



# Synthesis of 9H-fluoren-9-yl benzodithioates and their application as reversible addition–fragmentation chain transfer agents in living radical polymerization of styrene

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## ABSTRACT

The reversible addition–fragmentation chain transfer (RAFT) polymerization is one of living radical polymerizations. In this study, four different 9H-fluoren-9-yl benzodithiolates (FBDTs) were synthesized, and used along with azobis(isobutyronitrile) (AIBN), a radical initiator, in polymerization of styrene (ST) at the molar ratio of 3:1. This new transfer agent exhibited the typical characteristic living free radical polymerization behaviors such as good control of molecule weight and narrow molecule weight distribution. It was concluded that the FBDTs can be used as the RAFT agents in free radical polymerization of vinyl monomers.

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## 1. Introduction

Controlled/living polymerizations have come to prominent importance since Szwarc reported the “living” nature of the anionic polymerization of styrene (ST) and diene monomers in 1956 [1]. After several decades of intensive study on ionic living polymerization, considerable efforts are now being expended to develop free radical polymerizations that display the essential characteristics of living polymerization. One recent development in the field of controlled/living radical polymerization is the reversible addition–fragmentation chain transfer (RAFT) radical polymerization, first reported by Rizzardo et al. in 1998 [2]. By now, RAFT has evolved into a powerful synthetic tool for living polymerization. With an appropriate choice of a RAFT agent and reaction conditions, RAFT polymerization can be used to produce a polymer with predetermined molecular weight and narrow polydispersity. The RAFT polymerization technique can be applied not only to the synthesis of well-defined homopolymers, gradients, diblock copolymers, triblock copolymers, and star polymers, as well as more complex architectures, including microgels and polymer brushes, but also to modification of material surfaces [3–7].

Various RAFT agents, including dithioesters and trithiocarbonates, have been synthesized and applied to RAFT polymerization

[8–13]. In particular, dithioesters ( $S=C(Z)S-R$ ) are one of the most effective RAFT agents, where Z is an activating group that affects the reactivity of the thiocarbonyl moiety toward free radical addition, and R is a free radical leaving group that should be reactive enough to reinitiate the polymerization [14,3]. Thus, in addition to monomers and polymerization conditions, the effectiveness of RAFT agent depends strongly on the nature of the Z and R groups [15].

Due to its p– $\pi$  conjugated structure, the 9-fluorenyl free radical may be stable enough to be a good leaving group, and, at the same time, reactive enough to reinitiate radical polymerization of vinyl monomers. Thus, we attempted to synthesize 9H-fluoren-9-yl benzodithiolates and employ them in radical polymerization, in order to see if they can be used as RAFT agents. In this study, four 9H-fluoren-9-yl benzodithiolates (FBDTs) were synthesized, and used along with azobis(isobutyronitrile) (AIBN), a radical initiator, in polymerization of ST. This paper describes the synthesis of the novel BFDTs and preliminary results on their roles in the polymerization.

## 2. Experimental

### 2.1. Materials

All chemical reagents were purchased from Alfa Aesar, or Tianjin Shentai Chemicals and used as received, unless stated otherwise. AIBN was recrystallized from methanol and dried in

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vacuo overnight. ST was washed with an aqueous solution of sodium hydroxide (5.0 wt%) three times and then with deionized water until neutralized. After being dried with anhydrous magnesium sulfate, the ST was distilled under reduced pressure and kept in a refrigerator at 4 °C. All of the solvents used in this study were purified using standard laboratory procedures. All air/moisture-sensitive compounds were manipulated using the standard Schlenk technique in a dry nitrogen atmosphere. 9-Bromofluorene was prepared according to the method described elsewhere [16].

## 2.2. Measurements

Both  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 300 Ultra Shield spectrometer at 25 °C. Fourier transform infrared (FT-IR) spectra were recorded using FI-IR1730. The number- and weight-average molecular weights ( $M_n/M_w$ ) of polymers were determined with gel permeation chromatography (GPC) equipped with a refractive index detector, using a Shim-pack GPC-804 equipped with Shim-pack GPC-8025 columns calibrated with polystyrene (PS) as a standard. Tetrahydrofuran (THF) was used as an eluant at a flow rate of 1.0 mL min $^{-1}$  at 40 °C.

