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RAFT Polymerization of Styrene in the Presence of 2-Nonyl-benzoimidazole-1-carbodithioic Acid Benzyl Ester

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A novel dithiocarbamate, 2-nonyl-benzoimidazole-1-carbodithioic acid benzyl ester (***1a***), was synthesized and successfully used in RAFT polymerization of styrene in bulk with thermal initiation. The effect of molar ratio of styrene to RAFT agent on the polymerization was investigated. The linear relationship between $\ln([M]_0/[M])$ and polymerization time indicated that the polymerization was first-order with respect to monomer concentration. The molecular weights increased linearly with monomer conversion and were close to corresponding theoretical values. The molecular weight distributions (M_w/M_n) kept very narrow ($M_w/M_n < 1.1$) at a wide range of conversions of 14.2% to 73.3%. The obtained polymer had a strong ultraviolet absorption at 329 nm, which indicated that the ***1a*** moiety remained at the end of polymer chain.

Keywords: living polymerization; reversible addition-fragmentation chain transfer (RAFT); styrene; dithiocarbamate

1 Introduction

In recent years, considerable efforts (1–9) have been expended to develop free radical polymerizations that display the characteristics of living polymerizations, because living radical polymerization is one of the most effective ways to prepare well-defined polymer with predetermined molecular weight, narrow molecular weight distribution and functional groups (10). RAFT polymerization is one of the living free radical polymerization methods, and appears as the most versatile method. The RAFT process is a polymerization in the presence of a RAFT agent (Z-C (=S) S-R), which reacts by a series of reversible addition-fragmentation steps. As is well known, the structure of the RAFT agent (Z-C (=S) S-R) is most important to the RAFT process, and particularly, the Z group plays a special role in the compound properties (11, 13). There are four classes of thiocarbonylthio RAFT agents, depending on the nature of the Z group: dithioesters (Z is aryl or alkyl), trithiocarbonates (Z is substituted sulfur), dithiocarbonates (xanthates) (Z is substituted oxygen), and dithiocarbamates (Z is substituted nitrogen). Rizzardo et al. found that the electron-withdrawing groups on nitrogen atom of dithiocarbamates can significantly enhance the activity of dithiocarbamates (12, 13). Destarac et al. found the key parameter for the control of the radical polymerization of acrylates, styrene and vinyl acetate using novel dithiocarbamates, *N*,*N*-disubstituted or cyclic dithiocarbamates, as RAFT agents to be the conjugation of the lone pair of electrons of the nitrogen atom with carbonyl or aromatic groups (14). According to this research, the RAFT process can be achieved with the use of some dithiocarbamate derivatives, such as those derived from pyrrole and imidazole (12). Recently, Pan et al. reported that the free radical polymerizations of methyl acrylate under γ-ray irradiation in the presence of the dithiocarbamates with different *N*-groups. The results indicated that the conjugation structure of the *N*-group of dithiocarbamates played an important role in the living free radical polymerization (15). However, the mechanism of the γ-ray irradiation living free radical polymerization has been under debate (15, 16).

In this article, a novel dithiocarbamate, 2-nonyl-benzoimidazole-1-carbodithioic acid benzyl ester (Scheme 1, ***1a***), was synthesized and used as a RAFT agent in the thermal initiated RAFT polymerization of styrene to examine the effectiveness for controlled polymerization of styrene.

2 Experimental

2.1 Materials

Dimethyl sulphoxide (DMSO, analytical reagent, Shanghai Wulian Chemicals Co. Ltd, Shanghai, China) was purified

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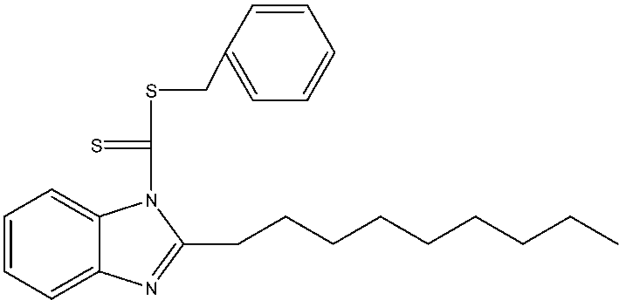

Sch. 1. Chemical structure of 2-nonyl-benzoimidazole-1-carbodithioic acid benzyl ester (***1a***).

