Polymer Bulletin 61, 287–297 (2008)
DOI 10.1007/s00289-008-0953-3

Polymer Bulletin

Synthesis and Characterizations of Triphenylamine End-Functionalized Polymers via Reversible Addition-Fragmentation Chain Transfer Polymerization

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Received: 22 February 2008 / Revised version: 14 May 2008 / Accepted: 16 May 2008

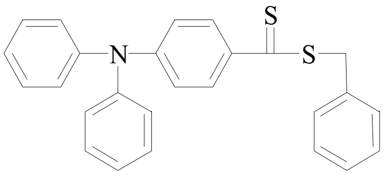
Summary

A novel reversible addition-fragmentation chain transfer (RAFT) reagent bearing triphenylamine (TPA) group, 4-diphenylamino-dithiobenzoic acid benzyl ester (DDABE), was designed and synthesized. It was used in the RAFT polymerizations of styrene (St) and methyl acrylate (MA) to prepare end-functionalized polymers. The results of the polymerization showed that the RAFT polymerizations could be well controlled using DDABE as the RAFT agent. Number-average molecular weight ($M_{n,GPC}$) increased linearly with monomer conversion, and molecular weight distributions were relatively narrow (PDI < 1.50). The results of chain-extension reaction, ^{1}H NMR spectra and UV/Vis spectra confirmed that most of the polymers chains were end-capped by the functional triphenylamine (TPA) groups. The effect of feed molar ratios of St/DDABE/AIBN on polymerization was investigated.

Introduction

The synthesis of well-defined polymers 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 polymerization (RAFT) [5-6] have extensively been reported. For NMP and ATRP, the synthesis of polymers with well-defined structures, such as block copolymers or polymers with complex architectures, 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 a widest range of monomers, and in principle, all classic radical polymerization can be used with the RAFT process in the presence of an efficient RAFT agents. According to the mechanism of RAFT polymerization proposed by Rizzardo et al. [5], the polymers obtained by RAFT polymerization are end-capped by the moieties derived from the RAFT agent. 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 RAFT polymerization (i.e., by selecting appropriate structures for the activating and leaving groups of the dithioester) [7-13]. Some chain-end functionalized polymers have been reported by designing the structures of RAFT agents. Chen et al. [14] synthesized of biotinylated stimuli-responsive polymer and diblock copolymer by RAFT polymerization using biotinylated trithiocarbonate as the RAFT agent. Wang et al. [15] reported the telechelic poly(n-butyl acrylate)s with dicarboxylic acid as functional groups via RAFT polymerization. It is well-known that TPA and its derivatives, can act as the hole-transport material, and play an important role in electronic devices such as organic light-emitting diodes (OLEDs) [16-17], organic photoreceptor devices and photo cells [18-19].

In this work, a functional dithiobenzoate, 4-diphenylamino-dithiobenzoic acid benzyl ester (DDABE) with Z group bearing the TPA moiety, was designed and synthesized. The DDABE was used as the RAFT agent to carry out the polymerizations of styrene (St) and methyl acrylate (MA). The polymers functionalized with TPA moieties at the chain ends were then obtained. Some of the optical properties of the obtained polymers were investigated, such as fluorescence intensity and UV absorption. The structure of the synthesized dithiobenzoate is presented in Scheme 1.



