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Block and star block copolymers by mechanism transformation. Part V. Syntheses of polystyrene/polytetrahydrofuran A_2B_2 miktoarm star copolymers by transformation of CROP into ATRP

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Abstract

Polystyrene (PSt)/polytetrahydrofuran (PTHF) A_2B_2 miktoarm star copolymers were prepared by transformation of cationic ring-opening polymerization (CROP) to atom transfer radical polymerization (ATRP). The synthetic approach involves the synthesis of PTHF with two secondary bromine groups in the center of a macromolecular chain, $(PTHF)_2Br_2$, by the CROP of THF with the symmetric tetrafunctional initiator α,ω-dibromosebasionyl dichloride [$ClCOCHBr(CH_2)_6CHBrCOCl$] in conjunction with silver perchlorate; $(PTHF)_2Br_2$ was used to initiate the polymerization of styrene to form $(PSt)_2(PTHF)_2$ star copolymer. The copolymer obtained was characterized by gel permeation chromatography and ^1H NMR spectrum. The hydrolysis of $(PTHF)_2Br_2$ was also investigated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Miktoarm star coplymers; Styrene; Tetrahydrofuran

1. Introduction

Block copolymers have been the subject of intense experimental and theoretical interests for more than two decades because of their practical applications as adhesives, surfactants, compatibilizers and thermoplastic elastomers. Recently, much attention has been focused on nonlinear polymers, such as miktoarm star copolymer because of its unique properties. Several reviews are available [1–3]. For example, the A_nB_m star copolymer might be expected to be a superior compatibilizer to the AB block copolymers.

Although there are several specific methods of synthesizing miktoarm star copolymers, two general strategies: one a chlorosilane approach, another involving divinyl compounds [2,3], have been developed. Both of them use living polymers with anionic or cationic ions.

The synthesis of A_2B_2 miktoarm copolymers was first reported by Xie and Xia [4] using a chlorosilane method. The synthetic approach involved the reaction of 1 mole of tetrachlorosilane with two moles of the living PS chain, resulting in the formation of the two-armed product. The remaining Si–Cl bonds continued to react with excess living PEO chains to form $(PS)_2(PEO)_2$ miktoarm star copolymer.

Different from the work of Xie and Xia, Iatrou and Hadjichristidis [5] used titration techniques monitored by SEC to prepare $(PSt)_2(PB)_2$. First, the living polystyrene (PSt) chains reacted with excess $SiCl_4$, followed by evaporation of the unreacted silane. The second PSt arm was incorporated by slow stoichiometric addition of one living PSt chain to react with $PSSiCl_3$, which was monitored by SEC. The last step involved the addition of a small excess of living polybutadiene (PB) chains for the preparation of the $(PSt)_2(PB)_2$.

The preparation of (polyisoprene)$_2$(polybutadiene)$_2$ copolymer was reported by Algaier [6]. In order to control the number of arms, two different methods were used. The first route was started by condensing one mole of silicontetrachloride with two moles of poly(isoprenyl) lithium (PILi), which had been end-capped by a few units of styrene (St) to avoid the formation of the three- or four-armed PI stars. The second route was started by linking two PILi chains with one molecule of silicon tetrachloride at −40°C to reduce the reactivity of PI chains. Both routes are completed by reaction of the two-armed intermediate $(PI)_2SiCl_2$ with an excess of poly(butadienyl) lithium.

Höcker and Latterman [7] prepared 4-miktoarm copolymers by adding living chains to bis(1-phenyl-vinyl) benzene, followed by a subsequent addition of monomer. Quirk and coworkers [8,9] have further developed this

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"living linking method" for the syntheses of A_2B_2 copolymers. In this case, A was PSt, and B was PI or PB.

According to the method of linking with divinyl compounds, Fernyhough et al. [10] reported the synthesis of $(PI)_2(PMMA)_2$ miktoarm star copolymers, in which the divinyl coupling agent was 1,1-(1,2-ethandiyl) bis (4-(1-phenylethenyl)) benzene.

