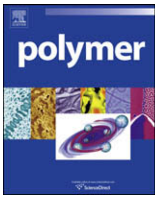
Polymer 49 (2008) 5431–5438

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Reversible addition–fragmentation chain transfer polymerizations of styrene with two novel trithiocarbonates as RAFT agents

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ARTICLE INFO

Article history:
Received 28 January 2008
Received in revised form
26 September 2008
Accepted 30 September 2008
Available online 10 October 2008

Keywords:
Styrene
Trithiocarbonate
RAFT

ABSTRACT

Two novel reversible addition–fragmentation chain transfer (RAFT) reagents bearing functional groups, S,S′-bis(9-anthrylmethyl) trithiocarbonate (BATTC) and S,S′-bis(1-naphthylmethyl) trithiocarbonate (BNTTC) were synthesized and used for the RAFT polymerizations of styrene (St). The polymerization results showed that the RAFT polymerizations could be well controlled using BNTTC or BATTC as the RAFT agents. For example, the polymerization rates were of first-order with respect to the monomer concentration, and the molecular weights of the obtained polystyrenes (PS) with narrow molecular weight distributions increased linearly with the monomer conversions and were close to their theoretical values in the presence of BNTTC or BATTC. The successful reaction of chain extension and analysis of ^{1}H NMR spectra confirmed the existence of the functional anthracene or naphthalene groups at the chain end of the correspondingly obtained PS. Optical properties of the obtained PS were characterized by fluorescence and UV absorption. Photochemical properties of the obtained PS end capped with anthracene were also described under irradiation of UV light.

1. Introduction

The ability to synthesize functional polymers in a controlled manner, i.e., with predetermined molecular weights, composition, and chain-end functionality, has become increasingly important in recent years. The "living"/controlled radical polymerization has recently emerged as one of the most effective synthetic routes to prepare well-defined polymers [1]. Among the "living"/controlled free radical polymerizations, nitroxide-mediated polymerization (NMP) [2], atom transfer radical polymerization (ATRP) [3,4], and reversible addition–fragmentation chain transfer (RAFT) [5,6] polymerization have extensively been reported. For NMP and ATRP, the synthesis of polymers with well-defined structures, such as some block copolymers and other complex architecture, has some limitations because the processes are not compatible with certain monomers or reaction conditions, or both. Compared with ATRP and NMP, the RAFT polymerization is suitable for much more monomers, and in principle, all classic radical polymerization can be used with the RAFT process in the presence of efficient RAFT agents such as dithioester [7,8], xanthate [9–11], trithiocarbonate [12–14], and dithiocarbamate [15–18]. According to the mechanism of RAFT polymerization proposed by Rizzardo et al. [5], the polymer obtained by RAFT polymerization contains the moieties of RAFT agent at the chain ends. As a result, in principle, the functional groups can be easily introduced into the chain ends of the polymers, by adjusting the structure of the RAFT agent used in the RAFT polymerization (i.e., by selecting appropriate structures for the activating and leaving groups (R groups) of the RAFT agent).

A number of well-defined polymers have been synthesized through RAFT polymerization [19–25]. Some chain-end functionalized polymers have been reported by designing the structures of RAFT agents. Hong et al. [26] synthesized biotinylated stimuli-responsive polymer and diblock copolymer by RAFT polymerization using biotinylated trithiocarbonate as RAFT agent. Wang et al. [27] reported the telechelic poly(n-butyl acrylate)s with dicarboxylic acid functional groups via RAFT polymerization. Zhou et al. [28] synthesized well-defined PS end capped by the anthracene moiety using a dithioester bearing anthracene as Z group as the RAFT agent. The facile synthesis of dumbbell-shaped dendritic-linear-dendritic triblock copolymer, [G-3]-PNIPAM-[G-3], consisting of third generation poly(benzyl ether) monodendrons ([G-3]) and linear poly(N-isopropylacrylamide) (PNIPAM), was reported by Ge et al. [29] via RAFT polymerization using [G-3]-based trithiocarbonate as RAFT agent.

There is considerable interest in the investigation of photosensitive polymers for technical applications such as photofabrication and information storage [30,31]. Anthracene [32] and naphthalene [33] are rigid conjugated molecule and sensitive to UV light.

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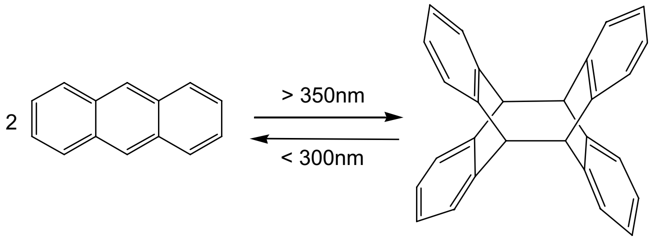
doi:10.1016/j.polymer.2008.09.065

Furthermore, anthracene is unique in combining the advantages of having easily accessible absorption spectra, exhibiting monomer (and often excirner) fluorescence and high photoreactivity, so anthryl-capped polymers could emerge using as the corresponding materials with luminophore properties [34,35]. The main photoreaction of anthracene functionality is [4 + 4] dimerization upon longwave UV irradiation (>350 nm) [36]. The dimer can be restored to the original monomer upon exposure to shortwave UV light (Scheme 1). This high photoreactivity of anthracene can be used for many applications. Yujun Zheng et al. [37] synthesized PEG-based hydrogel via the photodimerization of anthracene groups and demonstrated their photochemical properties including swellability, absorption spectrum, and topography. Katsunari Kataoka et al. [38] investigated the phase separation of anthracene-labeled polystyrene/poly(vinyl methyl ether) (PSA/PVME) blends induced by photo-cross-linking the PSA chains with linearly polarized light in the one-phase region of the blend.



Scheme 1. The reversible photodimerization of anthracene.

To the best of our knowledge, two bifunctional RAFT agents, S,S′-bis(9-anthrylmethyl) trithiocarbonate (BATTC) and S,S′-bis(1-naphthylmethyl) trithiocarbonate (BNTTC) have not been utilized previously in the syntheses of chain-end functionalized polymers. The structures of the RAFT agents are presented in Scheme 2. In this work, we synthesized the two novel bifunctional trithiocarbonates (BATTC and BNTTC), and used them as the RAFT agents for the synthesis of photosensitive group labeled PS with well-defined molecular weights and narrow molecular weight distributions. The optical properties of the obtained PS such as fluorescence, UV absorption and reversible photodimerization were investigated.