by vacuum distillation over anhydrous CaH_2. Styrene (analytical reagent, Shanghai Chemical Reagent Co. Ltd, Shanghai, China) 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 monomer was distillated twice under reduced pressure prior to use. Caron bisulfide (CS_2, analytical reagent, Shanghai Chemical Reagent Co. Ltd, Shanghai, China), tetrahydrofuran (THF, analytical reagent, Jiangsu Yangyuan Chemical Factory, Jiangsu, China), 2-nonyl-benzoimidazole (97%, Aldrich Chemical Company Inc., Milwaukee, USA), NaH (55%–65%, powder, Fluka Chemie, Netherlands), and benzyl bromide (chemically pure, Shanghai Chemical Reagent Co. Ltd, Shanghai, China) were used as received.

2.2 Synthesis of Dithiocarbamate and Polymerization

2.2.1. Synthesis of 2-Nonyl-benzoimidazole-1-carbodithioic Acid Benzyl Ester (1a)

A suspension of NaH (0.48 g, 20 mmol) in DMSO (20 mL) was first prepared, then 2-nonyl-benzoimidazole (4.88 g, 20 mmol) was added under vigorous stirring. The yellow solution was then stirred for another 10 h at room temperature. The solution was cooled to 20°C, and CS_2 (1.52 g, 20 mmol) was added dropwise. The resultant reddish orange solution was stirred for 10 h at room temperature, and then benzyl bromide (3.42 g, 20 mmol) was added. After the mixture was stirred for 10 h, water (20 mL) and then diethyl ether (20 mL) were added. The organic layer was separated, and the aqueous layer was extracted three times with diethyl ether (40 mL). The combined extracts were dried over $MgSO_4$ and filtered, and the solvent was evaporated. The crude product was subjected to column chromatography (silicagel H) with petroleum ether/ethyl acetate = 15 : 1 (v : v) as eluent. The main fraction was orange. The solvent was evaporated and the product dried under vacuum to yield an orange oil. The pure ***1a*** was obtained and the purity is above 94% (HPLC (Waters 515)).

2.3 Polymerization

The typical procedures were as follows: A dry ampoule was filled with 1 mL of mixture of styrene and ***1a*** ([styrene] : [***1a***] = 500 : 1 (mol : mol)). The content was purged with argon to eliminate oxygen for approximately 10 min. Then the ampoule was flame sealed and placed in an oil bath held by a thermostat at the desired temperature for the polymerization. The polymerization was stopped at a desired time by cooling the tube in ice water, then the ampoule was opened, the reaction mixture was diluted with 2 mL of THF, and precipitated in 250 mL of methanol. The polymer was filtrated and dried at room temperature under vacuum until a constant weight was obtained. The conversion of polymer was determined gravimetrically.

2.4 Characterizations

The molecular weights and polydispersities of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 column with molecular weight range 100–500,000 calibrated with PS standard samples. 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 tetramethylsilane as the internal standard. The UV absorption spectra of the samples in various solutions were determined on a Shimadzu- RF540 spectrophotometer.

3 Results and Discussion

3.1 Living Polymerization Character

The RAFT polymerizations of styrene with thermal initiation were carried out using ***1a*** as the RAFT agent in bulk with the molar ratio of $[\text{styrene}]_0$:$[\mathbf{1a}]_0$ = 500 : 1 at 110°C. The kinetic plot of $\ln([M]_0/[M])$ vs. polymerization time was shown in Figure 1. The linear relationship between $\ln([M]_0/[M])$ and polymerization time indicated that the polymerization was first order with respect to monomer concentration, and the number of radicals remained constant during the polymerization. Figure 1 also showed that there was no inhibition period in the polymerization. The number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were shown in Figure 2. The molecular weights increased linearly with monomer conversion and were agreement with their corresponding theoretical ones ($M_{n,th}$), calculated using the following equation:

$$M_{n,th} = \frac{[\text{styrene}]_0}{[\text{RAFT} - \text{agent}]_0} \times \text{conversion} \times M_{styrene} + M_{RAFT\ agent}$$