Scheme 1. The structure of DDABE

Experimental

Materials

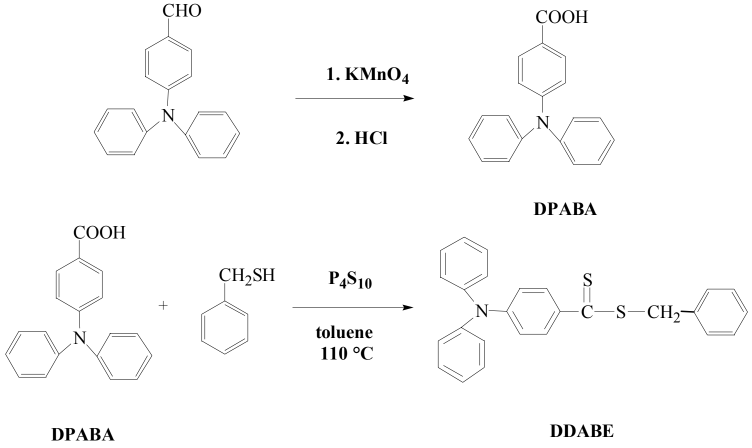
Unless otherwise specified, all chemicals were purchased from Shanghai Chemical Reagents Co., China. The monomers, styrene (St) and methyl acrylate (MA), were washed with an aqueous solution of sodium hydroxide (5 wt %) for three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, the monomers were distilled under reduced pressure and kept in a refrigerator under 0°C for short store. 4-(N, N-diphenylamino) benzaldehyde, benzyl mercaptan, and P_4S_{10} were purchased from Sigma-Aldrich Chemical Co. and used as received. Toluene was dried with 4-Å molecular sieves and distilled in vacuum.

Synthesis of 4-Diphenylamino benzoic acid (DPABA)

DPABA was achieved by the oxidation of 4-(N, N-diphenylamino) benzaldehyde with $KMnO_4$ [20]. ^{1}H NMR ($CDCl_3$, δ): 7.90, 2H (d); 7.32, 4H (t); 7.15, 6H (m); 6.99, 2H (d).

Synthesis of 4-Diphenylamino-dithiobenzoic acid benzyl ester (DDABE)

In a 250 mL three-necked round bottom flask equipped with thermometer and condenser, 3.36 g (7.5 mmol) of P_4S_{10}, 4.38 g (15 mmol) of 4-diphenylamino benzoic acid, 1.86 g (15 mmol) of benzyl mercaptan and 100 mL of toluene were added under stirring (Scheme 2). After bubbled with argon for 30 min at room temperature, the mixture was heated to 110°C and refluxed for 24 h. The reaction mixture was filtered, and the filtrate was evaporated using a rotatory evaporator. The crude product was washed thrice with petroleum ether and then further purified by column chromatography on silica oxide with petroleum ether-ethyl acetate (50 : 1, v/v) as an eluent. Yield: 35 %. The purity of the DDABE is about 99% determined from HPLC. ^{1}H NMR ($CDCl_3$, δ): 4.61, 2H (s); 6.90-6.92, 2H (d); 7.12-7.16, 6H (m); 7.27-7.31, 7H (m); 7.38-7.39, 2H (d); 7.98-8.00, 2H (d). Elem. Anal. Calcd. %: C, 75.87; H, 5.14; N, 3.40; Found: C, 75.77; H, 5.43; N, 3.01.



Scheme 2. Synthetic route of 4-Diphenylamino benzoic acid (DPABA) and 4-Diphenylamino-dithiobenzoic acid benzyl ester (DDABE).

RAFT Polymerization

The procedure of RAFT polymerization of St was as follows: a stock solution of 11 mL (96 mmol) of St, 117.9 mg (0.287 mmol) of DDABE and 15.7 mg (0.096 mmol) of AIBN were prepared, and aliquots of 1 mL were placed in each ampoule. The content was purged with argon for approximately 10 min to eliminate the oxygen. Then, the ampoules were flame sealed and placed in an oil bath held by a thermostat at 70°C to polymerize. After a preset reaction time, each ampoule was cooled with ice water and opened. The reaction mixture was diluted with tetrahydrofuran (ca. 2 mL) followed by precipitating in a large amount of methanol (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 procedures of the polymerization of MA were similar to that of St.

Characterizations

The molecular weights and polydispersities of the polystyrene (PS) and poly(methyl acrylate) (PMA) were determined using Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414), using HR 1, HR 2 and HR 4 (7.8×300 mm, 5 μm beads size) columns with molecular weights ranged

$10^2 \sim 5\times10^5$ g/mol. THF was used as an eluent at a flow rate of 1.0 mL/min and 30°C. The GPC samples were injected using a Waters 717 plus autosampler. PS and PMA were calibrated with polystyrene and poly(methyl methacrylate) standards from Waters, repectively. ^{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, and N 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 eluent at 30°C.

