Synthesis of 1,3-Benzodioxole End-Functionalized Polymers via Reversible Addition–Fragmentation Chain Transfer Polymerization

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ABSTRACT: Reversible addition–fragmentation chain transfer (RAFT) polymerization of styrene was carried out in the presence of a novel RAFT reagent, bearing 1,3-benzodioxole group, benzo [1,3]dioxole-5-carbodithioic acid benzo [1,3]dioxol-5-ylmethyl ester (BDCB), to prepare end-functionalized polystyrene. The polymerization results showed that RAFT polymerization of styrene could be well controlled. Number–average molecular weight ($M_{n(GPC)}$) increased linearly with monomer conversion, and molecular weight distributions were narrow ($M_w/M_n < 1.4$). The successful reaction of chain extension and analysis of ^{1}H NMR spectra confirmed the existence of the functional 1,3-benzodioxole group at the chain-end of polystyrene. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3535–3539, 2006

Key words: styrene; RAFT; functional material; 1,3-benzodioxole; piperonic acid

INTRODUCTION

Synthetic polymers containing functional groups of potential biological activity are of increasing importance[1]. Living radical polymerization has recently emerged as one of the most effective synthetic routes to prepare well-defined polymers[2]. The appearance of living free radical polymerization affords a very convenient way to prepare such materials. Among the living free radical polymerization, nitroxide-mediated polymerization (NMP),[3] atom transfer radical polymerization (ATRP),[4,5] and reversible addition fragmentation chain transfer polymerization (RAFT)[6,7] have extensively been reported. For NMP and ATRP, the synthesis of well-defined polymers, such as some block copolymers and other complex architecture, has been limited because the processes are not compatible with certain monomers or reaction conditions, or both.

For example, although NMP can be successfully used for making block copolymers based on styrene and its derivatives, it appears to have less utility for other systems. ATRP has limitations in monomers or initiators containing acid functionality and generates products contaminated by metal ions. However, in principle, all classic radical systems can be converted to the RAFT process in the presence of efficient transfer reagents.

According to the mechanism of RAFT polymerization proposed by Rizzardo et al.,[6] the polymer obtained by RAFT polymerization contains the structures of RAFT agent at the chain ends. As a result, chain-end functionality can, in principle, be easily introduced into the polymer, by adjusting the structure of the chain-transfer agent used during the RAFT polymerization (i.e., by selecting appropriate structures for the activating and leaving groups of the dithioester). A number of well-defined polymers have been synthesized through RAFT polymerization.[8–14] By designing the structures of RAFT agent, some chain-end-functionalized polymers have been reported. Chen et al.[15] synthesized light harvesting polymers by introducing functional dithiobenzoates into the acenaphthyl chromophore. Lima et al.[16] reported the linear α,ω-telechelic polymers with either hydroxyl or carboxyl end groups.

Piperonic acid is one of the sharp-tasting constituents in black pepper and is used as an insecticide.[17] Piperonylic acid has a characteristic structure, in which cyclic ether containing two oxygen atoms is fused to benzoic

acid. It can be used as antibacterial, antiviral, and fragrant material as well as other pharmaceuticals.[18]

The aim of this study is to produce a linear α,ω-telechelic polystyrene (PS) bearing 1,3-benzodioxole end group, which might be used in the biological area and lead to some very interesting properties. This work also reports some initial results, which demonstrates some principles of this strategy and illustrates the potential of this approach in the synthesis of functionalized biosensitive polymers at the chain ends.

EXPERIMENTAL

Materials

1,3-Benzodioxole-5-carboxylic acid, benzo[1,3]dioxol-5-yl-methanol, and P_4S_{10} are purchased from Aldrich and used as-received. Styrene (St) (CP, Shanghai Chemical Reagent Co., Ltd.) was washed with an aqueous solution of sodium hydroxide (5%) and then with distilled deionized water, dried with anhydrous magnesium sulfate overnight, finally distilled over calcium hydride under vacuum. 1,4-Dioxane (AR, Shanghai Chemical Reagent Co., Ltd.) was dried with CaH_2, and then distilled under vacuum. α,α'-Azobisisobutyronitrile (AIBN, CP; Shanghai Chemical Reagent Co., Ltd.) was purified by recrystallization from ethanol. All other reagents used in this study were of analytical grade and used as-received.