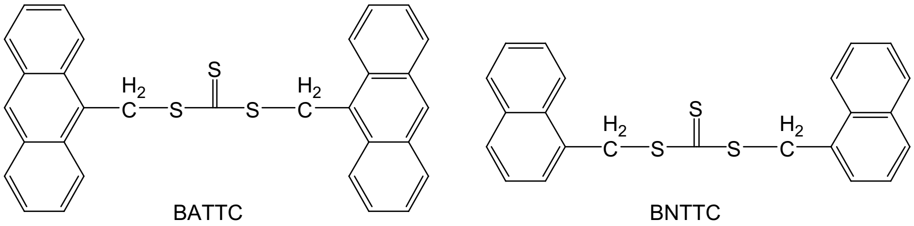
2. Experimental section

2.1. Materials

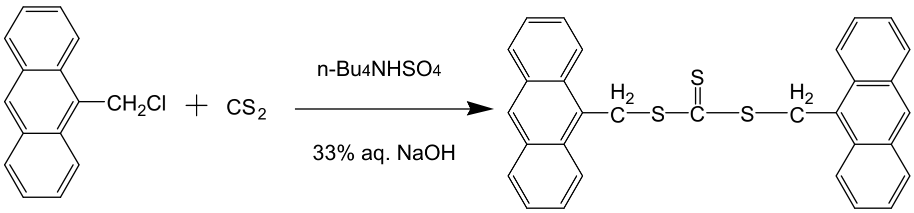
The monomer, styrene (St) was washed with an aqueous solution of sodium hydroxide (5 wt%) for three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, the monomer was distilled under reduced pressure and kept in a refrigerator under 0 °C for short store. 9-Chloromethyl anthracene, 1-chloromethyl naphthalene and n-Bu_4NHSO_4 were purchased from Aldrich Chemical Co. and used as received. 2,2′-Azoisobutyronitrile (AIBN) was recrystallized from ethanol. Tetrahydrofuran was dried with 4-Å molecular sieves and distilled in vacuum. Unless otherwise specified, all chemicals were purchased from Shanghai Chemical Reagents Co., China.

2.2. Synthesis of S,S′-bis(9-anthrylmethyl) trithiocarbonate (BATTC)

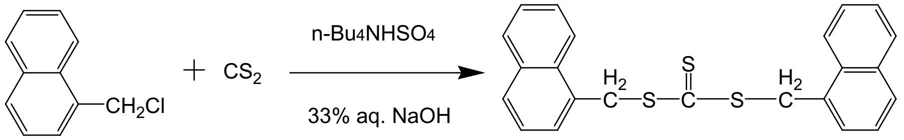
A mixture of 10 mL of CS_2 and 15 mL of 33% aqueous NaOH solution was stirred vigorously at room temperature in a 50 mL round-bottom flask with a magnetic stirrer. The phase transfer catalyst (n-Bu_4NHSO_4, 3 mol% to 9-chloromethyl anthracene used) was then introduced. After stirring for 10 min, 2 g (8.8 mmol) of 9-chloromethyl anthracene was added. The mixture was stirred vigorously at room temperature for about 5 h. To work up the reaction, the products were washed with THF (3 × 10 mL). Then recrystallization from THF gave a bright yellow crystal (Scheme 3). Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.66–5.72, 4H (s); 7.46–7.55, 4H (m); 7.56–7.65, 4H (m); 8.01–8.09, 4H (m); 8.22–8.29, 4H



Scheme 2. The structures of BATTC and BNTTC.



Scheme 3. Synthetic route of S,S′-bis(9-anthrylmethyl) trithiocarbonate (BATTC).



Scheme 4. Synthetic route of S,S′-bis(1-naphthylmethyl) trithiocarbonate (BNTTC).

(m); 8.46–8.56, 2H (s). Elem. Anal. Calcd. %: C, 75.88; H, 4.52; S, 19.60; Found: C, 75.70; H, 4.72; S, 19.41.

2.3. *Synthesis of S,S′-bis(1-naphthylmethyl) trithiocarbonate (BNTTC)*

The procedure for the synthesis of BNTTC is similar to that of BATTC (Scheme 4). Pure BNTTC was obtained as thin yellow crystal, and the purity was greater than 99% determined from HPLC. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 5.00–5.30, 4H (s); 7.38–7.48, 2H (m); 7.48–7.68, 6H (m); 7.75–7.94, 4H (m); 7.95–8.10, 2H (d). ^{13}C NMR (400 MHz, $CDCl_3$, δ): 223.37; 134.09; 131.90; 130.41; 129.30; 129.18; 128.71; 126.91; 126.39; 125.68; 123.81; 40.06. Elem. Anal. Calcd. %: C, 70.73; H, 4.65; S, 24.63. Found: C, 70.53; H, 4.77; S, 24.33.

2.4. *RAFT polymerization of St*

The typical procedure of RAFT polymerization of St was as follows: a stock solution of 11 mL (96 mmol) St and 3.9 mg (2.4×10^{-2} mmol) AIBN were prepared, and aliquots of 1 mL and 3.2 mg (6.5×10^{-3} mmol) of BATTC were placed in each ampoule. The content was purged with argon for approximately 10 min to eliminate the dissolved oxygen. Then the ampoules were flame sealed and placed in an oil bath held by a thermostat at 80 °C to polymerize. After a preset reaction time, each ampoule was cooled with ice water and opened. The reaction mixture was diluted with THF (ca. 2 mL) and then precipitated in petroleum ether (ca. 300 mL). The polymer was obtained by filtration and dried at room temperature in vacuum to a constant weight. The conversion of polymerization was determined gravimetrically. The other polymerization of St was carried out at 110 °C in bulk without AIBN.

2.5. *Characterizations*

The molecular weights and polydispersities of PS were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. ^{1}H NMR spectra of the polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance instrument, using $CDCl_3$ as a solvent and tetramethyl-silane as the internal standard. The fluorescence emission spectra of the polymers were obtained on an Ediburger FLS920 fluorescence spectrophotometer with THF as solvent at room temperature. The elemental analyses for C, H, N and S were performed on a LECO-CHNS microanalyzer. The UV absorption spectra of the samples in THF were determined on a UV 240 spectrophotometer. The purity of products was determined on high-performance liquid chromatograph (HPLC, mode 515, Waters) with the solvent of acetonitrile as the eluent at 30 °C.