Results and discussion

RAFT polymerizations of St and MA with DDABE as a RAFT agent

The RAFT polymerizations of St and MA using AIBN as an initiator at 70°C were carried out with DDABE as the RAFT agent. The results are showed in Figures 1 and 2, respectively. In Figure 1, the linear relationships between $\ln([M]_0/[M])$ and the reaction time for both of the RAFT polymerizations indicated that the concentration of free radicals remained constant during the polymerizations. The number-average molecular weights ($M_{n,GPC}$) increased almost linearly with monomer conversion and were close to the calculated value ($M_{n,th}$, calculated via Equation 1) as shown in Figure 2. The polydispersities were relatively narrow (PDI < 1.50). These results showed that DDABE was an effective RAFT agent for both of the RAFT polymerizations of St and MA.

$$M_{\mathrm{n,th}} = \frac{monomer\ \ weight}{mole\ of RAFT} \times conversion + M_{\mathrm{RAFT}} \qquad \textbf{(1)}$$

M_{RAFT}: molecular weight of RAFT agent.

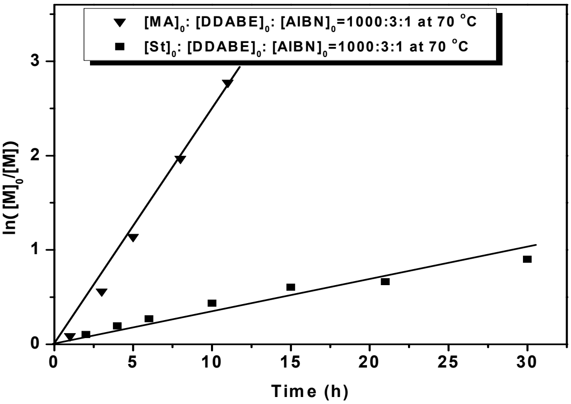


Figure 1. Relationships between ln ($[M]_0/[M]$) and the polymerization time for the RAFT polymerizations of St and MA at 70°C in bulk. ($[\text{monomer}]_0 : [\text{DDABE}]_0 : [\text{AIBN}]_0 = 1000 : 3 : 1$).

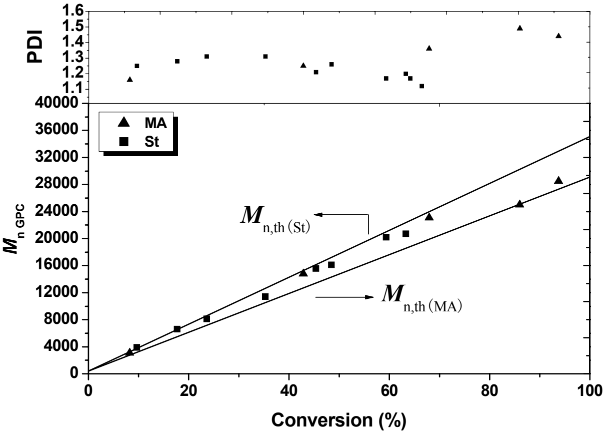


Figure 2. Dependence of number-average molecular weights ($M_{n,GPC}$) and PDIs on monomer conversions for the RAFT polymerizations of St and MA at 70°C in bulk. ($[monomer]_0 : [DDABE]_0 : [AIBN]_0 = 1000 : 3 : 1$).

In order to investigate the influence of the $[St]_0/[DDABE]_0/[AIBN]_0$ molar ratio on the RAFT polymerization of St, polymerizations with different feed molar ratios ($[St]_0$: $[DDABE]_0$: $[AIBN]_0$= 1000 : 3 : 1, 1000 : 6 : 2, 1000 : 10 : 3) were conducted. The results are showed in Figure 3 and Figure 4, respectively. As the ratio of $[St]_0$: $[DDABE]_0$ changed from 1000 : 3 to 1000 : 6, no obvious effect on polydispersity indexs (PDIs) was observed. The polymerization rates at the molar ratios of 1000 : 3 : 1 ($[St]_0$: $[DDABE]_0$: $[AIBN]_0$) was lower than that of 1000 : 10 : 3 (Figure 3). The reason may be due to the more effects from the increase of the initiator concentration than retardation effects by the increase of RAFT agent concentration [21-25]. In all cases, the $M_{n,GPC}$ increased almost linearly with monomer conversion, and it was close to the calculated value ($M_{n,th}$) with relatively low PDI values (PDI < 1.5) as showed in Figure 4.