Synthesis of benzo[1,3]dioxole-5-carbodithioic acid benzo[1,3]dioxol-5-ylmethyl ester (BDCB)

In a 50-mL three-necked round bottom flask equipped with thermometer and condenser, 2.22 g (5 mmol) of P_4S_{10}, 1.68 g (10 mmol) of 1,3-benzodioxole-5-carboxylic acid, 1.6 g (10 mmol) of benzo[1,3]dioxol-5-yl-methanol, and 1.5 g of $NaHCO_3$ were added to 40 mL of 1,4-dioxane, under stirring. After bubbled with argon for 30 min at room temperature, the reaction mixture was heated up to 95–100°C and refluxed for over 20 h. The reaction mixture was filtered, and the filtrate was evaporated using a rotatory evaporator. The crude product obtained was then dissolved in benzene, washed thrice with deionized water, and dried with Na_2SO_4 overnight. The crude product was obtained by evaporating the solvent under vacuum. It was further purified by column chromatography on

silica oxide with petroleum ether and ethyl acetate mixture (10 : 1, v/v) as an eluent.

^{1}H NMR: 4.52, 1H (s); 5.96, 2H (s); 6.04, 2H (s); 6.76–6.79, 2H (m); 6.86–6.87, 2H (m); 7.60, 1H (m); 7.71, 1H (m). Elem. Anal. Calcd. %: C, 57.83; H, 3.61; Found: C, 57.9; H, 3.96.
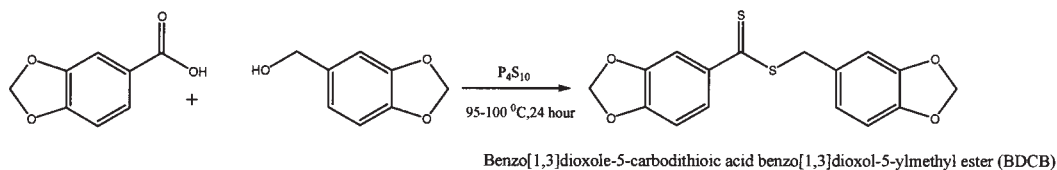
RAFT polymerization

A typical polymerization procedure is as follows: A solution of St and BDCB (prescribed molar ratio) was added to a dry tube, the content was bubbled with argon for 20 min, then the tube was flame sealed, placed in an oil bath held by a thermostat at a desired temperature. After the desired polymerization time, the tubes were taken out and cooled by iced water. Then, tubes were opened and the contents were dissolved in about 2 mL of tetrahydrofuran (THF) followed by precipitation into a large excess of methanol (about 200 mL). The polymers obtained were dried under vacuum until the weight reached constant, at room temperature. The conversions were determined gravimetrically.

Characterization

The molecular weights and molecular weight distributions 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 (NMR) instrument, using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. The elemental analyses for C, H, and N were performed on a LECO-CHNS microanalyzer.

RESULTS AND DISCUSSION

BDCB was synthesized by coupling 1,3-benzodioxole-5-carboxylic acid and benzo[1,3]dioxol-5-yl-methanol in the presence of P_4S_{10}, according to the literature.[19–21] This process affords a convenient and relatively short route to obtain dithioesters with func-

Benzo[1,3]dioxole-5-carbodithioic acid benzo[1,3]dioxol-5-ylmethyl ester (BDCB)

