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Synthesis of polystyrene end-capped with pyrene via reversible addition–fragmentation chain transfer polymerization

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Abstract

A novel benzodithioate compound with a pyrene structure in the R group, pyrenylmethyl benzodithioate (PMB) was synthesized. Using PMB as the chain transfer agent (CTA), the RAFT polymerizations of styrene with AIBN as an initiator were carried out in different reaction conditions. The results indicated that PMB was an effective CTA for the RAFT polymerizations of styrene with the "living"/controlled characteristics. The structures of the obtained polymers were characterized by ^{1}H NMR. The results showed that majority of the polymer chains contained the pyrene moiety in the chain end. The enhanced fluorescence property in $CHCl_3$ solution was observed. The chain-extension experiments of the obtained polystyrene (PS) with the monomers of styrene and methyl acrylate were successfully carried out.

Keywords: Pyrenylmethyl benzodithioate; RAFT; Styrene

1. Introduction

The living free radical polymerization offers chemists a powerful tool to synthesize polymers with pre-designed structures. The most widely used living radical polymerization techniques are stable free radical polymerization (SFRP) [1], atom transfer radical polymerization (ATRP) [2,3] and reversible addition–fragmentation chain transfer (RAFT) [4,5] polymerization. The RAFT polymerization has been considered as the most versatile and robust method, since it can be compatible with almost all monomers and reaction conditions that are applicable to conventional free radical polymerizations [6–14]. The RAFT process and its benefits are achieved simply by the addition of a suitable RAFT agent to the reaction mixture.

In Scheme 1, the simplified RAFT mechanism is depicted [15]. The structures of R and Z of the RAFT agent would exist in the chain ends of the final polymers. Thus, the end group of the polymer can be pre-designed by choosing the RAFT agent with the desirable structures. Our group has reported the successful synthesis of 1,3-benzodioxole and anthracene end-capped polymers via RAFT polymerization [16,17]. Pyrene is a widely used fluorescent 'reporter group' in the study of conformational behaviors of macromolecule [18,19], micelles [20], and supramolecules [21]. However, under the conditions the relationship between the pyrene and the target molecule is maintained through weak absorption or hydrogen bond. This weak relationship limited the application of pyrene in nonabsorption or high vibration systems. Through the design and synthesis of pyrene end-labeled polymers, the pyrene group can be attached firmly via a carbon–carbon bond at the polymer ends. This strategy could provide more accurate results and produce wide applications. To the best of our knowledge, there are relatively few reports on the synthesis of pyrene end-labeled polymers. Pyrene end-capped polymers that were reported can be prepared via anionic polymerization [22,23] and ATRP [24–26]. Recently, Nakayama and Okano [27] and Scales et al. [28] both reported the similar pyrene

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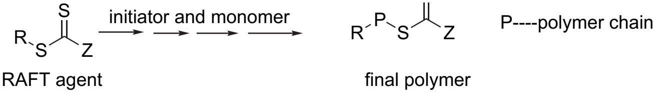


Scheme 1. Simplified commonly accepted RAFT process.

end-capped polymers via RAFT polymerization. However, the method they used contained several steps. Here we designed and synthesized a novel dithioester with pyrene structure in the R group. The RAFT polymerization of styrene (St) was successfully carried out using this pyrene containing dithioester as the RAFT agent. Pyrene end-capped polystyrene (PS) with the controlled molecular weight and narrow polydispersity was obtained via a simple method. It should be noted further that the fluorescence of pyrene can be maintained without affecting by the obtained polymer.

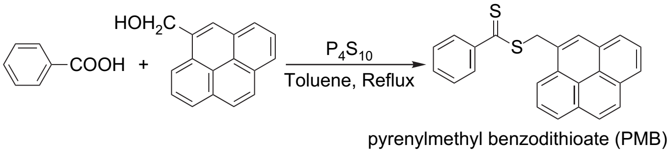
2. Experiment

2.1. Materials

All chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents Co. Ltd of China and J&K-Acros. 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 dried with anhydrous magnesium sulfate, the monomers were distilled under reduced pressure and kept in a refrigerator at 4 °C. Azobisisobutyronitrile (AIBN, 99%) was recrystallized twice from ethanol and dried in vacuum at room temperature overnight. Other materials were used without further purification.

