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Preparation and Characterization of Anthracene End-Capped Polystyrene via Reversible Addition-Fragmentation Chain Transfer Polymerization

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Summary

A novel benzodithioate compound with an anthracene structure (anthracen-9-ylmethyl benzodithioate, AMB) was synthesized. Using AMB as the chain transfer agent, the RAFT polymerizations of styrene with AIBN as an initiator were carried out in difference reaction conditions. The polymerization results showed that AMB was an effective RAFT agent for the RAFT polymerizations of styrene with the characteristics of "living"/controlled free radical polymerization. The structure of the obtained polymers was characterized by ^{1}H NMR. The results showed that the polymers contained an anthrancene moiety of AMB in the end and showed enhanced fluorescence property than AMB in DMF solution. The chain extension experiments of the obtained polymer with two different monomers (styrene and methyl acrylate) were successfully carried out.

Keywords:

Anthracen-9-ylmethyl benzodithioate, RAFT, Styrene, Fluorescence

Introduction

Fluorescent end labeled polymer is the most useful tool used in the investigating of polymer's behavior in solution [1- 2]. Many papers have reported the synthesis of different kinds of polymers end capped with the fluorescence [3-12] by conventional free radical polymerization [13]. Unfortunately, due to the inevitable bimolecular radical coupling and disproportionation reactions, the polymers made by conventional radical polymerization usually have a broad molecular weight distribution and lack control in molecular weight and architecture.

The appearance of the “living”/controlled free radical polymerization, such as nitroxide mediated polymerization (NMP)[14], atom transfer radical polymerization (ATRP)[15-16], and reversible addition fragmentation chain transfer (RAFT)[17-18] polymerization, has provide us a very convenient way to synthesize complex macromolecular architectures with controlled molecular weights and narrow molecular weight distributions. The RAFT polymerization is one of the most robust “living”/controlled free radical polymerization techniques, the main advantage of RAFT is that it can be used for a much wider range of functional and nonfunctional monomers and more importantly it can be used to polymerize monomers in an aqueous environment at low temperatures [19].

The RAFT process involves performance of a conventional free radical polymerization in the presence of certain thiocarbonylthio compound [Z-C(=S)-SR] that acts as highly efficient reversible addition-fragmentation chain transfer agent and provides the polymerization with “living”/controlled characteristics[19]. Following RAFT polymerization mechanism, nearly all polymer chains will have the thiocarbonylthio and R group as end groups. RAFT polymerization thus provides a means of introducing specifically photoactive moieties into polymer chains using appropriately functionalized RAFT agents [20-28]. Ghiggino et. al. reported to synthesis a functionalized RAFT agent, RAFT-AN, with anthracene containing in the R group[29-31]. Using the RAFT-AN, they were successful to introduce the anthracene group into the polymer ends. However, the stability of the resulting ester linkage limits the applications in a number of circumstances, such as in the presence of acid or base. They subsequently reported an alternative method to solve this problem by two step RAFT polymerization processes [32]. In the first step, a monomer structure containing RAFT agent was synthesized by adjusting the molar ratio of monomer to RAFT agent equals to one equivalence. Then using the obtained new RAFT agent, the polymerization was carried out to synthesized polymers with chromophores functionalized polymers.

However, the process is longer than the normal RAFT polymerization. We describe here an alternative method to introduce suitable chromophores into a RAFT agent. Furthermore, Rizzado and other researchers have reported that, the RAFT polymerization under a particular set of reaction conditions depend on the nature of the groups Z and R of RAFT agent. Considerable effort has been expended to synthesize RAFT agents with different group Z or different group R by various synthetic techniques [33-35]. Here, we reported the synthesis of a RAFT agent with a methyl anthrancene group as the R group. Then using this RAFT agent, it is easy to synthesize polymers end capped with a stable chromophores unit and the polymerization behavior has been studied also.

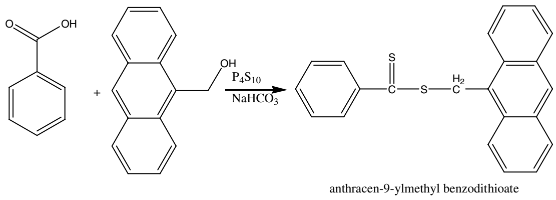
Experimental

Materials

All chemicals (analytical grade) used in this study were purchased from Shanghai Chemical Reagents Co. China and J&K-Acros. Styrene was washed with an aqueous solution of sodium hydroxide (5 wt %) three times and then with deionized water until neutralization. After being dried with anhydrous magnesium sulfate, the styrene was distilled under reduced pressure and kept in a refrigerator under 4 °C. Other materials were used without further purification.

