $\bar{D}$ values.

The major conclusions for the MALDI-TOF MS are given below. The main products were P-STXT-P adducts (bearing Na⁺ or K⁺ cation) that had been produced during the AIBN/TXT polymerization process. The signals for different fragment routes to P-STXT-P adducts were also observed. Both the signals for the fragment pieces *via* T-CMP process and for the side reaction (the fragment pieces in C—S single bond of P-STXT-P adducts) were obtained in the MALDI-TOF MS. Meanwhile, the pieces for the termination reaction of two main chain radicals were also observed.

Combining the polymerizations of MMA above as well as the results of ¹H-NMR and MALDI-TOF for PMMA samples, the characters of MMA polymerization *via* AIBN/TXT system could be well understood as follows. (1) The number-average molecular weight of PMMA for the AIBN/TXT system was mainly controlled by the ratio of AIBN/MMA because AIBN was the only initiator to initiate polymerization in the AIBN/TXT system. (2) The addition reaction of TXT molecules to PMMA chain radicals made TXT act as radical capture agent, which not only retarded propagation of PMMA chain radicals but also decreased the radical concentration in whole polymerization system; consequently, the polymerization was sharply slowed down with the participation of TXT. (3) The P-STXT radical, obtained by the addition reaction between the TXT molecule and main chain radical, was used as the dormant radical to control the polymerization. (4) Due to the existence of side reactions, the $\bar{D}$ values were over 1.5 in this AIBN/TXT polymerization system. As a consequence, these characters strongly indicated that, the AIBN/TXT polymerization system not only was an efficient polymerization system but also can achieve molecular weight promoting during the whole polymerization process, therefore showing some character of “livingness.”

In order to confirm the “livingness” of the AIBN/TXT system, the macro-initiator PMMA ($M_{n,GPC} = 4.7 \times 10^3$; $\bar{D} = 1.48$) had been used to initiate the polymerization of the second monomer (BA, TBMA, and MMA), and the results are plotted in Fig. 3. The linear increase of the molecular weights for these block copolymers was observed where the PMMA-*b*-PTBMA, PMMA-*b*-PMMA and PMMA-*b*-PBA increased to 5.3×10^3 , 6.3×10^3 and 6.8×10^3 , while the $\bar{D}$ values were 1.59, 1.66 and 1.80, respectively. The GPC curves for PMMA-*b*-PBA are shown in Fig. S9 (in ESI). The major difference between the AIBN/TXT system and TKMP process was that the TKMP process was not able to re-initiate the polymerization of the second monomer while the block polymers were successfully produced in the AIBN/TXT system. As Barner-Kowollik mentioned, once the spin trap in TKMP process was incorporated into the second main chain radical, this product might no longer fragment again. Thus, the re-initiating reaction for TKMP process was unsuccessful. However, in the AIBN/TXT system, the P-STXT-P adducts might decompose to the main chain radical and the P-STXT radical again, and the P-STXT radical might be used as the dormant agent in the re-initiating process. Meanwhile, the C—S bond in P-STXT-P adducts was broken in the side reaction. Both the fragment pieces for the two decomposing routes to P-STXT-P adducts

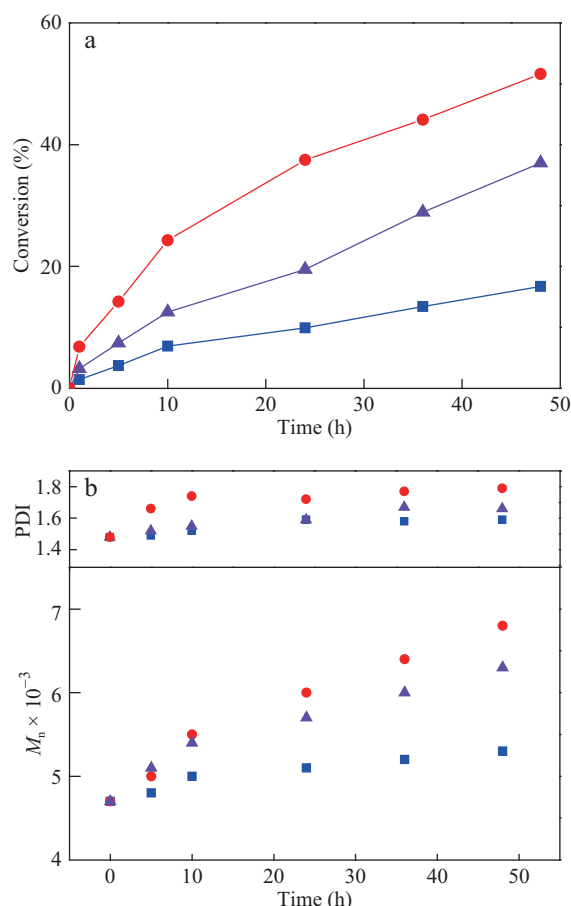


Fig. 3 (a) Conversion evolution of monomer versus time; (b) Evolution of M_n and $\bar{D}$ for the re-initiating reaction of BA (●), MMA (▲) and TBMA (■) in toluene at 70 °C

were observed in the MALDI-TOF MS. In the re-initiating reactions, the promoting of molecular weight was related to the existence of P-STXT radical while improved $\bar{D}$ was related to the side reactions. As a consequence, we might draw the conclusion that though the AIBN/TXT polymerization system was not living in a strict sense (due to the high $\bar{D}$), it could re-initiate the polymerization of the second monomer.

CONCLUSIONS

A cycloketyl thioketone, TXT was successfully synthesized by the Lawesson's reagent and had been utilized to construct an AIBN/TXT polymerization system. In this AIBN/TXT system, AIBN was used as the initiator while TXT was utilized as the dormant agent. This AIBN/TXT polymerization system was an efficient route to radical polymerization. The polymerization experiments and the end group analysis with $^1\text{H-NMR}$ and MALDI-TOF MS demonstrated that when the cycloketyl thioketone TXT was induced to a routine radical polymerization system like with AIBN as initiator, along with polymerization proceeding, TXT could capture polymeric chain radicals and *in situ* formed radicals analogous to CK radicals in CMP, which resulted in the propagation of polymer chains. Since the system involved the termination reaction as well as the

un-reversible fragmentation side reaction of C—S bonds, the $\bar{D}$ values were always higher than those for the other living polymerization systems. Re-initiating reaction had been achieved when PMMA was used as the macro-initiators. An ESR test is on-going and future work will focus on optimizing the TXT derivative to construct more efficient polymerization systems.

Electronic Supplementary Information

Electronic supplementary information (ESI) includes Experimental part, which is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2140-9>.

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