2.2. Synthesis of the RAFT agent

The pyrenylmethyl benzodithioate (PMB) was synthesized by coupling benzoic acid and pyrenylmethanol under P_4S_{10} (Scheme 2) [29−31]. A typical reaction procedure was as follows: benzoic acid (0.62 g, 5 mmol), pyrenylmethanol (1.18 g, 5 mmol), P_4S_{10} (1.11 g, 2.5 mmol) and 30 mL of toluene were added to a 100 mL three-neck round-bottom flask. The reaction mixture was stirred at room temperature for 0.5 h and then at 110 °C for about 20 h under argon atmosphere. The reaction solution was filtrated after cooling to room temperature. The solvent was removed by rotation evaporation and the resultant product was a dark reddish crystal solid. The crude product was purified by column chromatography on silica oxide with mixed petroleum ether and benzene from 20:1 to 10:1 (v/v). The pure PMB was obtained as a red crystal solid (0.39 g, 21%). m.p. 118.6−121.4 °C. ^1H NMR (400 MHz $CDCl_3$) δ 5.3 (s, 2H), 7.0−7.5 (m, 5H), 7.8−8.3 (m, 9H). ^{13}C NMR (100 MHz $CDCl_3$) δ 228.27, 145.10, 139.10, 132.94, 131.56, 131.72, 131.32, 130.02, 128.83, 128.29, 128.15, 127.81, 127.43, 126.61, 126.01, 125.93, 125.30, 123.33, 41.60. Elemental analysis Calcd (%): C 78.22, H 4.38, S 17.40; Found (%): C 77.86, H 4.83, S 16.51.



Scheme 2. Synthetic route of the RAFT agent (PMB).

2.3. Polymerization of St

A master batch of 8 mL (69.5 mmol) of styrene, 153.7 mg (0.417 mmol) of PMB and 22.8 mg (0.139 mmol) of AIBN was prepared, and aliquots of 1 mL were put into the 2 mL ampules. The reaction mixture was purged with argon for approximately 10 min to eliminate oxygen. Then the ampules were flame sealed. The polymerization reaction was performed at the pre-determined temperature. After the determined reaction time, each ampule was quenched in ice water, and then opened. The reaction mixture was diluted with about 2 mL of THF, and precipitated in about 200 mL of methanol. The final polymer was obtained by filtrating and drying at room temperature under vacuum to a constant weight. Conversion of styrene was determined gravimetrically.

2.4. Chain extension of PS

A pre-determined quantity of PS, obtained by RAFT process, was dissolved in styrene (or MA). The content was bubbled with argon for 20 min. The other procedures were the same as described above, except that the RAFT agent was replaced by the PS above.

2.5. Decomposition of dithioester group from PS

PS (0.805 g, $M_n = 8193$, PDI = 1.25) in 10 mL THF was added into a 50 mL round flask. Triethylamine (3 mL) and zinc powder (1.5 g) were added under the nitrogen atmosphere. The reaction mixture was stirred under nitrogen atmosphere at 30 °C for 48 h. The resulted solution was precipitated into 250 mL methanol. A white powder (0.56 g, 69%) was obtained after filtration followed by vacuum drying.

2.6. Characterization

The molecular weights (M_ns) and polydispersity indices (PDIs) of polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector, using HR 1, HR 3, and HR 4 columns with molecular weight range 100−500,000 calibrated with polystyrene standard samples. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. ^1H NMR spectra of the polymers were recorded on an INOVA400 nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. Elemental analyses (EA) of C, H and N were measured by the EA1110 CHND-S. The fluorescence intensity was measured by FLS920.

3. Results and discussions

The pyrenylmethyl benzodithioate (PMB) was synthesized for the first time via the simple one step method as shown in Scheme 2. The PMB was purified by the column separation to produce a red crystal. The structure of PMB was confirmed by ^{1}H NMR, ^{13}C NMR and elemental analysis. The PMB was used as RAFT agent to give rise to the controlled free radical polymerization of styrene with AIBN as the initiator. Fig. 1 shows the kinetic plots of the RAFT polymerization with [styrene]$_0$:[PMB]$_0$:[AIBN]$_0$ of 500:2:1 at 70 °C. The polymerization exhibited fast and linear kinetics as the polymerization time shorter than 12 h, while the polymerization slowed down to a relatively low rate as the time longer than 15 h. The decomposition rate of AIBN at 70 °C in styrene is 4.72×10^{-5} s^{-1}, e.g. $t_{1/2} = 4.08$ h [32], which means that the free radicals from AIBN decomposition would be exhausted after 12 h. As a result, the concentration of overall propagating free radicals would fall into a relatively low and constant level, which showed the decrease in polymerization rate. The dependences of M_n and PDI on monomer conversion are shown in Fig. 2. It can be noted that the M_ns increased linearly with monomer conversion, and the M_ns from GPC results were very close to the corresponding theoretical values ($M_{n(th)}$). The PDIs of polymers were in the range of 1.1–1.3.

