

Atom Transfer Radical Polymerization of Styrene Using a Bifunctional Initiator

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A bifunctional alkyl halide, namely 1,2-bis(2'-bromobutyryl) ethane (BBrBE), was synthesized and used to initiate the bulk atom transfer radical polymerization (ATRP) of styrene (St) at 110°C in the presence of CuBr/2,2'-bipyridyl. The narrow polydispersity of polystyrene (PSt) with precisely two arms could be synthesized. The initiate ability of the two active bromide functional groups at both sides of BBrBE for St and the propagation ability of the two arms were confirmed to be similar by the characterization of the individual arms obtained upon hydrolysis of the ester link between the core and the branches.

Keywords Living free radical polymerization, atom transfer radical polymerization, bifunctional initiator, polystyrene

Introduction

Compared with ionic polymerization techniques, radical processes offer the advantages of being applicable to a wide variety of vinyl monomers and having ease of preparation. Recent advances in controlled/"living" radical polymerization have made it viable for the syntheses of well-defined macromolecules.^{1,2} More progress on better control of polymerization was achieved using nitroxide-mediated,³ metal mediated,⁴ and atom transfer radical polymerization (ATRP).⁵⁻¹² Controlled radical polymerization yielded polymers with predetermined molecular weight and narrow polydispersity, and has

been successfully applied in macromolecular engineering to synthesize various block and graft copolymers as well as hyperbranched and star-shaped polymers. For example, Matyjaszewski^{13,14} reported the preparations of two-arm polystyrene using α , α' -dibromoxylene as the initiator and hexa-arm stars using hexakis(bromomethyl)benzene as the initiator by ATRP of styrene, and Fukuda¹⁵ synthesized a well-defined anthracene-labelled two-arm polystyrene. However, the details pertaining to the characterization of the arms of the polymers have not been presented in these reports. Following the nitroxide route, Hawker synthesized tri-arm polystyrene and characterized them by comparing their molar masses with those of their individual arms. And the latter ones were isolated by cleavage of the central core.¹⁶ Gnanou reported ATRP of styrene using octafunctional initiator, and well-defined star PSt was obtained below 15—20% of conversion, but the significant intermolecular termination occurred beyond this conversion.¹⁷

In this paper, we synthesize a bifunctional initiator, 1,2-bis(2'-bromobutyryl) ethane (BBrBE) for the preparation of two-arm polystyrene, demonstrate the use of the dibromide as an effective initiator for ATRP of styrene, and report the characterization of well-defined two-arm polymers by a controlled/"living" radical process for the first time since polystyrene with two equal arms could be synthesized up to 80% of conversion.

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Experimental

BBrBE was synthesized by the reaction of α -bromobutyl acid with ethylene glycol in the presence of *p*-toluene sulfonic acid. The desired BBrBE could be separated as colorless oil by passing the reaction mixture through a column packed with silica gel and eluting with dichloromethane. $^1\text{H NMR}$ (CDCl_3 , 200MHz) δ : 0.97 (t, $J = 8$ Hz, 6H, 2- CH_3), 2.02 (q, $J = 8$ Hz, 4H, 2- CH_2), 4.01 (t, $J = 7$ Hz, 2H, 2-CH), 4.29 (s, 4H, 2- OCH_2). Styrene was stirred overnight over CaH_2 and distilled prior to use. CuBr was purified in acetic acid, washed with methanol and dried under vacuum (100°C/(2 mmHg)) to offer white powder. 2, 2'-Bipyridyl (bpy) was used as received. All other solvents used were purified by standard procedures.

Polymerization of styrene

The general procedure is as follows. Into a 30 mL dry glass tube with a magnetic stirrer, CuBr (0.063 g, 0.44 mmol), bpy (0.206 g, 1.32 mmol), St (8.8 g, 0.085 mol) were put, then BBrBE (0.079 g, 0.22 mmol) was added. The tube was closed with three-way stopcocks. After three freeze-pump-thaw cycles were performed, the tube was sealed under vacuum, and finally placed in an oil bath kept at 110°C. After a prescribed time, the polymerization tube was cooled down to room temperature rapidly and then opened. Several drops of the polymerization solution were put into NMR tube, then NMR spectrum was measured using D-chloroform (CDCl_3) as solvent. Based on the change of the integral value of the peak of vinyl hydrogen, the conversion was calculated according to Eq. (1).

$$\text{Conversion} = [(I_{5.4}/2)/(I_{5.4}/2 + I_{1.7}/3)] \times 100\% \quad (1)$$

where $I_{5.4}$ is the integral value of the peak at 4.69—6.04, $I_{1.7}$ is the integral value of the peak at 0.88—2.54. The rest of contents were passed through neutral alumina column to remove the metal salts. The polymer obtained was precipitated from an excess of methanol, then filtered, and dried at 40°C in vacuum oven for 24 h.