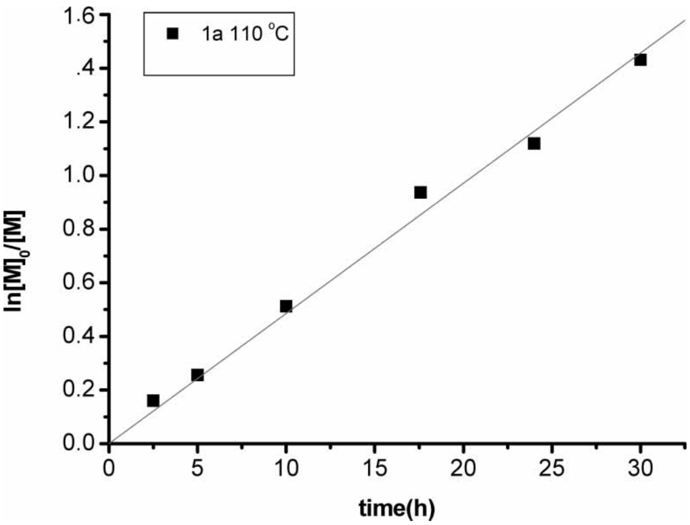

Fig. 1. Kinetic plots of the polymerization of styrene in the presence of ***1a***, $[\text{styrene}]_0 : [\mathbf{\mathit{1a}}]_0 = 500 : 1$.

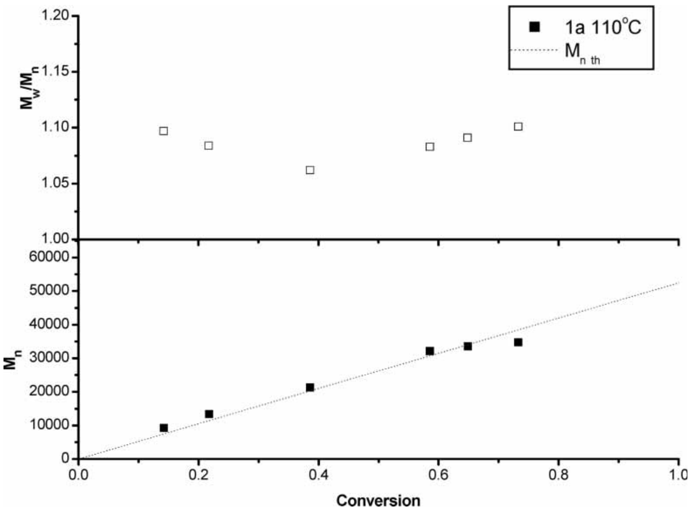

Fig. 2. M_n and M_w/M_n vs. conversion for the polymerizations of styrene in the presence of ***1a***, $[\text{styrene}]_0 : [\mathbf{\mathit{1a}}]_0 = 500 : 1$.

Where, $[\text{styrene}]_0$ and $[\text{RAFT-agent}]_0$ are the initial concentrations of styrene and RAFT agent, and $M_{styrene}$ and $M_{RAFTagent}$ are molecular weights of styrene and RAFT agent, respectively. The M_w/M_ns were very narrow ($M_w/M_n < 1.1$) at a wide range of conversions of 14.2% to 73.3%. These results showed that the novel dithiocarbamate, 2-nonyl-benzoimidazole-1-carbodithioic acid benzyl ester (***1a***), was an effective RAFT agent for the RAFT polymerization of styrene.

3.2 Effect of Ratios of [styrene]$_0$: [1a]$_0$

The polymerizations of styrene were carried out in bulk with different molar ratios of $[\text{styrene}]_0 : [\mathbf{\mathit{1a}}]_0$ to investigate the effect of ratios of $[\text{styrene}]_0 : [\mathbf{\mathit{1a}}]_0$ on RAFT polymerization of styrene. The results are shown in Table 1 and Figure 3. From Table 1 and Figure 1, it can be seen that the RAFT agent (***1a***) had excellent control over the polymerization of styrene with thermal initiation up to a very high molar ratio of $[\text{styrene}]_0 : [\mathbf{\mathit{1a}}]_0$. When molar ratio of $[\text{styrene}]_0 : [\mathbf{\mathit{1a}}]_0$ increased from 500 : 1 to 3000 : 1, the polymerizations of styrene were well controlled although M_w/M_ns had a little increase with the increasing of molar ratio. The controlled molecular weight was up to 82400 g.mol^{-1} with a M_w/M_n of 1.28. However, when the molar ratio increased to more than 3000 : 1, the M_w/M_ns were more than 1.5 and the molecular weights ($M_{n.GPC}$) determined from GPC result were significantly deviated from their corresponding theoretical values, indicating poor control over the polymerizations of styrene.