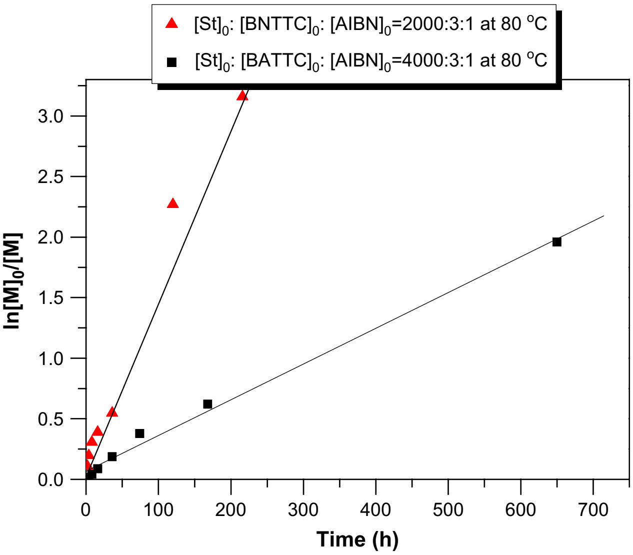


Fig. 1. Relationships between ln([M]0/[M]) and the polymerization time for the RAFT polymerizations of St in the presence of BATTC and BNTTC at 80 °C ($[St]_0$:$[BATTC]_0$:$[AIBN]_0$=4000:3:1; $[St]_0$:$[BNTTC]_0$:$[AIBN]_0$=2000:3:1) in bulk.

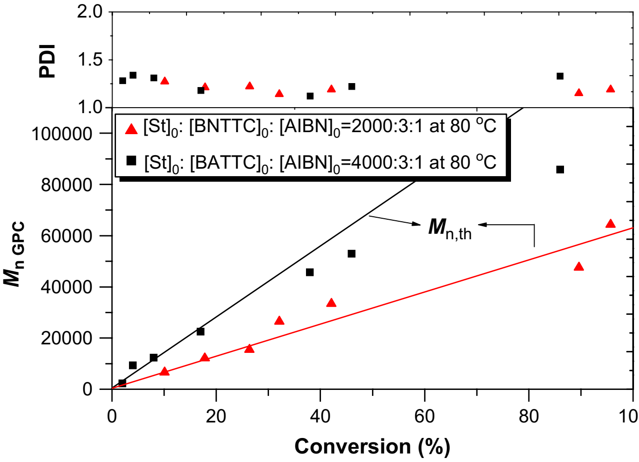


Fig. 2. Dependence of the molecular weights and PDIs on the monomer conversions for the RAFT polymerizations of St in the presence of BATTC and BNTTC at 80 °C ($[St]_0$:$[BATTC]_0$:$[AIBN]_0 = 4000$:3:1, $[St]_0$:$[BNTTC]_0$:$[AIBN]_0 = 2000$:3:1) in bulk.

3. Results and discussion

3.1. *RAFT polymerizations of St with BATTC and BNTTC as RAFT agents*

The RAFT polymerizations of St using AIBN as an initiator at 80 °C were carried out in the presence of BATTC or BNTTC ($[St]_0$:$[BATTC]_0$:$[AIBN]_0 = 4000$:3:1, $[St]_0$:$[BNTTC]_0$:$[AIBN]_0 = 2000$:3:1). The results are shown in Figs. 1 and 2, respectively. As shown in Fig. 1, the linear relationships between $\ln([M]_0/[M])$ and the reaction time for the RAFT polymerizations indicated that the concentration

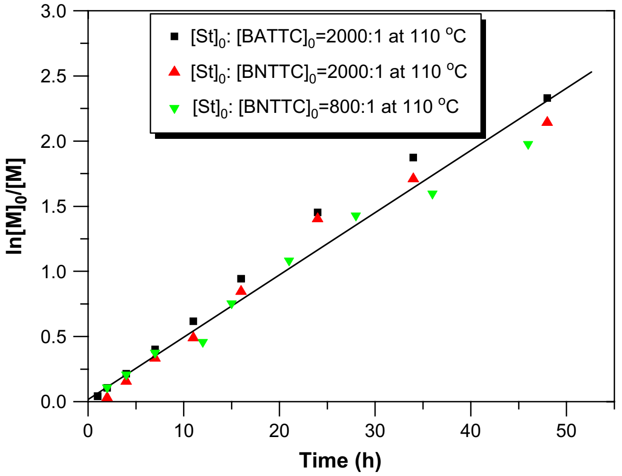


Fig. 3. Relationships between $\ln([M]_0/[M])$ and the polymerization time for the thermal-initiated RAFT polymerizations of St at 110 °C ($[St]_0$:$[BATTC]_0 = 2000$:1, $[St]_0$:$[BNTTC]_0 = 2000$:1, $[St]_0$:$[BNTTC]_0 = 800$:1) in bulk.

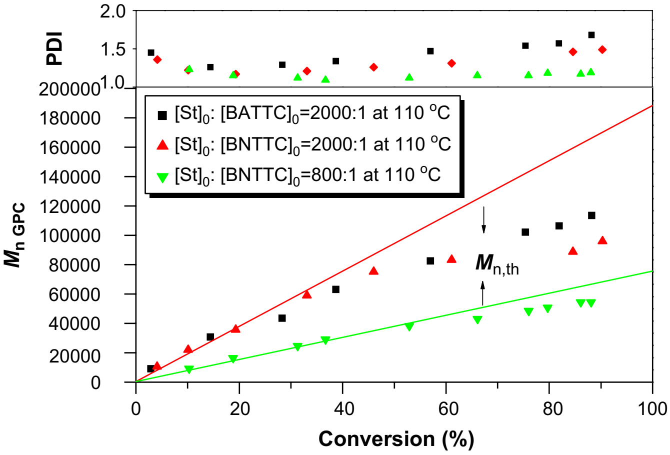


Fig. 4. Dependence of the molecular weights and PDIs on the monomer conversions for the thermal-initiated RAFT polymerization of St at 110 °C ($[St]_0$:$[BATTC]_0$ = 2000:1, $[St]_0$:$[BNTTC]_0$ = 2000:1, $[St]_0$:$[BNTTC]_0$ = 800:1) in bulk.