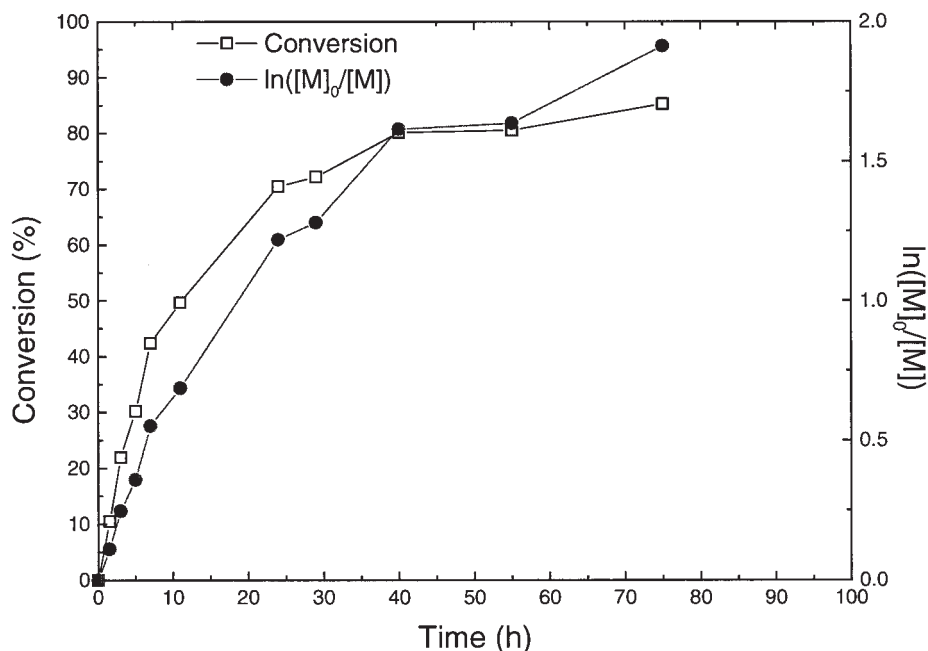**Scheme 1**   Synthetic route of benzo[1,2]dioxole-5-carbodithioic acid benzo[1,2]dioxol-5-ylmethyl ester (BDCB)

Figure 1 Kinetics of RAFT polymerization of styrene. Polymerization conditions: $[Styrene]_0 : [BDCB]_0 : [AIBN]_0 = 500 : 2 : 1$; 70°C.

tional groups. The structure of BDCB has been confirmed by EA and ^{1}H NMR spectrum. The results were listed in experimental sections. The purity of this RAFT agent is >98% and >99%, respectively, determined from GC and HPLC.

The BDCB obtained was used as the chain transfer agent in RAFT polymerization of styrene, using AIBN as an initiator in bulk. Figures 1 and 2 show the polymerization results with a molar ratio of $[Styrene]_0 : [BDCB]_0 :$ $[AIBN]_0 = 500 : 2 : 1$, at 70°C. From Figure 1, it can be seen that the monomer conversion increases with the polymerization time. The dependences of M_n and M_w/M_n on monomer conversion are shown in Figure 2. From Figure 2, it can be seen that the M_n's increase linearly with monomer conversion, while the M_n's from GPC results are somewhat higher than those of the corresponding theoretical values ($M_{n,th}$), which indicates that the equilibrium between active and dormant chains