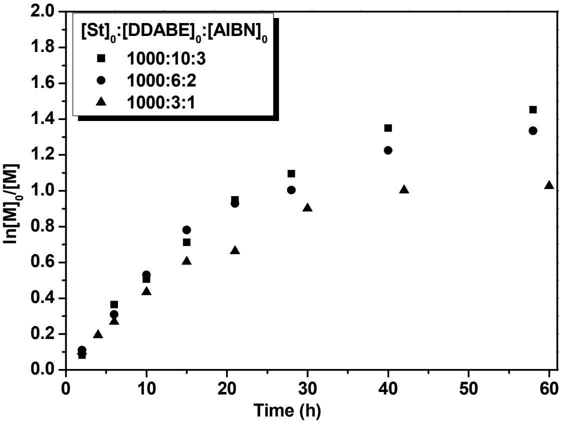


Figure 3. Relationships between ln ($[M]_0/[M]$) and polymerization time for the RAFT polymerizations of St at 70°C in bulk at different molar ratios of $[St]_0$/ $[DDABE]_0$/$[AIBN]_0$.

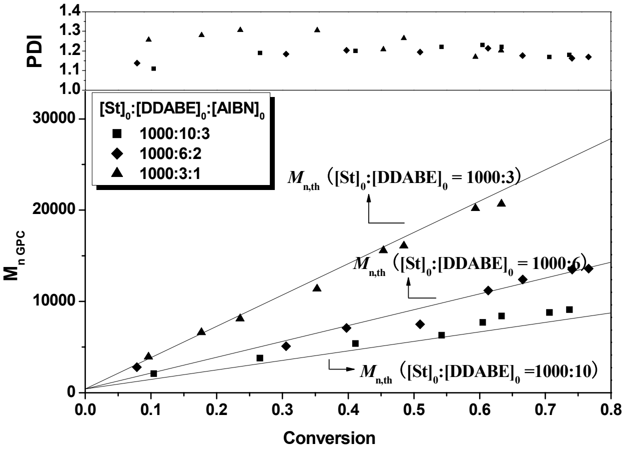


Figure 4. Dependence of the $M_{n,GPC}$ and PDIs on the monomer conversions for the RAFT polymerizations of St at 70°C in bulk under different feed molar ratios of $[St]_0/[DDABE]_0/[AIBN]_0$.

End Group Analysis and the Chain Extension

The structures of polymers obtained were characterized by ^1H NMR. The spectra of PS and PMA obtained via RAFT polymerization using DDABE as the chain transfer agent are showed in Figure 5 and Figure 6, respectively. The signals of the aromatic protons (a) and benzylic protons (b) from DDABE of PS were observed at chemical shifts of 7.2-8.0 and 3.4 ppm in Figure 5. In Figure 6, the signals at 7.90-8.00 (a), 7.25-7.40 ppm (d), 7.05-7.20 ppm (b,e,f,g), and 6.80-6.95 ppm ppm (c) could be attributed to the protons of the TPA group (a,b,c,d), and phenyl protons on the R group of DDABE (e, f, g). These results indicated that the TPA moieties of DDABE were attached to polymer chain-ends. Furthermore, the molecular weight of PS can be calculated from the ^1H NMR spectrum ($M_{n,NMR}$ = 7300 g/mol, by Equation 2) in Figure 5, which was deduced from the assumption that each polymer chain end was capped with TPA group.

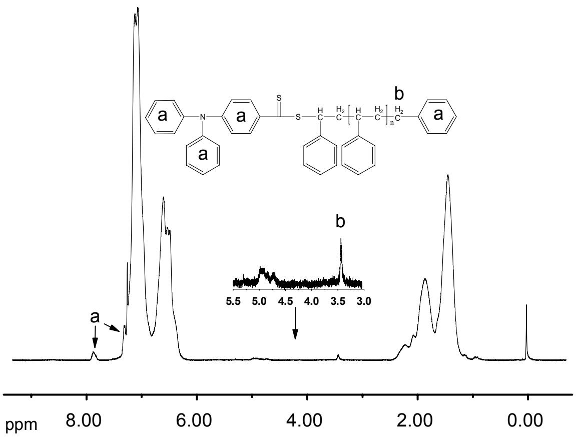


Figure 5. Typical ^1H NMR spectrum of PS prepared via RAFT polymerization using DDABE as the RAFT agent. (solvent: $CDCl_3$, TMS as the internal standard, $M_{n\,GPC}$ = 6600 g/mol, PDI = 1.28).