The structure of the obtained PS was also characterized by ^{1}H NMR spectra given in Fig. 3. The chemical shifts at $\delta = 7.6$–8.2 ppm were attributable to the protons in the pyrene group which serves as the R group in PMB. The appearance of the pyrene group proton signals indicated that the moieties of PMB remained intact at the chain ends of PS. It should be noted that the samples used for NMR analyses were carefully purified by successive dissolution/precipitation cycles with THF and methanol.

Furthermore, the molecular weight ($M_{n(NMR)}$) can be calculated from the ratio of protons in PS to the protons of pyrene at the chain ends of PS. The equation is showed as below:

$$M_n = \left(\frac{I_{0.9-2.0}/3}{I_{7.6-8.2}/9}\right) \times \text{Molecular weight of styrene}$$

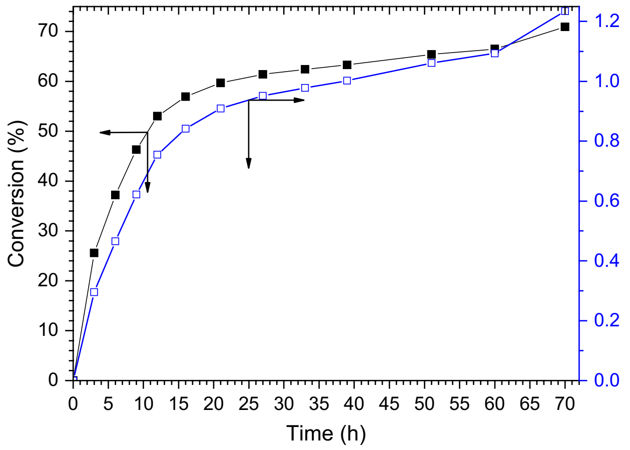


Fig. 1. Conversion and logarithmic plot of conversion vs time in the polymerization of styrene with PMB as the RAFT agent and AIBN as the initiator at 70 °C in bulk. [styrene]$_0$:[PMB]$_0$:[AIBN]$_0$ = 500:2:1.

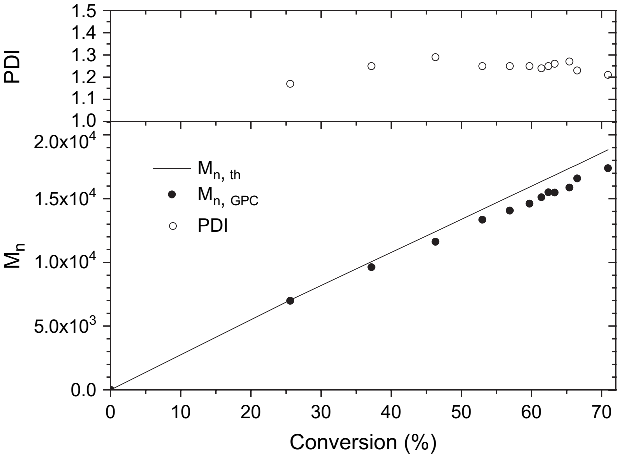


Fig. 2. Relationships of M_ns and PDIs with conversion in the RAFT polymerizations of styrene using PMB as the RAFT agent and AIBN as the initiator at 70 °C in bulk. [styrene]$_0$:[PMB]$_0$:[AIBN]$_0$ = 500:2:1.

where $I_{0.9-2.0}$: integral of the signals at 0.9–2.0 ppm and $I_{7.6-8.2}$: integral of the signals at 7.6–8.2 ppm.