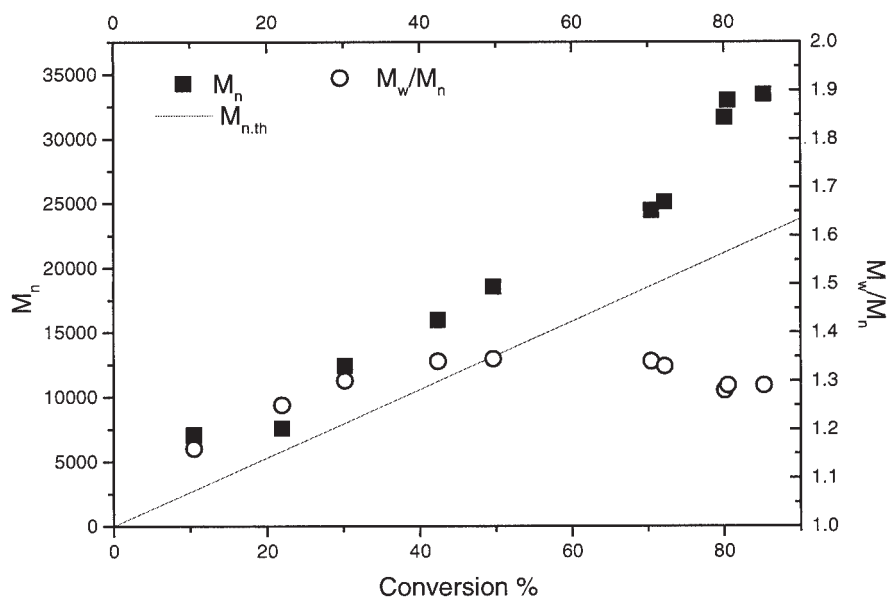**Figure 2** Dependence of M_n and M_w/M_n on conversion. Polymerization conditions: $[Styrene]_0 : [BDCB]_0 : [AIBN]_0 = 500 : 2 : 1$; 70°C.
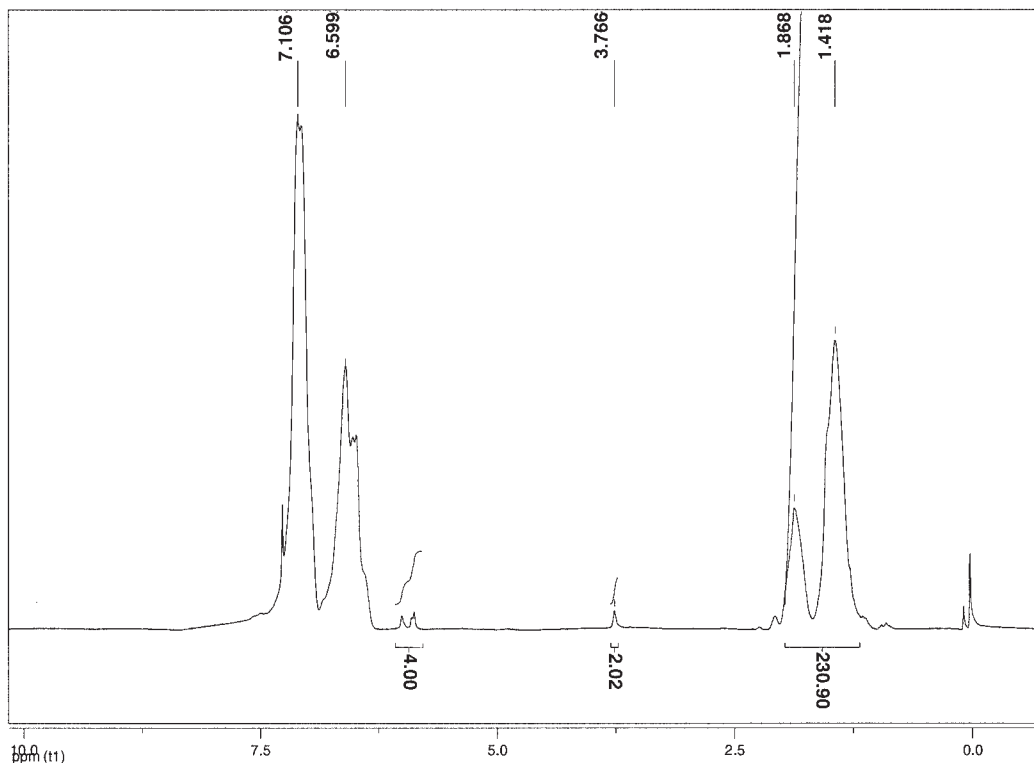
Figure 3 ^{1}H NMR spectrum of polystyrene with $M_n = 7060$ and $M_w/M_n = 1.16$.

may be not so efficient. The M_w/M_n's of polymers are narrow (M_w/M_n in the range of 1.1–1.4).

The structure of the obtained PS was also characterized by ^{1}H NMR. The result is shown in Figure 3. The chemical shift at $\delta = 3.766$ ppm (a) is attributed to the methylene protons in the benzyl group, which serves as the R group in BDBC. The signals of $\delta = 5.60$–5.80 ppm (b) are ascribed to the methylene protons adjacent to oxygen in the 1,3-benzodioxole group. The area ratio of (a) to (b) is 2, fairly in agreement with the theoretical ratio of these two groups in a RAFT agent. At the same time, the presence of these groups in the RAFT agent indicates that the moieties of BDCB remained intact at the chain end of PS. It is noted that the samples used for NMR analyses were carefully purified by successive dissolution/precipitation cycles with THF and methanol.

Furthermore, the molecular weight ($M_{n,\text{NMR}}$) can be calculated from the ratio of protons in PS to the protons of RAFT agent covalently tethered at the chain ends of PS. The equation is as follows:

$$M_n = \left(\frac{I_{0.9-2.0}}{3} \Big/ \frac{I_{5.6-5.8}}{4} \right)$$

$$\times \text{ Molecular weight of styrene}$$

$I_{0.9-2.0}$ is the integral of the signals at 0.9–2.0 ppm; $I_{5.6-5.8}$ is the integral of the signals at 5.6–5.8 ppm.