## 2.3. Synthesis of 9H-fluorene-9-yl benzodithiolates (FBDTs)

Four different FBDTs were synthesized using the same synthetic route; therefore, the synthesis of only 9H-fluorene-9-yl 4-methoxybenzodithioate (FBDT-1) is described here. 4-Bromoanisole (10 mmol) was dissolved in 5 mL anhydrous THF, and introduced over 15 min to a round bottomed flask containing anhydrous THF (2 mL), magnesium turnings (10.5 mmol), and a crystal of iodine. The mixture was heated to 60 °C and refluxed for 1 h. The reaction mixture was then cooled to 0 °C, followed by the slow addition of carbon disulfide (10 mmol) using a degassed syringe. When the reaction mixture became deep orange-colored, it was cooled to room temperature. After 40 min, a solution of 9-bromofluorene (10 mmol in 5 mL anhydrous THF) was introduced, and the reaction mixture was refluxed for 1 h, then cooled in an ice-water bath, followed by slow addition of deionized water. The product was extracted into ethyl acetate (2 × 100 mL). The organic layers were combined, and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was purified using column chromatography on silica using ethyl acetate and petroleum ether (1/40), followed by recrystallization using the same solvents.

**Data for 9H-fluorene-9-yl 4-methoxybenzodithioate (FBDT-1):** pink needle-like crystals; yield 85%; m.p. 165–167 °C:  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3/\text{TMS}$ ),  $\delta$  (ppm) 8.20 (d,  $J$  8.92 Hz, 2H, 2 × *H*-Ph), 7.91 (d,  $J$  7.58 Hz, 2H, 2 × *H*-Ph), 7.65 (d,  $J$  7.57 Hz, 2H, 2 × *H*-Ph), 7.47 (t,  $J$  7.48 Hz, 2H, 2 × *H*-Ph), 7.35 (t,  $J$  7.54 Hz, 2H, 2 × *H*-Ph), 7.04 (d,  $J$  8.93 Hz, 2H, 2 × *H*-Ph), 6.77 (s, 1H,  $-\text{CH}-$ ), 3.91 (s, 3H,  $-\text{OCH}_3$ );  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3/\text{TMS}$ ),  $\delta$  (ppm) 53.21, 113.81, 120.33, 125.29, 127.77, 128.76, 129.54, 137.32, 140.89, 142.90, 225.47 (C=S); IR (KBr,  $\text{cm}^{-1}$ ) 3039, 2947, 2890, 1601, 1499, 1446, 1309, 1263, 1237 (C–S) 1178, 1042 (C=S), 1012, 882, 844, 734; MS for  $\text{C}_{21}\text{H}_{16}\text{S}_2$ , ( $\text{M}^+$ ), measured value (calculated value):  $m/z$ , 349.1 (348.48).

**Data for 9H-fluorene-9-yl 4-methylbenzodithioate (FBDT-2):** purplish red needle-like crystals; yield 64%; m.p. 90–91 °C:  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3/\text{TMS}$ ),  $\delta$  (ppm) 8.03 (d,  $J$  8.25 Hz, 2H, 2 × *H*-Ph), 7.90 (d,  $J$  7.56 Hz, 2H, 2 × *H*-Ph), 7.64 (dd,  $J$  7.53 Hz, 2H, 2 × *H*-Ph), 7.46 (t,  $J$  7.40 Hz, 2H, 2 × *H*-Ph), 7.33 (dd,  $J$  13.97, 7.42 Hz, 4H, 4 × *H*-Ph), 6.74 (s, 1H,  $-\text{CH}-$ ), 2.38 (s, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3/\text{TMS}$ ),  $\delta$  (ppm) 20.59, 53.35, 120.36, 120.72, 125.14, 125.28, 126.82, 127.20, 127.56, 127.81, 128.82, 129.25, 140.93, 142.03, 142.72, 144.33, 227.64 (C=S); IR (KBr,  $\text{cm}^{-1}$ ) 3034, 2917, 2865, 1603, 1446, 1386, 1305, 1235 (C–S), 1181, 1121, 1045 (C=S),

877, 817, 735, 644; MS,  $\text{C}_{21}\text{H}_{16}\text{S}_2$ , ( $\text{M}^+$ ), measured value (calculated value):  $m/z$ , 332 (332.48).