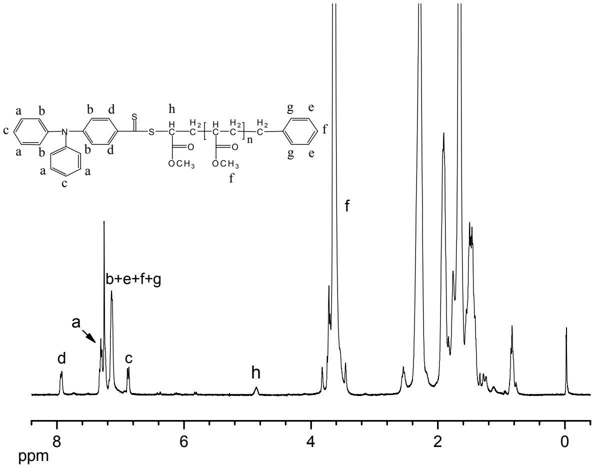


Figure 6. ^{1}H NMR spectrum of PMA prepared via RAFT polymerization using DDABE as the RAFT agent. (solvent: $CDCl_3$, TMS as the internal standard, $M_{n\,GPC}$ = 8400 g/mol, PDI = 1.28).

With the $M_{n,\ NMR}$ and $M_{n,\ GPC}$, the living polymer chains, i. e., the content of polymers capped with TPA group in the products (C_{PS}), was about 90% calculated with Equation 3. Since both of DDABE and polymer showed characteristic UV/Vis absorption peak of TPA group at 424.6 nm, the numer-average molecular weights of polymers can also be measured through the UV/Vis spectrum. The calibration curve was obtained by DDABE in THF at room temperature. The results showed that 84% of polymer ($M_{n,GPC}$ = 6600 g/mol, PDI = 1.28) was end-capped with TPA group calculated from the intesity of UV/Vis absorption, and that the corresponding molecular weight from UV/Vis was 7800 g/mol, which was a little higher than that obtained from NMR results for the same polymer sample. The differences of the obtained two C_{PS} values may be caused by the measure error in NMR and UV/Vis methods.

$$M_n = \left(\frac{I_{0.90\sim2.40}}{3} / \frac{I_{7.70\sim8.00}}{2} \right) \times MW_{St} + M_{n\ DDABE} \qquad \textbf{(2)}$$

$I_{0.90\text{-}2.40}$: the integral of the signals at 0.90-2.40 ppm;
$I_{7.70\text{-}8.00}$: the integral of the signals at 7.70-8.00 ppm.
MW_{St} : molecular weight of St.

$$C_{PS}\ (\%) = M_{n,\ GPC} / M_{n,\ NMR} \qquad \textbf{(3)}$$

An additional method of confirming the "living"/controlled fashion of the polymerization is to carry out the chain-extension reaction. A typical chain extension experiment of the PS was carried out using the PS ($M_{n,GPC}$ = 8500 g/mol and PDI = 1.22), obtained by $[St]_0$: $[DDABE]_0$: $[AIBN]_0$ = 1000 : 3 : 1 at 70°C for 6 h, as the macro-RAFT agent and MA as the second monomer. The chain-extension reaction was performed with the molar ratio of 1000 : 3 : 1 ($[MA]_0$:$[PS]_0$:$[AIBN]_0$) at 70°C for 6 h with 82.1% conversion. GPC curves of the original and chain-extended polymers are showed in Figure 7. The $M_{n,GPC}$ increasd from 8500 to 25000 g/mol, and the PDIs of the polymers had a little change, from 1.22 of PS to 1.36 of PS-*b*-PMA. The peak of original PS disappeared thoroughly, indicating that the most of the original polymer