Hydrolysis of the two-arm polystyrene

The two-arm polymer (0.8 g) was added into 30 mL of THF in a 150 mL round-bottomed flask fitted with a refluxing condenser. Then 10 mL of KOH solution (1 M, in ethanol) was added into the flask. The reaction was performed at 70°C for 48 h while stirring. Then the mixture was evaporated to dryness under reduced pressure. Concentrated hydrogen chloride (30 mL, 37%) was added, the mixture was stirred at room temperature for 2 h, then evaporated to dryness. The residual was dissolved in 100 mL of CH_2Cl_2 and washed with water until neutrality. The product was finally precipitated in methanol, and the hydrolyzed polymer was collected by filtering, then dried in vacuum oven.

Measurements

The structure of reactants, intermediates and polymers was characterized by $^1\text{H NMR}$ spectroscopy using a 500 MHz Bruker spectrometer, CDCl_3 as solvent and tetramethylsilane as standard. Molecular weight and molecular weight distribution of the two-arm polystyrene and its hydrolyzed products were determined by gel permeation chromatographs (GPC) on a Waters 150C instrument with three columns (10 nm, 10^2 nm and 10^4 nm), using polystyrene standard as calibration and THF as eluate at 25°C with flow rate of 1 mL/min.

Results and discussion

The bifunctional initiator BBrBE was used as initiator of ATRP for synthesizing two-arm polystyrene. The conditions and results are listed in Table 1. It was observed that as polymerization proceeded, the conversion and molecular weight increased, the molecular weight distribution became narrower as the same phenomenon observed in conventional ATRP. Assuming that each PST macromolecule contain one molecule of BBrBE, the theoretical number molecular weight ($M_{n,\text{th}}$) was calculated according to Eq. (2).

$$M_{n,\text{th}} = \text{Conv.} \times ([M]/[I]) \times 104 + 358 \quad (2)$$

where $[M]$ and $[I]$ are the moles of St and BBrBE added respectively; 104 and 358 are molecular weights of St and BBrBE respectively. The results are listed in Table 1.

Table 1 Conditions and results of ATRP of St using initiation system of BBrBE/CuBr/bpy^a

No.	Time (h)	Conv. (%)	$M_{n,th}^b$	$M_{n,NMR}^c$	$M_{n,GPC}^d$	M_w/M_n^d
1	2.5	28.2	11600	7800	9000	1.35
2	5	40.1	16400	20600	20200	1.23
3	8	53.6	21800	22800	24400	1.19
4	12	61.2	24900	28500	28900	1.13
5	16	70.2	28500	32300	33000	1.15
6	20	76.3	30600	36000	37200	1.14
7	24	83.3	33400	38400	39000	1.15

^a Polymerization conditions: [St]:[I]:[CuBr]:[bpy] = 385:1:2:6 (molar ratio); temperature: 110°C, bulk polymerization. ^b $M_{n,th}$, calculated according to Eq. (2). ^c $M_{n,NMR}$, calculated based on ¹H NMR data. ^d $M_{n,GPC}$ and M_w/M_n , measured on a Waters 150C GPC instrument.

Fig. 1 is a ¹H NMR spectrum of the polymer obtained (Sample No. 1 in Table 1). The facts that the peak at 4.01 corresponding to methine proton next to bromine atom and carbonyl group of BBrBE completely disappeared, and the peak of methyl protons at 0.97 was shifted to a new position at 0.76 in Fig. 1 indicated that the two bromides of BBrBE took part in the initiation reaction and two-arm PSt was formed. The signal at 3.79 corresponds to methylene proton adjacent ester oxygen. The signal at 4.45 is indicative of methine proton next to bromine atom at the end of the polymer. Based on the integral values of the peak at 0.76 ($I_{0.8}$) and the peaks at 6.37 ~ 7.24 ($I_{7.0}$) representative of benzene protons, number average molecular weight $M_{n,NMR}$ was calculated according to Eq. (3)

$$M_{n,NMR} = (6I_{7.0}/5I_{0.8}) \times 104 + 358 \quad (3)$$

The results are listed in Table 1.