3.3 End Group Analysis and Chain Extension Reaction

In order to confirm the mechanism of the polymerization, ^{1}H-NMR was used to examine the structure of the polymers. The typical spectrum is shown in Figure 4. The signals at 7.3–7.8 ppm (peak ***a*** in Figure 4) and 0.89 ppm (peak ***b*** in Figure 4) corresponded to the protons for the aromatic group and methyl group of dithioester moieties, respectively, which indicated that the **1a** moiety remained at the end of the polymer chain. The signals at 6.5–7.1 ppm (peak ***c*** in

Table 1. The polymerization results of styrene at different ratios of $[\text{styrene}]_0/[\mathbf{1a}]_0$ in 110°C

Time(h)	$[\text{M}]_0 : [\mathbf{\mathit{1a}}]_0$	$M_{n(th)}$	$M_{n(GPC)}$	conv. (%)	M_w/M_n
5	500 : 1	8700	10700	15.9	1.09
10	500 : 1	19100	22000	35.9	1.08
5	1000 : 1	18200	19900	17.1	1.08
10	1000 : 1	39000	35600	37.0	1.12
5	2000 : 1	43400	42000	20.7	1.13
10	2000 : 1	80900	66400	38.7	1.20
5	3000 : 1	65800	58500	20.9	1.20
10	3000 : 1	114900	82400	36.6	1.28
10	6000 : 1	246400	127200	39.4	1.59
10	10000 : 1	408400	174800	39.2	1.64

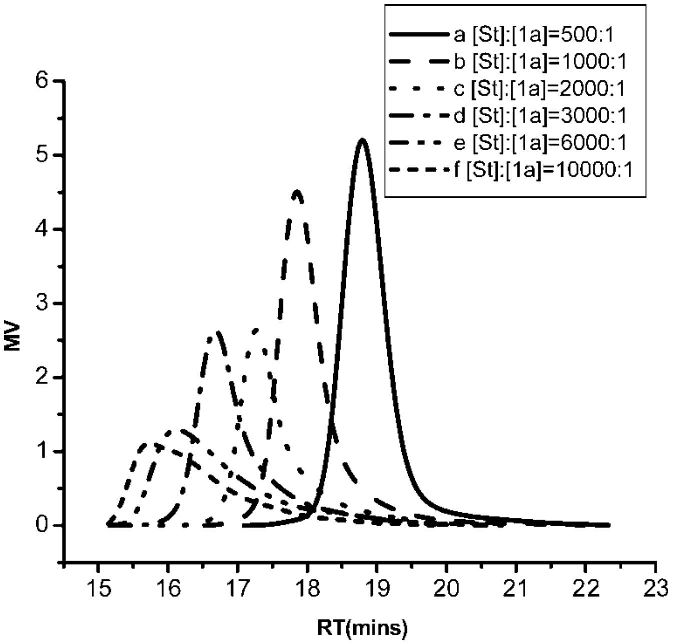

Fig. 3. GPC elution profiles for polystyrenes by thermal polymerization of styrene in the presence of various concentrations of ***1a*** at 110°C for 10 h. (a: $M_n = 22000$, $M_w/M_n = 1.08$, 35.8% conversion; b: $M_n = 35600$, $M_w/M_n = 1.12$, 37.0% conversion; c: $M_n = 66400$, $M_w/M_n = 1.20$, 38.7% conversion; d: $M_n = 82400$, $M_w/M_n = 1.28$, 36.6% conversion; e: $M_n = 127200$, $M_w/M_n = 1.59$, 38.4% conversion, and f: $M_n = 174800$, $M_w/M_n = 1.64$, 39.2% conversion).