Synthesis of the anthracen-9-ylmethyl benzodithioate (AMB)

The AMB was synthesized by coupling benzoic acid and anthracen-9-ylmethanol under P_4S_{10} according to the literatures [36-38]. A typical reaction procedure is as follows: Benzoic acid (1.22 g, 10 mmol), anthracen-9-ylmethanol (2.08 g, 10 mmol), P_4S_{10} (2.22 g, 5 mmol) and 40 mL toluene were added to a 100 mL three neck round flask. The solution was stirred at room temperature for half an hour and at 110 °C for about 20 hours under argon atmosphere. The reaction solution was filtrated after cooling and the filtrate was washed with deionized water till clear. The organic solution layer was dried with anhydrous $NaSO_4$ for 24 hours. The solvent was removed by rotation evaporation and the obtained product was a dark yellowish solid. The crude product was purified by column chromatography on silica oxide with mixed petroleum ether and benzene (10:1) as eluent. The purity of AMB was greater than 98.7% (Shimadzu 14B); ^1H NMR ($CDCl_3$), 4.57 (s, 2H); 7.3-8.2 (m, 14); Elemental analysis Calcd (%) C 76.73, H 4.65; Found (%) C 76.66, H 4.88.



Scheme 1 Synthesis route of the AMB

Polymerizations

The following procedure was typical. A master batch of 8 mL (69.5 mmol) of styrene, 95.7 mg (0.278 mmol) of AMB and 22.8 mg (0.139 mmol) of AIBN was prepared, and aliquots of 1mL were placed in ampules. The content was purged with argon for approximately 10 minutes to eliminate the oxygen. Then the ampules were flame sealed. The polymerization reaction was performed at the appropriate temperature. After the determined reaction time, each ampule was quenched in ice water, and opened. The reaction mixture was diluted with a little of THF (about 2 mL), and precipitated in large amount of methanol (about 300 mL). The polymer was obtained by filtrating and dried at room temperature under vacuum to constant weight. Conversion of styrene was determined gravimetrically.

Chain Extension of PS

A predetermined quantity of PS, obtained by polymerization of styrene by RAFT process, is dissolved in styrene. The content bubbles with argon for 20 minutes. The rest of the procedure is the same as described above, except that RAFT agent was replaced by the PS synthesized above.

Characterization

The molecular weights (M_n) and its polydispersity (PDI) 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 column with molecular weight range 100-500,000 calibrated with polystyrene standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 $mLmin^{-1}$ 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.

Results and discussions

RAFT polymerization of styrene using AMB as RAFT agent

Using AMB as the RAFT agent and AIBN as the initiator, the RAFT polymerization of styrene was carried out at 70 °C ($[Styrene]_0 : [AMB]_0 : [AIBN]_0 = 500 : 2 : 1$). The corresponding GPC curves at different conversions shown in Figure 1 were symmetrically monomodal and narrow peaks. The GPC molecular weights increased in direct proportion to monomers conversion and the polydispersity (PDI) remained at a very narrow level (PDI < 1.2) throughout the reaction. Number-average molecular weights were fitting well with the theoretical values $M_{n,th}$ ($M_{n,th} = [St]_0 \times Mw_{st} \times conversion/[RAFT\ agent]_0 + Mw_{RAFT\ agent}$). Figure 2 presents the kinetics of polymerization of styrene. There was a distinct change in rate of polymerization at approximate 5 hour. The rate of polymerization was high at early stage of polymerization and then decreased. The pseudo-first-order plot was obtained after period of about 4 hours.

The effects of different ratios of St/AMB and temperatures on polymerization were also studied. The results are listed in Table 1, which shows that the polymerizations in all entries are conducted in a way of controlled RAFT polymerization. However, rate retardation can be observed, that is, a decrease in the rate of polymerization with an increasing RAFT agent concentration. The conversion was 48.3% as the molar ratio $[St]_0:[AMB]_0:[AIBN]_0 = 500:2:1$ at 90 °C after 41.3 hours polymerization, however , the conversion was 48.4% after 65.5 hours polymerization with molar ratio of $[St]_0:[AMB]_0:[AIBN]_0 = 500:3:1$. Such rate retardation phenomena have already been reported for some monomer/RAFT agent combinations and have extensively been discussed in the literatures [39-45]. The underlying cause of rate retardation is still