It could be observed that there are some differences between $M_{n,GPC}$, $M_{n,NMR}$ and $M_{n,th}$. As the conversion was low, the data obtained from experiment were lower than those calculated from conversion, because the molecular distribution was somewhat wide, the part of low molecular weight played an important role. As the conversion increased, double radical termination maybe occurred. Thus the real molecular weight was slightly higher than the data calculated from conversion. But $M_{n,GPC}$ and $M_{n,NMR}$ agreed with $M_{n,th}$ on the whole. The basic agreement demonstrates that the polymerization can be controlled. The results are the same as those of the polymerization of St using ethyl α -bromobutyrate as initiator.¹⁸

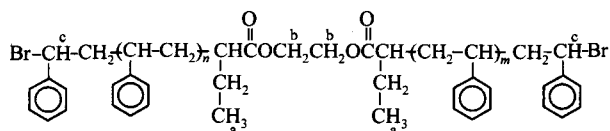
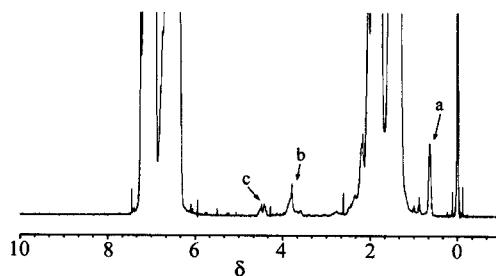


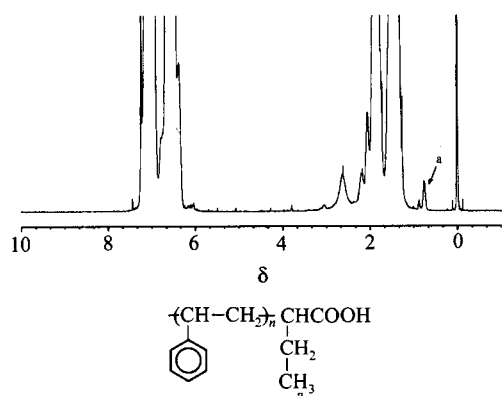
Fig. 1 ¹H NMR spectrum of PSt in CDCl₃ obtained using BBrBE/CuBr/bpy as initiative system (No. 1 in Table 1).

In order to study whether the two functional groups in the same molecule of BBrBE can initiate monomer almost at the same time, and whether they have the same possibility to propagate, the hydrolysis of the two-arm PSt was carried out. Then proton NMR and GPC curve of the hydrolyzed product were measured. The results are listed in Table 2. M_n of the hydrolyzed PSt is almost one half of the corresponding two-arm PSt. M_w/M_n values from 1.16 to 1.39 and the GPC curves show single symmetric peak. The structures of the hydrolyzed polymers analyzed by ¹H NMR spectroscopy (Fig. 2) show that the hydrolysis of the two-arm polystyrene was completed. From these facts, it can be concluded that the hydrolyzed PSt is one arm of the two-arm PSt, and each bromide in the initiator molecule has almost the same possibility of participating in initiation and propagation.

Table 2 Determination of the actual functionality of PSt

No	$M_{n,GPC}$ of two-arm PSt	M_w/M_n of two-arm PSt	$M_{n,GPC}$ of hydrolyzed PSt	M_w/M_n of hydrolyzed PSt	f_{GPC}^a	$M_{n,NMR}$ of two-arm PSt	$M_{n,NMR}$ of hydrolyzed PSt	f_{NMR}^b
1	9000	1.35	4500	1.43	2	7800	4500	1.73
2	20200	1.23	10300	1.39	1.96	20600	11200	1.84
3	24400	1.19	12800	1.28	1.90	22800	12100	1.88
4	28900	1.13	13800	1.22	2.09	28500	14100	2.02
6	37200	1.14	18400	1.19	2.02	36000	17700	2.03

^a The ratio of the $M_{n,GPC}$ of the two-arm PSt to that of the hydrolyzed PSt. ^b The ratio of the $M_{n,NMR}$ of the two-arm PSt to that of the hydrolyzed PSt.

**Fig. 2** ¹H NMR spectrum of hydrolyzed PSt (No. 1 in Table 1).

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