**Data for 9H-fluorene-9-yl 4-bromobenzodithioate (FBDT-3):** purple needle-like crystals; yield 73%; m.p. 115–117 °C:  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3/\text{TMS}$ ),  $\delta$  (ppm) 8.03 (d,  $J$  7.86 Hz, 2H, 2 × *H*-Ph), 7.91 (d,  $J$  7.55 Hz, 2H, 2 × *H*-Ph), 7.67 (dd,  $J$  16.12, 8.53 Hz, 4H, 4 × *H*-Ph), 7.47 (t,  $J$  7.53 Hz, 2H, 2 × *H*-Ph), 7.35 (t,  $J$  7.46 Hz, 2H, 2 × *H*-Ph), 6.69 (s, 1H,  $-\text{CH}-$ );  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3/\text{TMS}$ ),  $\delta$  (ppm) 53.80, 120.22, 125.37, 127.31, 127.70, 128.48, 128.65, 132.83, 141.06, 142.86, 144.60, 228.14 (C=S); IR (KBr,  $\text{cm}^{-1}$ ) 3046, 2924, 2852, 1572, 1445, 1235 (C–S), 1179, 1045 (C=S), 876, 833, 735, 689; MS,  $\text{C}_{20}\text{H}_{13}\text{BrS}_2$ , ( $\text{M}^+$ ), measured value (calculated value):  $m/z$ , 397.1 (397.35).

**Data for 9H-fluorene-9-yl benzodithioate (FBDT-4):** salmon pink needle-like crystals; yield 68%; m.p. 77–80 °C:  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3/\text{TMS}$ ),  $\delta$  (ppm) 8.10 (d,  $J$  7.86 Hz, 2H, 2 × *H*-Ph), 7.92 (d,  $J$  7.62 Hz, 2H, 2 × *H*-Ph), 7.66 (d,  $J$  7.25 Hz, 3H, 3 × *H*-Ph), 7.50 (dd,  $J$  16.85, 7.60 Hz, 4H, 4 × *H*-Ph), 7.47 (t,  $J$  7.47 Hz, 2H, 2 × *H*-Ph), 6.74 (s, 1H,  $-\text{CH}-$ );  $^{13}\text{C}$  NMR (300 MHz,  $\text{CD}_3\text{COCD}_3/\text{TMS}$ ),  $\delta$  (ppm) 53.88, 120.21, 125.30, 127.71, 127.87, 128.64, 128.73, 131.64, 141.04, 142.60, 143.12, 226.18 (C=S); IR (KBr,  $\text{cm}^{-1}$ ) 3053, 2924, 2872, 1443, 1237 (C–S), 1084, 1049 (C=S), 872, 737, 687, 646; MS,  $\text{C}_{20}\text{H}_{14}\text{S}_2$ , ( $\text{M}^+$ ), measured value (calculated value):  $m/z$ , 319.1 (318.46).

## 2.4. Polymerization of ST

Polymerization of ST was initiated by AIBN with or without FBDT at 65 °C. A stock solution of ST, FBDT, and AIBN in a predetermined molar ratio was prepared. An aliquot (1.5 mL) was taken from the stock solution and placed into a polymerization ampoule. The contents were purged with nitrogen for 10 min to remove oxygen, and then the ampoule was sealed. The polymerization reaction was performed at an appropriate temperature for a desired amount of time. Then the polymerization reaction was quenched using a cold water bath. The reaction mixture was diluted with THF and precipitated into a large amount of methanol. The polymer was dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained. The conversion yield (%) of the polymerization was gravimetrically determined.

## 2.5. Chain extension of PS

A predetermined quantity of PS (0.5 g), which was obtained by the initial polymerization of ST at 85 °C in the presence of FBDT and AIBN at the molar ratio of 3:1 for 5 h, was then dissolved in additional ST (50 mL). The resulting PS solution was polymerized under the same conditions as those described above.

## 3. Results and discussion

The synthetic procedure employed to synthesize the FBDT is shown in Scheme 1. Depending on the substituent at the *para* position of bromobenzene, four different FBDTs were synthesized in the same process: formation of Grignard reagent, dithio carbonylation, and formation of dithioester group. The syntheses were simple, but the isolation yields of the products largely depended on the substituted bromobenzene (64–85%). The chemical structures of the products were confirmed by NMR, IR, and mass spectral data. They were all needle-like crystals, so they could be obtained as highly pure solids via recrystallization.

First, polymerization of ST was conducted in the presence of FBDT-3 and AIBN in a nitrogen atmosphere at 65 °C, where the initial molar ratio of [ST]/[FBDT-3]/[AIBN] was 1440:18:1. Aliquots were withdrawn at predetermined time intervals during the

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