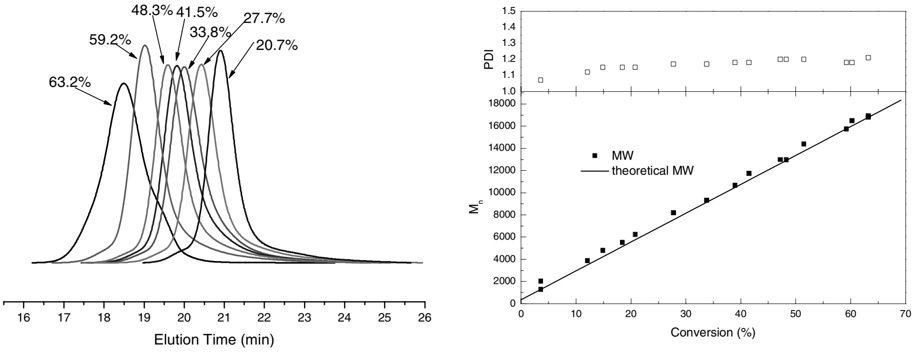


Figure 1 Corresponding GPC curves, molecular weights and molecular weight distributions vs monomers conversions. 70 °C, $[Styrene]_0 : [AMB]_0 : [AIBN]_0 = 500 : 2 : 1$

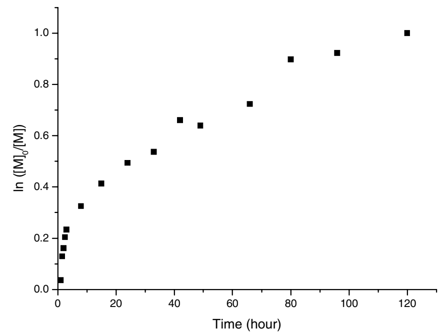


Figure 2 The plots of $\ln([M]_0/[M])$ vs time for styrene RAFT polymerization at 70 °C. $[Styrene]_0 : [AMB]_0 : [AIBN]_0 = 500 : 2 : 1$

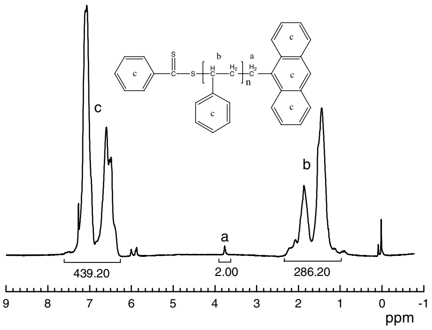


Figure 3 ^1H NMR spectra of PS mediated by AMB with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Mn, $_{GPC}$ = 10660, PDI = 1.18

debated within the scientific community, but the majority of the evidence indicates that the slow fragmentation the intermediate macro-RAFT radicals is the primary cause. At the same time, the molecular weight distribution increased from 1.11 to 1.18 as the mole ratio of $[St]_0/[AMB]_0$ increased from 500:3 to 500:2, which may be caused by the more side reactions as the result of decreasing concentration of $[AMB]_0$.

Table 1 RAFT polymerization of styrene using AMB as the RAFT agent in different conditions.

Entry	Time (h)	$[St]_0:[AMB]_0:[AIBN]_0$	Temperature (°C)	Conv. (%)	$M_{n, th}$	$M_{n, GPC}$	PDI
1	46	500:2:1	70	44.2	11514	13540	1.18
2	41.3	500:2:1	90	48.3	12920	13660	1.15
3	65.5	500:3:1	90	48.4	8750	10030	1.11

The chain ends of PS prepared by the RAFT polymerization using AMB as the RAFT agent were analyzed by ^1H NMR spectroscopy (Figure 3). In Figure 3, the signals at σ = 3.76 ppm are correspond to the methylene protons nearby the anthranene units in AMB, the signals at σ = 6.4-7.5 ppm are ascribed to aromatic protons of phenyl group in styrene, the signals at σ = 0.9-2.4 ppm are belong to the alkyl protons in styrene, All of the above indicate that the RAFT agent moieties are attached to the polymer chain ends, which complies with the RAFT mechanism. Furthermore, the polymer molecular weight can be calculated from the signal ratio of the AMB to styrene in the Figure 3 using following equation:

$$M_{n,\,NMR} = ((I_{0.9\text{-}2.4}/3)/(I_{3.76}/2))*104+344 \tag{1}$$

Where, $I_{0.9\text{-}2.4}$ and $I_{3.76}$ means the integral value of the peak at 0.9 ~ 2.4 and 3.76 ppm respectively, 104 and 344 means the molecular weight of styrene and AMB respectively. The calculated molecular weight from the ^1H NMR spectroscopy, $M_{n,\,NMR}$, is 10265. The $M_{n,\,NMR}$ is closed to the $M_{n,\,GPC}$ (10660), which means that the polymers obtained from the AMB mediated RAFT polymerization of styrene are almost all capped with the AMB moiety.