The molecular weight calculated from the ^{1}H NMR spectroscopy was 8723 g/mol, which was deduced from the assumption that every polymer chain end was capped with a pyrene ring. The molecular weight from GPC was 6980. Thus the actual concentration of pyrene end-capped PS can be estimated by 6980/8723 (0.8). This result indicated that 80% chains of the polymers were end-functionalized with the group of pyrene. The polymers showed characteristic UV–vis absorption peak of pyrene group at 344.5 nm [27]. Thus, the degree of pyrene end-functionalizing in polymers also can be measured through the UV–vis spectrum. The calibration curve was obtained by pyrenylmethanol in chloroform. The results showed that there were 90% of polymer 1 ($M_n = 8200$, PDI = 1.23) and 79% of polymer 2 ($M_n =$ 23,300, PDI = 1.25) end-capped with pyrene. The result

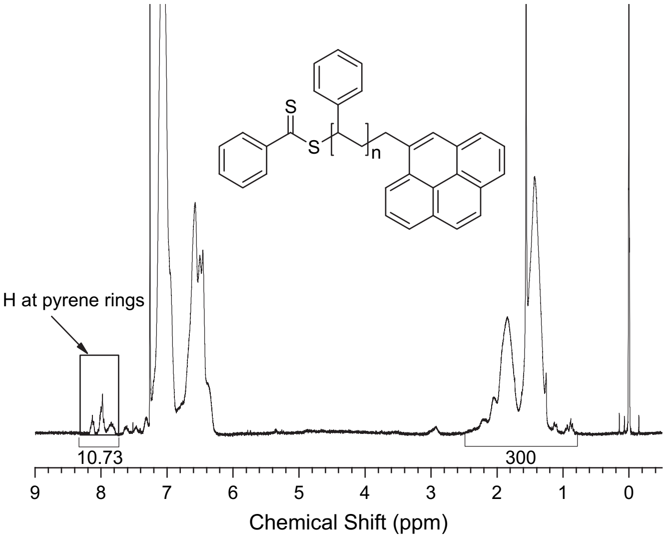


Fig. 3. ^{1}H NMR characterization of the PS obtained from the PMB mediated RAFT polymerization with the $M_n = 6980$ and PDI = 1.17.

obtained from UV–vis (90% for $M_n = 8200$) was higher than that obtained from NMR (80% for $M_n = 6980$) with the similar molecular weight. The difference may be caused by the measurement error in NMR. The signal of pyrene in NMR spectrum is very weak. It is hard to calculate the exact value of the integral within the NMR spectrum, which should be responsible for the error caused. Lower percentage of pyrene end-capped polymer chain in higher molecular weight should be caused by more side reaction (transfer to monomer, termination, etc.) at higher conversion than that of lower conversion. Furthermore, some polymers that were formed from the initiator also would result in the non-pyrene end-capped chains.

Generally the polymer obtained from RAFT polymerization should be end-labeled with the functional dithio-groups in the other end. However, it is difficult to figure out the percent of ditho-group end-labeled in the other end from the ^{1}H NMR spectrum in present work. This is because the RAFT agent (PMB) contained the same benzene group with styrene. Therefore, the chain-extension behavior of the obtained polymers was carried out to confirm the dithio-group end functionality of the polymers. Fig. 4 shows the GPC traces of the original PS and the two chain-extended polymers using styrene and MA as the second monomers, respectively. Initially the polymer ($M_n = 3780$, PDI = 1.14) was added to the solution of fresh styrene and AIBN with the molar ratio of $[\text{styrene}]_0:[\text{macro-RAFT}]_0:[\text{AIBN}]_0 = 500:3:1$. The polymerization is carried out at 90 °C for 0.75 h to result in a 19.4% of conversion. The GPC traces of original macro-RAFT agent and the chain-extended polymers (listed in Fig. 4) showed that the molecular weight increased from 3780 g/mol for the original polymer to 4770 g/mol after chain extension, while the PDI remained the same. Secondly the same original polymer as the macro-RAFT agent was added to the solution of fresh MA and AIBN with the molar ratio of $[\text{MA}]_0:[\text{macro-RAFT}]_0:[\text{AIBN}]_0 = 500:3:1$. A block copolymer PS-*b*-PMA with $M_n = 5140$ and PDI = 1.17 was obtained with a conversion of 22.6% after 0.75 h at 90 °C. No peak of the original polymer was observed in the GPC curves of the chain-extended polymers. This result confirmed that the original polymer was end-labeled with the dithio-groups in high level, which was consistent with the common point of view in the RAFT polymerization [33].