of free radicals remained constant during the polymerizations. The number-average molecular weight ($M_{n,GPC}$) values increased almost linearly with monomer conversion and were close to the calculated value ($M_{n,th}$, calculated via equation (1)) when conversion is less than 50% as shown in Fig. 2. The polydispersities were relatively narrow (PDI < 1.34).

$$M_{n,th} = \frac{\text{monomer weight}}{\text{mole of RAFT}} \times \text{conversion} + M_{RAFT} \tag{1}$$

The thermal-initiated RAFT polymerizations of St with different ratios at 110 °C in bulk were also carried out using BATTC or BNTTC as RAFT agent. The results are shown in Figs. 3 and 4. The linear relationships between ln([M]$_0$/[M]) and the reaction time were observed from Fig. 3. The number-average molecular weights ($M_{n,GPC}$) and molecular weight distributions are shown in Fig. 4 along with monomer conversions. The molecular weights increased linearly with the monomer conversions and were lower than the theoretical molecular weights ($M_{n,th}$, $M_{n,th} = [St]_0/[\text{RAFT agent}]_0 \times \text{Conversion} \times M_{\text{styrene}} + M_{\text{RAFT agent}}$) at high conversions in the cases of high mole ratio of $[St]_0$:[RAFT agent]$_0$ (2000:1). However, when the ratio of $[St]_0$:[RAFT agent]$_0$ decreased to 800:1, the agreement between $M_{n,GPC}$ and $M_{n,th}$ was good and molecular weight distribution was relatively narrow (PDI < 1.25). It was likely due to the existence of transfer side reactions at high conversions with a high mole ratio of $[St]_0$:[RAFT agent]$_0$. The rates of thermal-initiated RAFT polymerizations of St at 110 °C in the cases of $[St]_0$/$[BNTTC]_0$ = 800:1 and $[St]_0$/$[BNTTC]_0$ = 2000:1 were almost same.

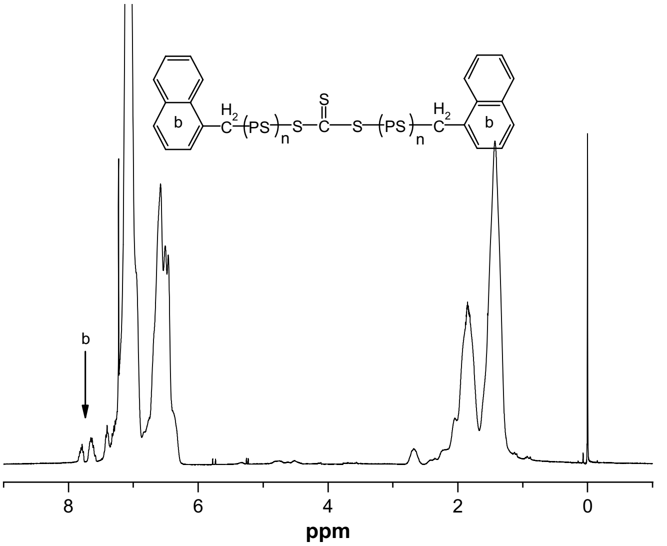


Fig. 6. Typical ^{1}H NMR spectrum of PS prepared via RAFT polymerization using BNTTC as the RAFT agent. (Solvent: $CDCl_3$, TMS as the internal standard, $M_{n\ GPC}$ = 6600 g/mol, PDI = 1.27).

These results showed that BATTC and BNTTC were effective RAFT agents for AIBN-initiated RAFT polymerization at 80 °C and thermal-initiated RAFT polymerizations of St at 110 °C in bulk.

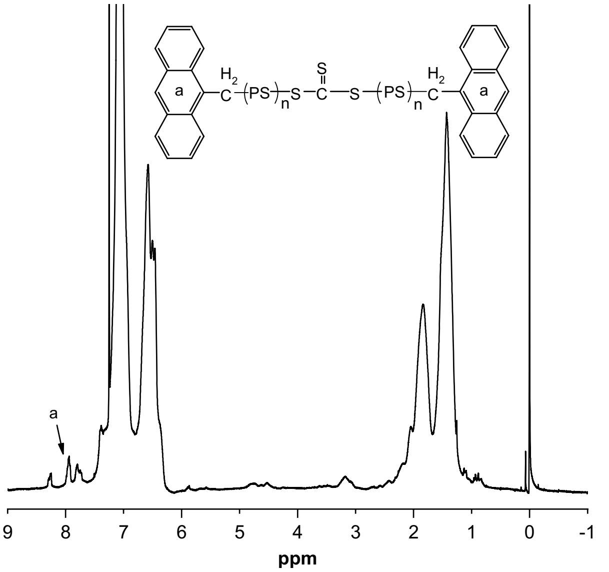


Fig. 5. Typical ^{1}H NMR spectrum of PS prepared via RAFT polymerization using BATTC as the RAFT agent. (Solvent: $CDCl_3$, TMS as the internal standard, $M_{n\ GPC}$ = 5100 g/mol, PDI = 1.33).

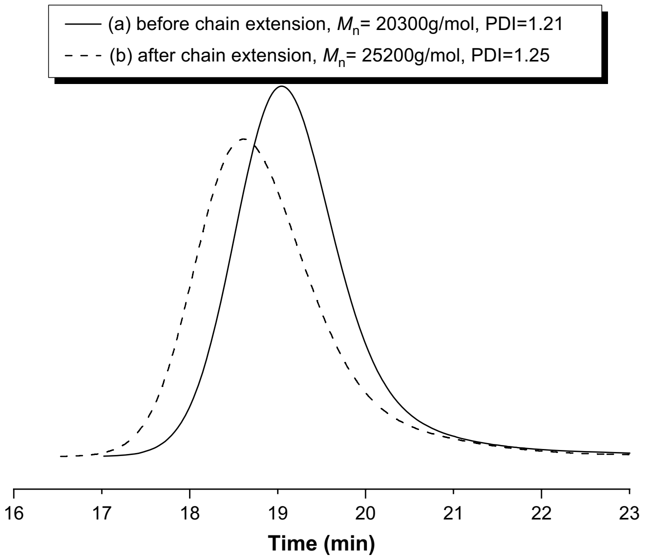


Fig. 7. GPC curves for before (a) and after (b) the chain extension of the anthracene end-labeled PS as macro-RAFT agent, original PS before chain extension obtained by the RAFT polymerization of St using BATTC as RAFT agent. Chain extension: $[St]_0$:[macro-RAFT agent]$_0$:$[AIBN]_0$ = 1000:3:1, temperature = 80 °C, 13 h, conversion = 22.5%.