Figure 4) corresponded to the protons of the aromatic group in the polystyrene. Furthermore, the M_n of the synthesized polystyrene was assumed from both GPC and ^{1}H-NMR spectroscopy. The M_n of 13400 g/mol, inferred from GPC, is close to the M_n of 10900 g/mol, duduced from the ^{1}H-NMR spectroscopy (ratio of the aromatic protons (peak ***c*** in Figure 4) of the polystyrene to the protons of the methyl group (peak ***b*** in Figure 4) of RAFT agent ***1a***. In addition, the chain extension reaction, which is the alternative way to verify the functionality of the polymer prepared by RAFT polymerization, was also carried out using the obtained polystyrene as the macro-RAFT agent. Typical chain extension reaction was carried out with adding fresh styrene monomer ($[\text{styrene}]_0 : [\text{macro-RAFT}]_0 = 500 : 1$) at 110°C or fresh MA ($[\text{MA}]_0 : [\text{AIBN}]_0 : [\text{macro-RAFT}]_0 = 1500 : 1 : 3$) at 80°C and 60°C for 5 h, respectively. The GPC curves of the original and extended polymer are shown in Figure 5.

There was an obvious peak shift from the macro-RAFT agent to product, and the peak of original polymer disappears, which demonstrated that the macro-RAFT agent was completely converted into the product of chain extension reaction. For the chain extension with styrene, the M_w/M_n after chain extension almost remained the same as that for the macro-RAFT agent. However, for block copolymers (PS-*b*-PMA) after chain extension reactions with MA both at 80°C and 60°C, the M_w/M_ns were a little broader than the one for the macro-RAFT agent, especially at a higher temperature (80°C), the M_w/M_n of 1.06 for the macro-RAFT agent increased to 1.36 for the PS-*b*-PMA block copolymer. This may be due to the fact

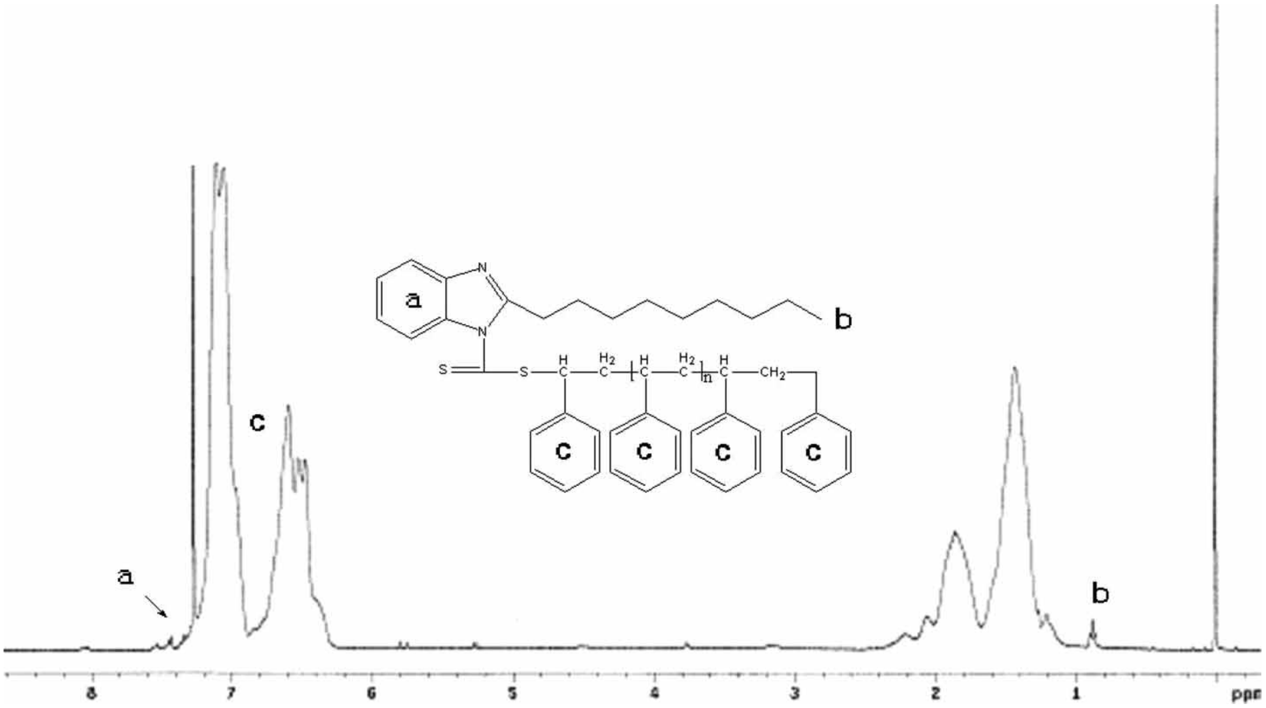

Fig. 4. ^{1}H-NMR spectra of (***1a***) PS ($M_n = 13400$, $M_w/M_n = 1.08$).