Furthermore, the effects of RAFT agent concentration and temperature on the polymerization behaviors were also investigated. Figs. 5 and 6 show the polymerization kinetics and relationships between M_ns, PDIs and conversions in different molar ratios of monomer, RAFT agent and AIBN at 90 °C. The polymerization rate decreased with an increase in polymerization time. These results were similar to those showed in Fig. 1. At the early period of the polymerization (0–3 h), there was considerable concentration of AIBN-derived free radicals. As the time was prolonged, the AIBN was exhausted to result in very small or even no "fresh" free radical decomposed from AIBN in the polymerization system. The polymerization rate was dropped. The decomposition rate of AIBN at 90 °C is one order larger than that at 70 °C ($k_d = 4.86 \times 10^{-4}\ \text{s}^{-1}$ at 90 °C and $4.72 \times 10^{-5}\ \text{s}^{-1}$ at 70 °C) [32], which will result in the early exhaust of AIBN, e.g. the polymerization rate turning

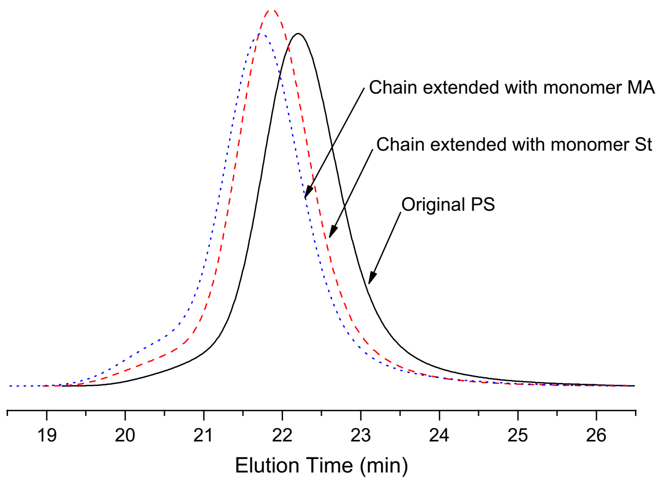


Fig. 4. The GPC traces of the original PS and the chain-extended polymers with styrene and MA as the second monomers, respectively.

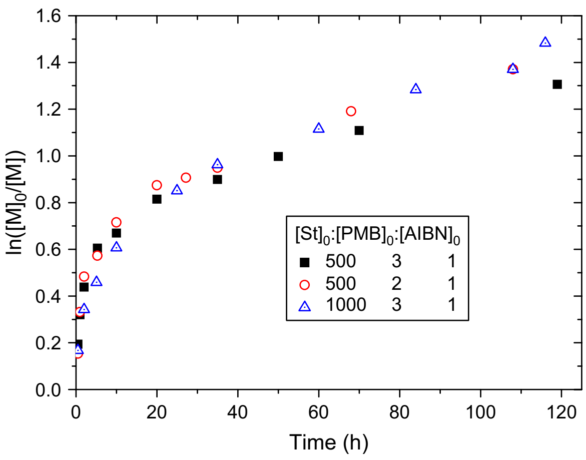


Fig. 5. Kinetic plots of RAFT polymerizations of styrene at different molar ratios of styrene, PMB and AIBN at 90 °C in bulk.

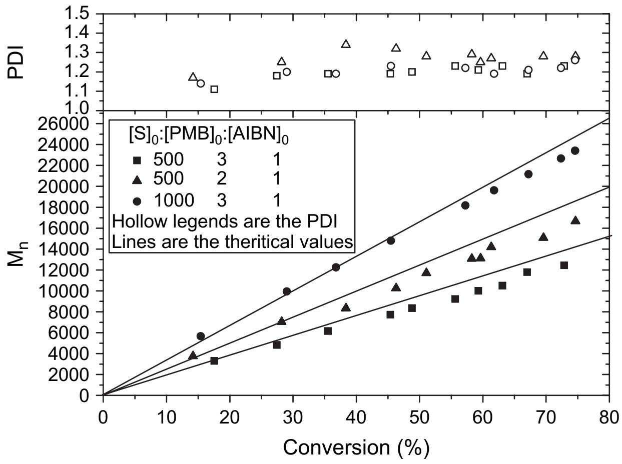


Fig. 6. Relationships of M_ns and PDIs with conversion in the RAFT polymerizations of styrene at different molar ratios of styrene, PMB and AIBN at 90 °C in bulk.