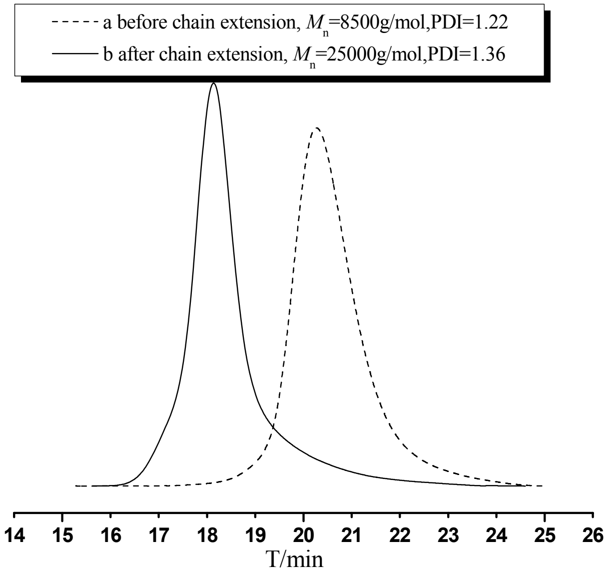


Figure 7. GPC curves for the chain extension of PST used as macro-RAFT agent. (a) polymer before chain extension, (b) polymer after chain extension ($[MA]_0$: [macro-RAFT agent]$_0$: $[AIBN]_0$ = 1000 : 3 : 1, temperature = 70°C, 6 h, conversion = 82.1%).

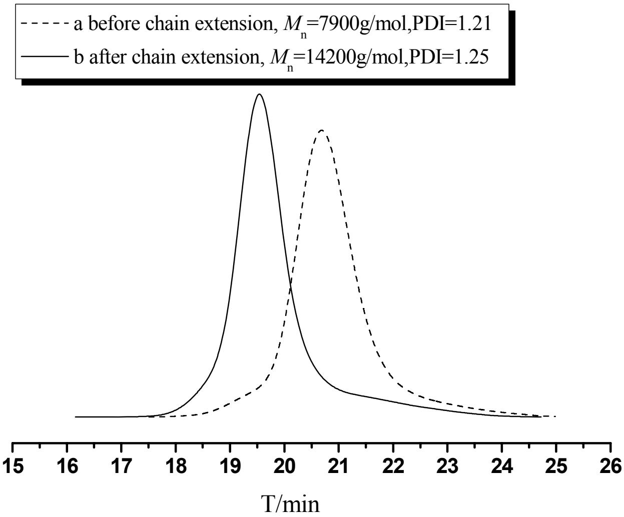


Figure 8. GPC curves of the chain extension of PMA used as macro-RAFT agent. (a) polymer before chain extension, (b) polymer after chain extension ($[St]_0$: [macro-RAFT agent]$_0$: $[AIBN]_0$ = 1000 : 3 : 1, temperature = 70°C, 6 h, conversion = 23.3%).

chains contained the moiety of RAFT agent, and can be reactived with MA. This result was consisted with the results showed in ^{1}H NMR characterization.

Furthermore, the chain extension of obtained PMA was also carried out using St as the second monomer at 70°C. The GPC traces of the original PMA and the chain-extended block copolymer are showed in Figure 8. There was also an obvious peak shift from PMA (M_n = 7900 g/mol, PDI = 1.21) to PMA-*b*-PS (M_n = 14200 g/mol, PDI = 1.25, $[St]_0:[PMA]_0:[AIBN]_0$ = 1000:3:1, at 70°C for 6 h with 23.3% conversion). The results indicated that the original polymer was still active.

Thus, all the above evidence showed that DDABE was an effective RAFT agent for the RAFT polymerizations of St and MA under these experimental conditions.