The molecular weight calculated from the ^{1}H NMR spectroscopy results is 7820 g/mol, which is higher than the $M_{n,\text{GPC}}$ (7060 g/mol). This result indicated that not all of the polymer chains were end capped with the BDBC moiety, some polymer chains have one end bearing the cyano isopropyl group, which is derived from AIBN. However, the result also further
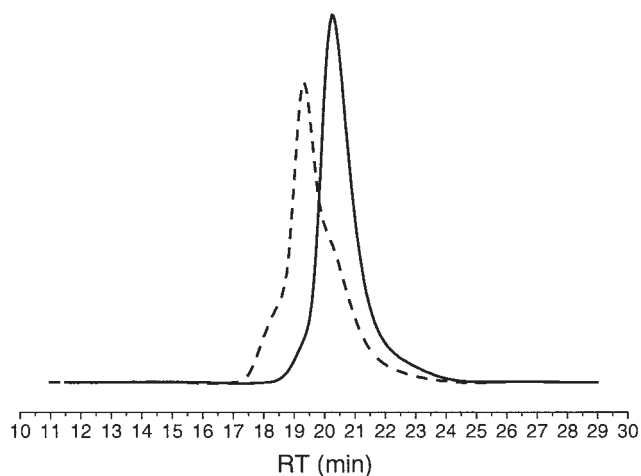

Figure 4 GPC curves of the original polymer and the chain extended polymer.

TABLE I
Effects of Polymerization Temperature and Concentration of RAFT Agent on the Polymerization of Styrene

Entry	$[St]_0 : [BDCB]_0 : [AIBN]_0$	Temp. (°C)	Time (h)	Conv. (%)	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n
1	500 : 2 : 1	70	1.5	10.5	3,060	7,060	1.16
2	500 : 2 : 1	70	5	30.2	8,190	12,400	1.25
3	500 : 2 : 1	70	24	70.4	18,430	27,860	1.29
4	500 : 2 : 1	90	2	40.2	10,800	14,470	1.34
5	500 : 2 : 1	90	5	48.9	12,740	17,300	1.33
6	500 : 2 : 1	90	24	63.0	16,740	21,890	1.31
7	500 : 3 : 1	90	25	60.9	10,900	15,280	1.27

confirmed that the polymer was end functionalized with BDBC group.

The polymer containing RAFT agent structure at the chain ends can be used as the macro-RAFT agent to carry out chain extension reaction by adding fresh monomer. The polymer with $M_n = 8880$, $M_w/M_n = 1.21$ was added to the solution of fresh styrene and AIBN with the molar ratio of $[St]_0 : [\text{macro-RAFT}]_0 : [AIBN]_0 = 500 : 2 : 1$. The polymerization was carried out at 70°C for 2.5 h and resulted in a 37% of conversion. The GPC traces of original macro-RAFT agent and the chain-extended polymer were shown in Figure 4. It can be found that the molecular weight increased from 8880 g/mol for the original polymer to 16,940 g/mol for the polymer after chain extension. However, the molecular weight distribution increased slightly from 1.21 to 1.36. The results of the chain extension further confirmed the existence of the functional 1,3-benzodioxole group at the chain-end of PS.

The effect of polymerization temperature and the concentration of BDCB on the RAFT polymerization of styrene have also been investigated. The results are listed in Table I. By comparison of the results at 70°C (entries 1–3 in Table I) with those at 90°C (entries 4–6 in Table I), we can see that the polymerization rate is higher, as expected, at higher temperature, while the polymerization is also well controlled. The same results has also been reported in the literature.[22] Increasing the BDCB concentration in the polymerization system results in a better controllable polymerization. However, the polymerization rate decreases a little with increasing of the concentration of BDCB.

CONCLUSIONS

A synthetic pathway to obtain well-defined α,ω-telechelic PS bearing 1,3-benzodioxole group was demonstrated. The process involved: (i) the synthesis of the RAFT agent BDBC, containing two 1,3-benzodioxole structures and (ii) the polymerization of styrene, using BDBC as the RAFT agent and AIBN as an initiator. The RAFT polymerization of styrene in the presence of BDBC showed characters of living free radical polymerization.

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