Chain extension

To further reveal the "living" behavior of the polymerization, the obtained polymers were used as macro-RAFT agents to conduct chain-extensions of styrene and methyl acrylate (MA) using AIBN as the initiator. The chain extensions results are showed in Figure 4. The molecular weight of original polymer increased from 9940 to 13470 and 14490 after 3h at 70 °C using styrene (conversion : 37.4%) and methyl acrylate (conversion 38%) as the second monomer, respectively. There was an obvious peak shift from the original polymer to the chain extension products in Figure 4. The peak of original polymer disappeared, which indicated that the original polymers were reacted into new polymers in the chain extension reaction. On the other hand, the polydispersity (PDI: 1.33 and 1.34) of the chain extension products were a little larger than the original polymer (PDI: 1.20). This may be caused by the little portion homopolyerization of St and MA initiated by AIBN and the dead polymer existed in the original polymer (macroRAFT agent), which was discussed above. Therefore, the most of the chains were still living at the end of the polymerization. These results indicated that the original polymers were active and the polymerization had the "living"/controlled nature.

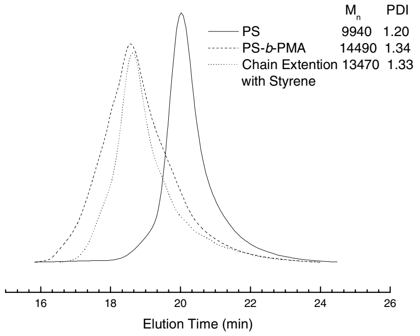


Figure 4 GPC curves for the chain extension of PS used as macroRAFT agent. $[\text{monomer}]_0 : [\text{AMB}]_0 : [\text{AIBN}]_0 = 500 : 2 : 1$ with the polymerization temperature as 70°C

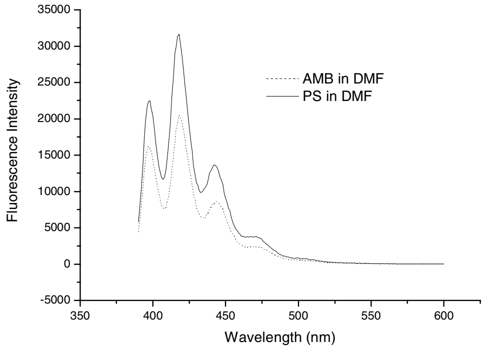


Figure 5 Fluorescence spectra of PS and AMB in DMF at room temperature. PS: $M_n = 9300$, PDI = 1.17. The concentration of all solutions are 5.01×10^{-5} M, $\lambda_{ex} = 374$ nm

Fluorescence study

Figure 5 shows the fluorescence spectra of obtained PS and the AMB in DMF, the excitation wavelength is 374 nm. The results demonstrated that in these two cases, the emission spectra were similar. There were three peaks in the spectrum and the maximum of emission were all around 444 nm, which was confirmed with the references [31]. Furthermore, the polymer obtained has high fluorescence intensity than the original RAFT agent AMB. As concerned with the structure of AMB, which is showed in Scheme 1, there is a sulfur atom adjacent to the anthracene. The sulfur atom is a well known fluorescence quenching agent [32], which is considered as the results of the decrease in the oscillator strength of the S_0 --- S_1 transition. Compare the structures of the RAFT obtained PS and AMB, the sulfur atom is far from the chromophore e. g. anthracenyl in the polymer, while it linked near to the chromophore in AMB. As the result, the fluorescence strength shows some difference.

Conclusion

In this work, a novel RAFT agent with an anthracenyl structure (AMB) was synthesized and the RAFT polymerization of styrene using AMB as the RAFT agent and AIBN as the initiator was studied. The polymerization results showed characteristic “living”/controlled free radical polymerization behaviors. The successfully chain extension experiments and the ^{1}H NMR spectroscopy confirmed the polymerization of styrene in the presence of AMB complied with the RAFT mechanism. The polymers contained with anthrancene moiety in the end. The block copolymer of MA and styrene with controlled molecular weight and narrow polydispersity was successfully prepared. The RAFT polymerization of styrene using AMB as the RAFT agent showed an obvious retardation. The polymer showed stronger fluorescence intensity than the AMB in DMF.

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