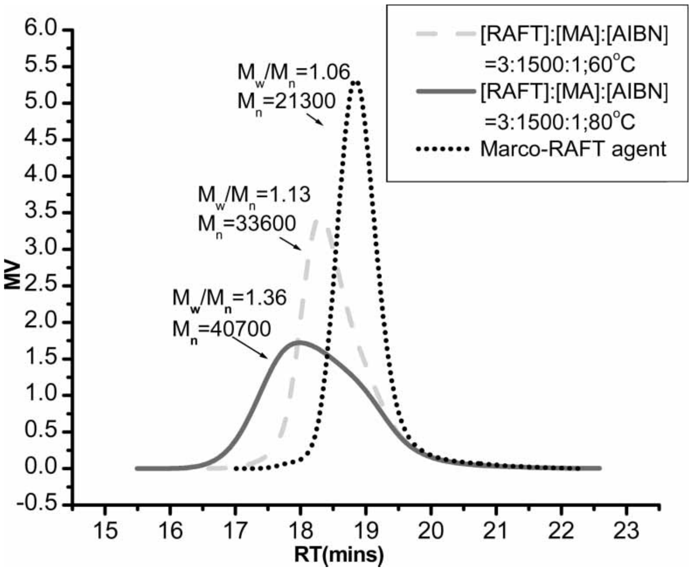

Fig. 5. GPC curves of chain extension reaction.

that some homopolymerization of MA initiated by AIBN occurred and that some dead polymers existed in the copolymers at higher temperature (17, 18). This evidence supported the fact that the RAFT polymerization of styrene using ***1a*** as RAFT agent under thermal initiation was well controlled in RAFT mechanism.

3.4 *Optical Properties of the Polymer*

Figure 6 presents the UV spectra of ***1a*** and the polymer in the same molar concentration (1.0×10^{-5} M^{-1}). The both of polymer and ***1a*** had a UV absorption maximum at 329 nm, and in same concentration, they had also the same absorbance intensity.

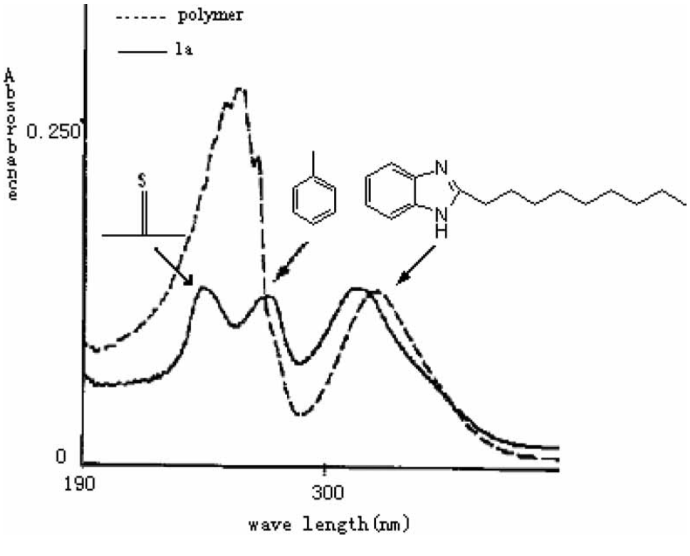

Fig. 6. UV absorption spectra of the polymer ($M_n = 13400$, $M_w/M_n = 1.08$) and ***1a***.

4 Conclusions

A novel RAFT agent (***1a***) was successfully synthesized, and could be used to prepare well-defined polystyrene with narrow molecular weight distribution. The ^{1}H-NMR spectra of the polymer after chain extension and the UV absorption spectrum indicated that the polymerization was a RAFT process and the RAFT agent moiety was attached to the end of the resulting polymer.

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