Wright and Young [11] reported the synthesis of $(PSt)_2(PI)_2$ copolymers by the above two methods at the same time. In the first method, 2 moles of polydienyl lithium were reacted with 1 mole of 1,3-bis (1-phenylethenyl) benzene. This difunctional adduct was then used to initiate the polymerization of St. The second route is similar to that of Xie and Xia.

By living cationic polymerization, Bae and Faust [12] prepared the first example of amphiphilic A_2B_2 star copolymer, where A is polyisobutylene (PIB) and B is poly(methyl vinyl ether) (PMeVE). The synthetic approach involved the living coupling reaction of living PIB, using 2,2-bis-[4-(1-tolylethenyl)phenyl]propane (BDTEB) as a living coupling agent, followed by the chain ramification reaction of methyl vinyl ether (MeVB) at the junction of the living coupled PIB, thus the A_2B_2 star copolymer was formed.

The disadvantages of the methods mentioned above are the high-vacuum techniques, troublesome procedures and difficulty in controlling the number of arms. In order to overcome these problems, mechanism transformation has been developed. Early studies involved converting propagation center of the first block into another type of initiation site that can initiate the second monomer to polymerize. Several articles reported that the well-defined block copolymers were made by the transformation of initiating site from living anionic to living cationic [13–17], from living cationic to living anionic [18–21] and from living coordination to living cationic polymerization [22]. However, these techniques require many steps and the monomers available are limited.

Recently, the developing living radical polymerization, mainly nitroxide-mediated stable free-radical polymerization and atom transfer radical polymerization (ATRP), have opened a new and potentially wide route for the preparation of well-defined macromolecules because many monomers can undergo free-radical polymerization [23–27]. In previous articles, PTHF–PSt, PSt–PTHF–PSt, PTHF–PSt–PTHF and PDOP–PSt block copolymers have been prepared by mechanism transformation of the initiating site [28–32]. Matyjaszewski and coworkers [28,33,34] reported a general method of preparing block copolymers without any modification of the initiating sites by transformation of living cationic polymerization into ATRP. However, there is no report on the application of mechanism transformation for preparation of miktoarm star copolymer. The present work study synthesis of the hitherto unknown A_2B_2 star copolymers, where A is PSt and B is polytetrahydrofuran (PTHF), by the transformation from cationic ring-opening polymerization (CROP) into ATRP without modification of the initiating site.

2. Experimental section

2.1. Materials

St, CuBr (AR, Shanghai No. 1 Chemical Reagent Factory, 98%), 2,2′-bipyridine(bpy, Aldrich) were purified by the method described in our previous paper [32]; the reagents used for the cationic polymerization of THF were purified as before [35]. All other reagents were of analytical grade, and used as received.

2.2. Synthesis of α,ω-dibromosebasionyl dichloride

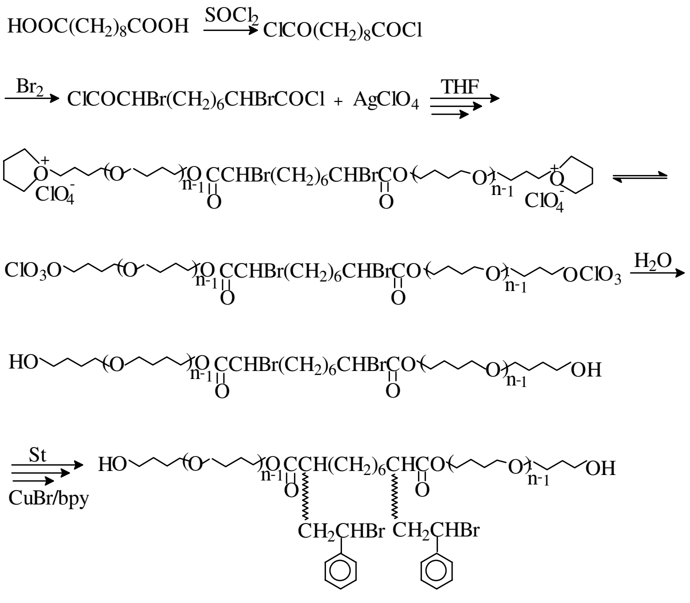
α,ω-Dibromosebasionyl dichloride (DBSDC) was prepared as follows: 4.04 g of sebasic acid (0.02 mol), 7 ml of $SOCl_2$ (0.1 mol) were added into a 25 ml two-necked flask equipped with anhydrous $CaCl_2$ tube for protection from moisture. The mixture was refluxed for 2 h while stirring. Then, about 10 ml of dried liquid Br_2 (0.2 mol) was added dropwise into the reaction mixture in 5 h. The mixture was heated at 95°C while stirring for additional 24 h. After removal of volatile compounds at 65°C under reduced pressure for several hours, a slight-yellow liquid product was obtained in 98.5% of yield.