Optical properties of the RAFT agent (DDABE) and the corresponding polymers

Triphenylamine is a rigid and conjugated molecule with strong fluorescence. Incorporating TPA moiety into DDABE, which acted as a RAFT agent in the RAFT polymerization of St, can produce the PS with TPA end-capped at the polymer chain. The expectation was confirmed by the ^{1}H NMR spectrum of PS (Figure 5). Therefore, the fluorescence of DDABE and the PS were investigated, the fluorescence spectra are showed in Figure 9. It can be observed that the PS with TPA end-labeled exhibited strong fluorescence emission in a wide wavelength region, and the wavelength of the maximum fluorescence intensity was around 475 nm. DDABE exhibited a little higher intensity of fluorescence emission than the obtained PS with the same concentration of TPA moiety. The fluorescence intensity are reported to be dependent on the environment of fluorescent chromophore [26]. The attachment of the polystyrene chain to the TPA moiety may change the polarity of the TPA, which may result in the change of the fluorescence emission.

Furthermore, according to the high sensitivity of TPA group to UV light, the measurements of UV spectroscopy of the TPA-based RAFT agent and the corresponding polymers in THF were carried out. Figure 10 shows the UV spectra of DDABE and the corresponding PS. It can be found that both DDABE and the corresponding PS showed strong UV absorption at round 424 nm, corresponding to the absorption by the TPA moiety. In addition, the intensity of absorption of DDABE was stronger than that of the corresponding polymers at the same concentration. Meanwhile, it was also found that the molecular weight of the polymer had no obvious effects on the UV absorption, which further indicated that most of polymer chains were end-capped by TPA moieties from the Z group of DDABE.

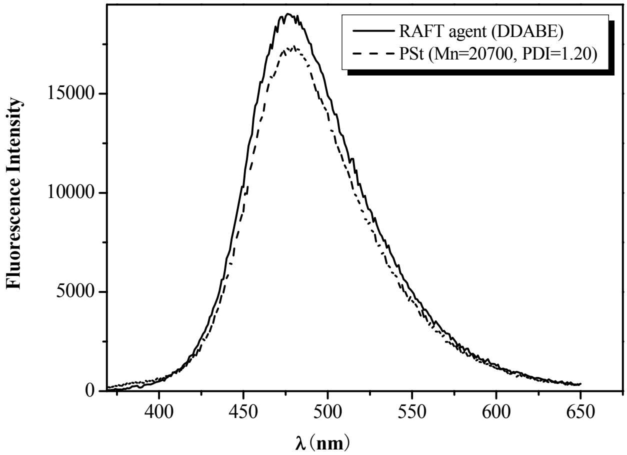


Figure 9. Fluorescence spectra of DDABE and the obtained PS in THF at room temperature. The concentration of TPA moiety is 5.00×10^{-5} M for DDABE and PS, λ_{ex} = 346 nm.

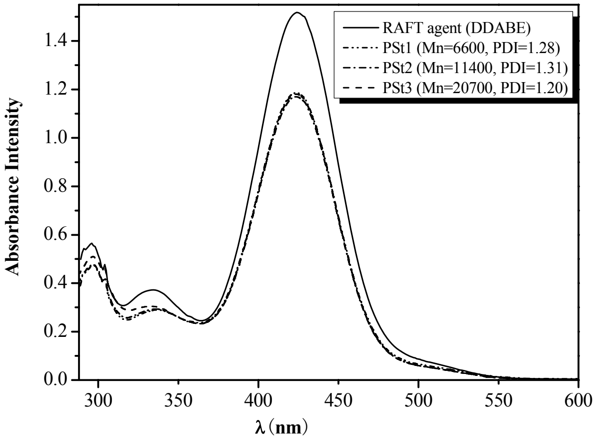


Figure 10. UV-Vis spectra of DDABE and the corresponding PS in THF. The concentration of TPA moiety is 5.00×10^{-5} M.

Conclusions

A novel dithiobenzoate (DDABE) bearing triphenylamine moiety in Z group was synthesized and used in the RAFT polymerizations of St and MA. The RAFT polymerizations of St and MA were well-controlled. The obtained polymer was characterized by ^{1}H NMR and UV spectroscopy. Most of the polymer chains were end-capped by the TPA moieties. The obtained PS showed typical optical properties of TPA, such as fluorescence emissions and UV absorption.

Acknowledgements. The financial supports of this work by the National Nature Science Foundation of China (No.20574050), 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), and the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20040285010) are gratefully acknowledged.

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