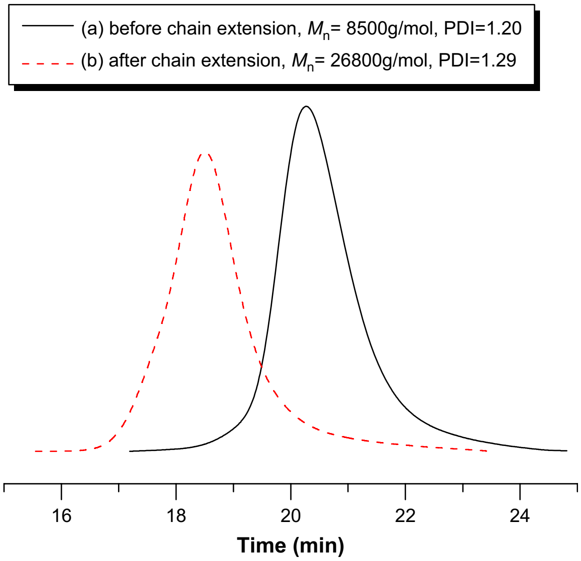


Fig. 8. GPC curves for before (a) and after (b) the chain extension of the naphthalene end-labeled PS as macro-RAFT agent, Original PS before chain extension obtained by the RAFT polymerization of St using BNTTC as RAFT agent. Chain extension: $[St]_0$:[macro-RAFT agent]$_0$:$[AIBN]_0$ = 1000:3:1, temperature = 80 °C, 14 h, conversion = 58.3%.

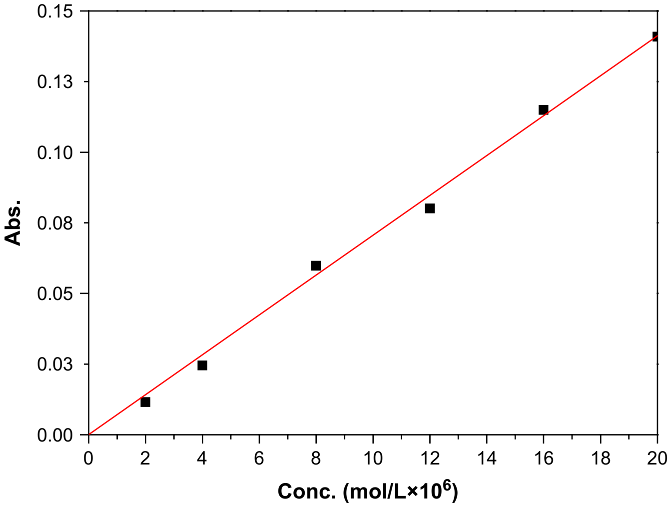


Fig. 10. UV–vis calibration curve of BATTC.

3.2. *End group analysis and the chain-extension experiment*

The structures of polymers obtained were characterized by ^{1}H NMR. The spectra of PS obtained via RAFT polymerization using BATTC and BNTTC as RAFT agents with AIBN initiation are shown in Figs. 5 and 6, respectively. The signals of the anthryl protons (a) from BATTC of PS were observed at 7.5–8.5 in Fig. 5. The signals at 7.5–8.0 ppm corresponded to the naphthyl protons (b) from BNTTC of PS (Fig. 6). These results indicated that the functional anthryl or naphthyl groups of the RAFT agents were attached to polymer-chain ends.

An additional method of confirming the "living"/controlled fashion of the polymerization is chain-extension reaction. A typical chain-extension experiment of the anthracene end-labeled PS was carried out using PS (M_n = 20,300 g/mol and PDI = 1.21) as the macro-RAFT agent and St as the second monomer ($[St]_0$:[macro-RAFT agent]$_0$:$[AIBN]_0$ = 1000:3:1, at 80 °C for 13 h with 22.6% conversion). GPC curves of the original and chain-extended polymers are shown in Fig. 7. There was a peak shift, and the molecular weight of the polymer increased from 20,300 to 25,200 g/mol, and the PDI of the chain-extended PS had a little increase, from 1.21 to 1.25. This may be caused by the small amount of homopolymerization of St and the dead polymer existing in the original polymer [39,40]. Furthermore, the chain extension of the naphthalene end-labeled PS was also carried out using St as the second monomer with AIBN initiating at 80 °C. The GPC traces of the original PS and the chain extended polymer are shown in Fig. 8. There was also a peak shift from the macro-RAFT agent (M_n = 8500 g/mol, PDI = 1.20) to the extended PS ($[St]_0$:[macro-RAFT agent]$_0$:$[AIBN]_0$ = 1000:3:1, at 80 °C for 14 h with 58.3% conversion) as shown in Fig. 8. The molecular weight of the polymer increased from 8500 to 26,800 g/mol, and the PDI of the polymer changed from 1.20 to 1.29. The results indicated that the original polymer was still active.

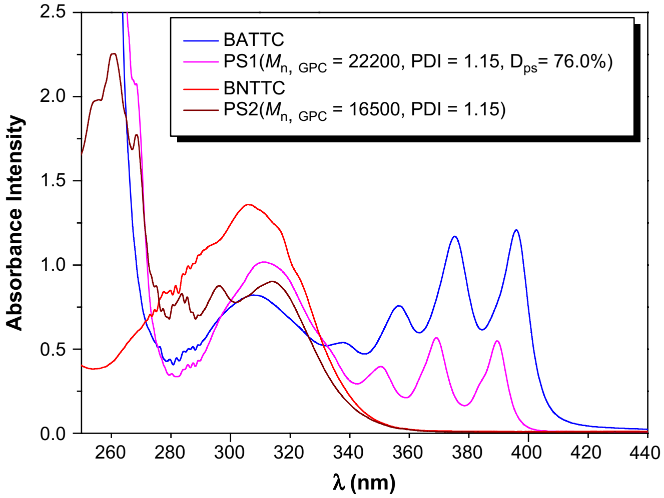


Fig. 9. UV–vis spectra of the RAFT agents (BATTC and BNTTC) and the corresponding PSs (PS1 and PS2 were obtained with BATTC and BNTTC as RAFT agent respectively) with THF as solvent at room temperature. The concentration of all solutions is 1.0×10^{-4} mol/L.