point appeared much earlier at 90 °C (about 3 h) than at 70 °C (about 12 h). In addition, the results in Fig. 5 also indicated that the polymerization rate was almost the same for the molar ratios of $[\mathrm{St}]_0$:$[\mathrm{PMB}]_0$:$[\mathrm{AIBN}]_0$ from 500:3:1 to 500:2:1. These results indicated that the polymerization was without retardation, similar to the RAFT polymerization of styrene using CPDB as the RAFT agent. The pyrene methyl R group of PMB showed the same effect of phenyl R group of phenyl dithiobenzoate in the RAFT polymerization of styrene [34]. Fig. 6 shows the good controllability of PMB in the RAFT polymerization of styrene in these cases.

Pyrene is the widely used fluorescence dye in the investigation of polymer morphology [18] and micelle behavior [20]. The PS obtained in this study is end-labeled with pyrene as mentioned above. The fluorescence spectrum of the obtained PS in $CHCl_3$ solution was characterized by using the excitation wavelength of 350 nm (Fig. 7). The results indicated that the strong fluorescence appeared in the solution of PS. There were three typical peaks in the spectrum and the maximum of emission was all around 380 nm, which was consistent with that reported [35]. In a control experiment, the $CHCl_3$ solution of PMB with the same pyrene moiety concentration as the PS solution did not show fluorescence. This was considered as the result of the adjacent sulfur existed in the structure of PMB (see Scheme 2). The sulfur atom is a well known fluorescence quenching agent [36]. From the structures of the RAFT obtained PS and PMB, the sulfur atom is far from the chromophore, e.g. pyrene in the polymer, while the sulfur atom is near to the chromophore in PMB. Therefore their fluorescence intensities are different. In order to further investigate this hypothesis, the fluorescence spectrum for pyrene containing PS without the dithio-group is also showed in Fig. 7. The dithioester end group was decomposed with alkaline. The result showed that there was no obvious difference between the fluorescence spectra for the polymers with and without dithioester group. The result confirmed that the distance between dithioester and pyrene would have great effect on the fluorescence quenching effects.

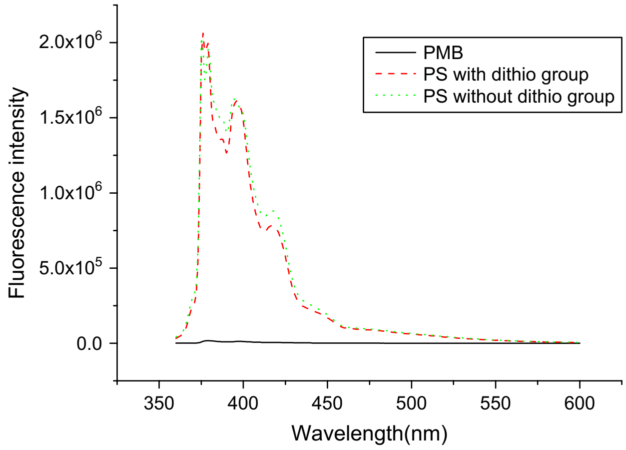


Fig. 7. Fluorescence spectra of pyrene containing PS with and without dithioester group and PMB in $CHCl_3$ with the exciting wavelength of 350 nm. Concentration of PMB unit in the PS and PMB solutions is 1×10^{-4} mol/L.

4. Conclusion

A novel pyrenylmethyl benzodithioate (PMB) with pyrene structure in the R group was designed and successfully synthesized. The RAFT polymerization of styrene using PMB (as the RAFT agent) and AIBN (as the initiator) was studied. The obtained polymers showed controlled molecular weights and narrow polydispersity indexes (PDI = 1.1–1.3). The polymerization rate decreased to a low level after the exhaustion of AIBN both at 70 °C and 90 °C. The structure of the obtained polymer was characterized by ^{1}H NMR spectroscopy. It was found both from NMR and UV–vis method that above 80% chains of the polymers contained the pyrene structure in the ends. The block copolymer of MA and styrene is prepared via the successful chain extension of the obtained PS. The RAFT polymerization of styrene using PMB as the RAFT agent did not exhibit obvious retardation. In addition, the obtained PS showed strong fluorescence intensity in $CHCl_3$. The easy way to prepare the pyrene end-labeled polymers provides a useful tool in the polymer morphology field.

Acknowledgments

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