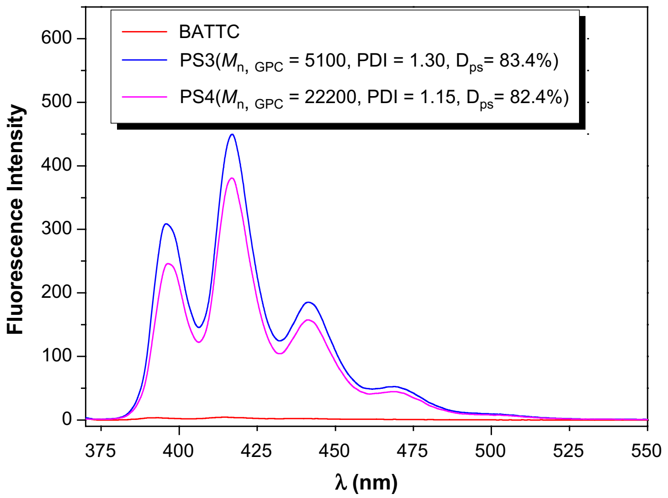


Fig. 11. Fluorescence spectra of BATTC and the corresponding PSs, obtained using BATTC as the RAFT agent, in THF at room temperature. The concentrations of anthracene moiety are 5.00×10^{-5} M for BATTC and PSs, λ_{ex} = 369 nm.

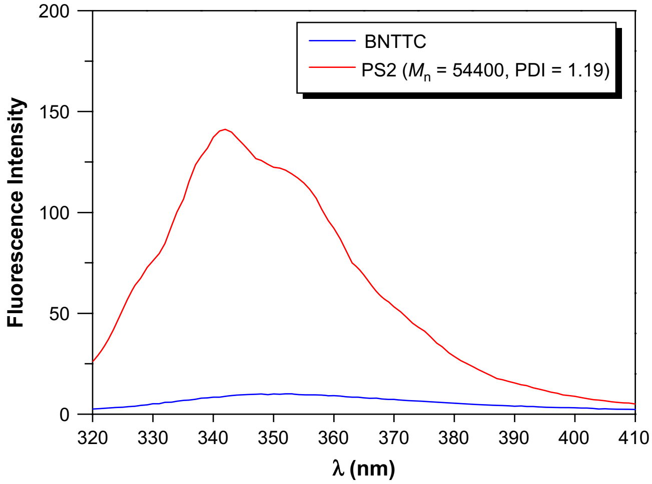


Fig. 12. Fluorescence spectra of BNTTC and the corresponding PS, obtained using BNTTC as the RAFT agent, in THF at room temperature. The concentrations are 5.00×10^{-5} M for BNTTC and PS, λex = 280 nm.

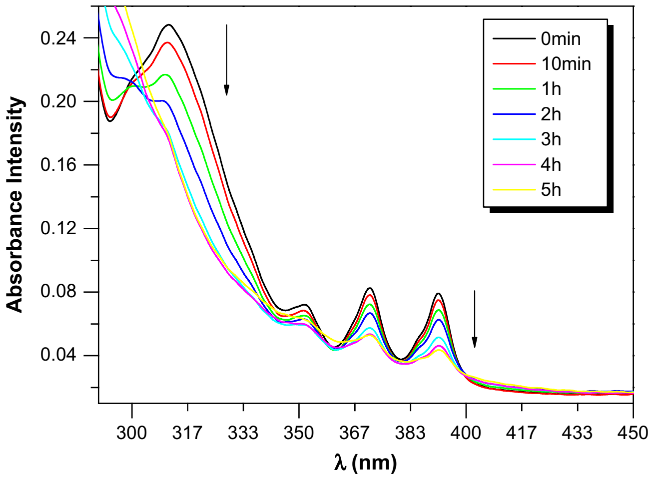


Fig. 14. UV–vis spectra of an anthryl-capped PS solid film under different irradiation times at 365 nm. Sample PS with $M_{n,\ GPC}$ = 3900 g/mol and PDI = 1.31 obtained using BATTC as the RAFT agent.

Thus, all the above evidences showed that the BATTC and BNTTC were effective RAFT agents for the RAFT polymerizations of St under these experimental conditions.

3.3. Optical properties of the RAFT agents and the corresponding polymers

According to the mechanism of RAFT polymerization, the functional group of RAFT agent would exist at the chain ends of the obtained PS, which was confirmed by the ^{1}H NMR spectrum of PS (Figs. 5 and 6). Therefore, the UV spectra of the RAFT agents and the corresponding PS in THF at the same concentration were measured because of the high sensitivity of the anthracene and naphthalene to the UV light. The results are shown in Fig. 9. It can be found that both BATTC and the corresponding PS (PS1) showed two characteristic absorption peaks, corresponding to the absorption of the anthracene moiety (between 350 nm and 410 nm) and trithiocarbonate moiety (310 nm) [41]. The absorption peak of the anthracene moiety had a small blue shift (~7 nm), which may be due to the weak interaction between the pendant phenyl groups of the PS skeleton and the anthracene group in polymer-chain end. At the same time, both PSs (PS2) obtained using BNTTC as RAFT agent and BNTTC had a maximum absorption peak around 302 nm corresponding to the naphthalene moiety (280 nm) [42] and trithiocarbonate moiety (310 nm). In addition, both anthracene end capped PS and BATTC showed strong absorption peak at 369 nm. Thus, the degree of anthracene end-functionalizing (D_{ps} (%)) in PS can be measured through the UV–vis spectrum. The calibration curve was obtained by BATTC at room temperature in THF with the concentrations of anthracene group that ranged from 2.00×10^{-6} to 2.00×10^{-5} (Fig. 10). The results showed that there was 76.0% for PS1, 83.4% for PS3 ($M_{n,\ GPC}$ = 5100, PDI = 1.30) and 82.4% for PS4 ($M_{n,\ GPC}$ = 22,200, PDI = 1.15) end capped with anthracene, respectively. All of the results further indicated that the PS chains were attached with anthracene and naphthalene moieties in R groups of the RAFT agents.

Anthracene and naphthalene are rigid conjugated molecules with strong fluorescence. Thus, we investigated the fluorescence of

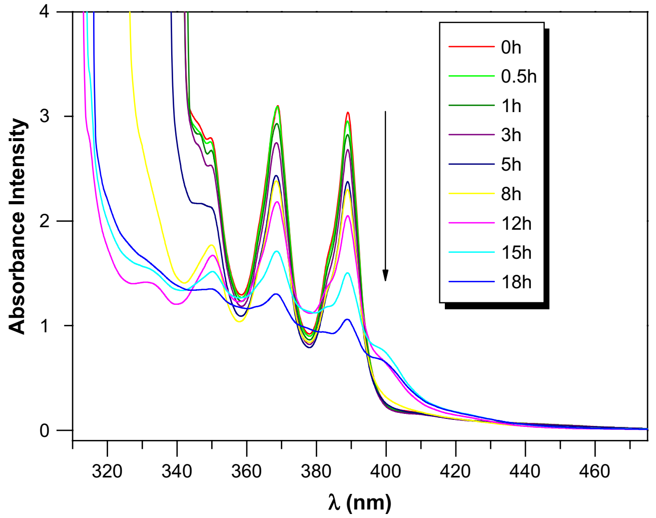


Fig. 13. UV–vis spectra of an anthryl-capped PS solution under different irradiation times at 365 nm. Sample PS with $M_{n,\ GPC}$ = 3900 g/mol and PDI = 1.31 obtained using BATTC as the RAFT agent. The initial concentration of PS was 5.00×10^{-4} M in THF.

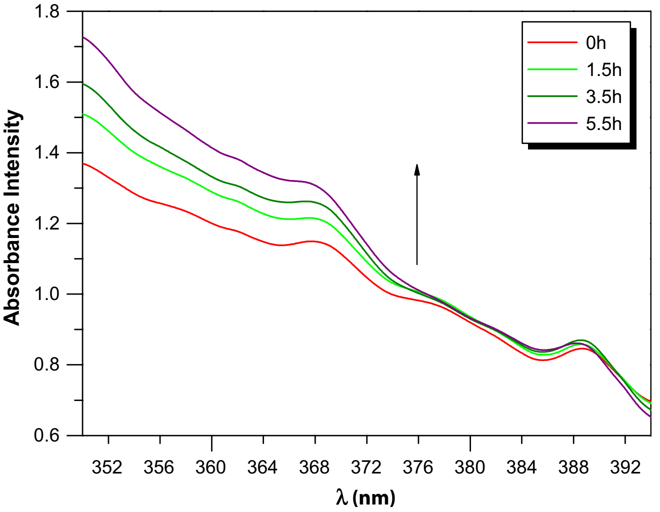


Fig. 15. UV–vis spectra of the anthryl-capped PS solution, which had been exposed to 365 nm light for 18 h, under different irradiation times at 254 nm. Sample PS with *Mn*, GPC = 3900 g/mol and PDI = 1.31 obtained using BATTC as the RAFT agent. The initial concentration of PS was 5.00×10^{-4} M in THF.

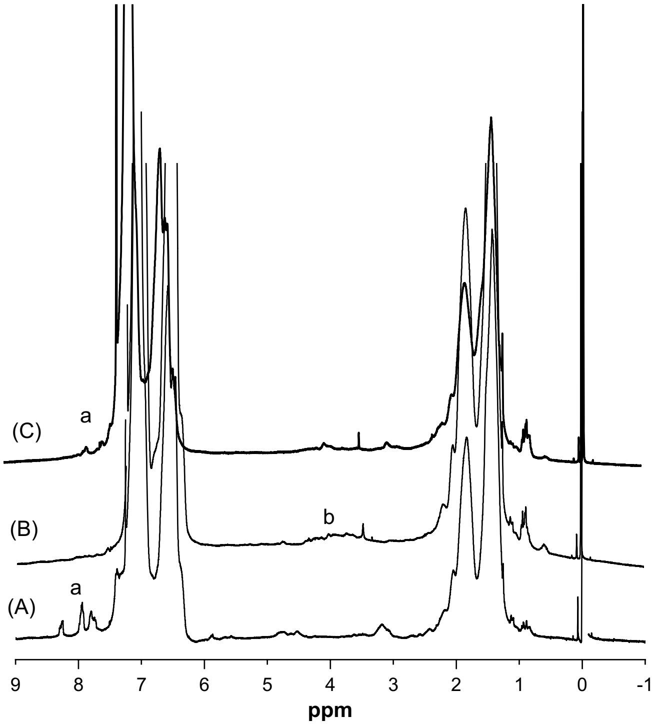


Fig. 16. Changes in ^{1}H NMR spectra of PS (Mn GPC $= 5100$ g/mol, PDI $= 1.33$) end capped with anthracene moiety in $CDCl_3$ at different irradiation conditions: (A) no irradiation; (B) 365 nm irradiation for 5 days; (C) further exposure to 254 nm for 3 days.

the RAFT agents and the corresponding PSs in THF. Fig. 11 shows the typical fluorescence emission spectra of BATTC and the corresponding PSs (PS3 ($M_{n,\,GPC} = 5100$, PDI $= 1.30$, $D_{PS} = 83.4\%$) and PS4 ($M_{n,\,GPC} = 22{,}200$, PDI $= 1.15$, $D_{PS} = 82.4\%$)) in THF at room temperature with the same concentration of anthracene groups. It can be observed that anthracene end-labeled PSs exhibited strong fluorescence emission from 375 nm to 520 nm which was characteristic of the anthracene chromophore with excitation wavelength of 369 nm, and the fluorescence intensity of PS was much stronger than BATTC and increased with the space between anthracene chromophore and dithioester group. It could be explained that the introducing St units between anthracene chromophore and dithioester group would suppress the fluorescence quenching of the anthracene dye [43–45]. For PS obtained using BNTTC as RAFT agent, the emission spectrum (Fig. 12) shows the characteristic absorption peak of naphthalene around 345 nm in THF at room temperature with excitation wavelength of 280 nm [41]. Furthermore, it can also be found that BNTTC exhibited almost no fluorescence emission under the same concentration.

It is well known that anthracene is unique in combining the advantages of having easily accessible absorption spectra, exhibiting monomer (and often excimer) fluorescence and high photoreactivity. Therefore, the photoreactivity of PS end capped with anthracene moiety was investigated in degassed THF solution (10^{-3}–10^{-4} M) and the solid film at room temperature, using 365 nm UV lamp and 254 nm UV lamp as light source. Figs. 13 and 14 respectively show the UV–vis absorption of a 5.00×10^{-4} M THF solution and a solid film of PS ($M_n = 3900$, PDI $= 1.31$). Upon irradiation with 365 nm light, the absorption maximum at 300–400 nm, characteristic of trithiocarbonate moiety and anthracene moiety, decreased with the irradiation time. It is likely due to the undergoing dimerization of anthracene groups and decomposition of trithiocarbonate groups in PS [46]. Subsequently, the PS solution which had been exposed to 365 nm light for 18 h was irradiated at 254 nm. The absorption intensity increased slightly with the irradiation time due to the regeneration of the anthracene group (Fig. 15).

^{1}H NMR spectroscopy was used to delineate the effect of irradiation by UV light on the structure of PS end capped with anthracene moiety. The result is shown in Fig. 16. It indicated that 365-nm irradiation has no effect on the PS backbone proton peaks. However, 365-nm exposure causes the peaks (a) of the anthracene protons to disappear in intensity and a new peak (b) at 4.0 ppm corresponding to bridgehead protons to appear. Further exposure of PS solution to 254-nm UV light caused the peaks ($\delta = 7.5$–8.5 ppm) of the anthracene protons to appear as shown in Fig. 16(C). These changes maybe attributed to the formation of [4 + 4] dimers [36].

GPC curves in THF of PS recorded before and after polymer irradiation with UV light confirm the photoreaction process. The results are shown in Fig. 17. After irradiation with 365 nm UV light for 5 days, the molecular weight and PDI of anthryl-capped PS (PS6) had a little change (Fig. 17(A)), whereas the molecular weight of naphthyl-capped PS (PS9) almost decreased to half (Fig. 17(B)). It

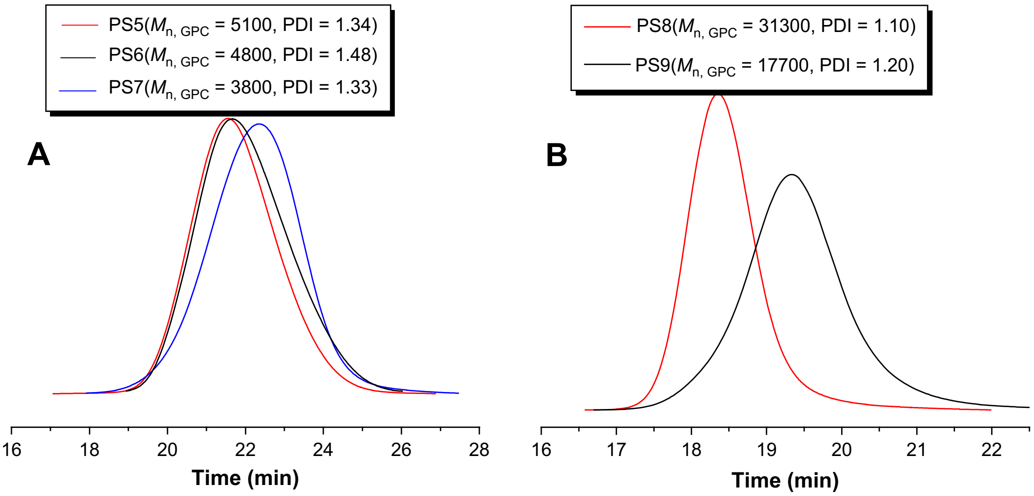


Fig. 17. Variations of the GPC traces of PSs end capped with anthracene (A) and naphthalene (B) groups during the photoconversions. (PS5: original PS end capped with anthracene group, PS6: PS5 irradiated with 365 nm UV light for 5 days, PS7: PS6 irradiated with 254 nm UV light for 3 days. PS8: original PS end capped with naphthalene group, PS9: PS8 irradiated with 365 nm UV light for 5 days.)

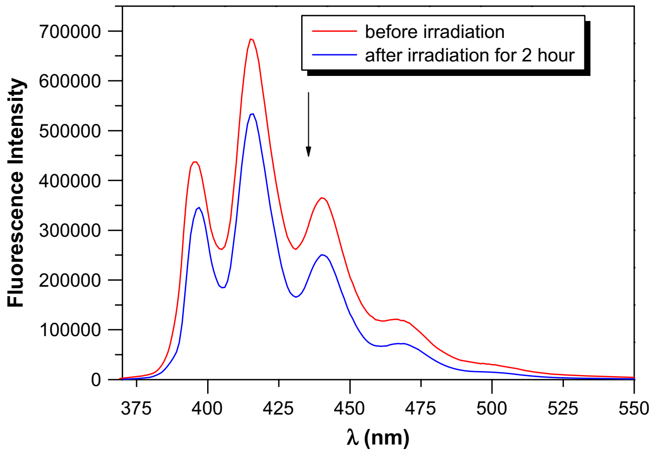


Fig. 18. Fluorescence spectra of the anthryl-capped PS (*M*n, GPC = 3900 g/mol and PDI = 1.31) before and after irradiation by 365 nm-UV light measured in THF. The concentration PS was 5.00×10^{-4} M.

can be explained that anthryl-capped PS simultaneously underwent decomposition of trithiocarbonate groups and dimerization of anthracene groups. However, just decomposition of trithiocarbonate groups occurred in naphthyl-capped PS. Furthermore, after irradiation at 254 nm, the photodimerised PS (PS6) partly restored, as proved by GPC in Fig. 17(A).

The fluorescence of the anthryl-capped PS before (0 h) and after (2 h) irradiation with 365 nm UV light was also investigated. The results are shown in Fig. 18. It could be found that the fluorescence intensity of PS after irradiation at 365 nm UV light became weaker than the original PS. It further confirmed the photoreactivity of the anthracene groups in PS.

4. Conclusions

Two novel trithiocarbonates (BATTC and BNTTC) bearing functional groups in R group were synthesized and successfully used in the RAFT polymerizations of St to prepare functional PS via a facile way. Both of them showed good controllability for both AIBN-initiated and thermal-initiated RAFT polymerization of St. The successful reaction of chain extension and analysis of ^{1}H NMR spectra of the obtained PS confirmed the existence of the functional anthracene group at the chain end of PS. The obtained PS showed typical optical properties of the anthracene and naphthalene chromophores, such as fluorescence and UV absorption and reversible photodimerization.

Acknowledgments

The financial supports of this work by the National Nature Science Foundation of China (No. 20874069), the Science and Technology Development Planning of Jiangsu Province (No. BK2007702 and BK2007048), the Nature Science Key Basic Research of Jiangsu Province for Higher Education (No. 05KJA15008) are gratefully acknowledged.

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