^{1}H NMR ($CDCl_3$), δ: 1.38–1.53 (m, 8H, $CH_2(CH_2)_4CH_2$), 2.04–2.21 (m, 4H, $2CHBrCH_2$), 4.52 (t, 2H, $2CHBrCH_2$).

IR (neat) ν: 1782 cm^{-1} (C=O).

2.3. Synthesis of macroinitiator $[-(CH_2)_3CHBrCO-PTHF]_2$, $[(PTHF)_2Br_2]$ by CROP

Macroinitiator $(PTHF)_2Br_2$ was synthesized by CROP of THF with DBSDC in combination with silver perchlorate as initiator [35]. A typical procedure was as follows: a 50 ml two-necked flask with a magnetic bar was evacuated and purged with pure nitrogen alternatively three times, 10.5 ml of methylene chloride and 0.341 g (0.865 mmol) of DBSDC were then added. Stirring was commenced. Under nitrogen atmosphere, 0.374 g (1.73 mmol) of silver perchlorate was transferred into the flask at −15°C. After 1 h, 19.5 ml (240 mmol) of THF was added with a syringe. The samples used for measurements of polymerization conversion and molecular weight (MW) were withdrawn from the polymerization system at definite time intervals. The polymerization was stopped by adding excess distilled water. The mixture was filtered to remove AgCl, and unreacted THF was removed in vacuum. Then the residue was dissolved in methylene chloride, and washed with distilled water until neutralization, subsequently methylene chloride was removed with a rotary evaporator; the residue was dissolved in THF and the solution was added into methanol at −30°C. The product $(PTHF)_2Br_2$ was precipitated, collected by filtration, and finally dried at 40°C/0.2 Torr for 24 h. For



Scheme 1.

kinetic study, the product was directly obtained after removal of methylene chloride in vacuum, and no precipitation was performed.

2.4. Hydrolysis of $(PTHF)_2(Br)_2$

The procedure of hydrolysis of $(PTHF)_2(Br)_2$ was similar to the method described in our previous paper [35]. The hydrolyzed product was dried at 40°C/0.2 Torr for 24 h.

2.5. ATRP of St initiated with $(PTHF)_2Br_2$

The A_2B_2 star copolymer was synthesized by the bulk polymerization of St initiated by $(PTHF)_2Br_2$ in combination with CuBr/bpy. A typical procedure was as follows: a glass tube with a magnetic bar was charged with 0.4 g (0.035 mmol) of $(PTHF)_2Br_2$, 0.010 g (0.07 mmol) of CuBr, 0.033 g (0.21 mmol) of bpy and 4.0 ml (35 mmol) of St. The system was degassed by three freeze–pump–thaw cycles. The tube was sealed under vacuum, and placed in a thermostat at 110°C while stirring. The polymerization was terminated after a definite time interval. The tube was opened, and conversion was determined by ^{1}H NMR. The reaction mixture was dissolved in THF and the solution was passed through a short neutral alumina column to remove the copper complexes. After precipitation from solution in THF into methanol, the solid was collected by filtration. After dried under vacuum at 40°C overnight, 1.5 g of A_2B_2 copolymer was obtained.

2.6. Characterization

MW and molecular weight distribution (MWD) were determined on a Waters 150C gel permeation chromatography (GPC) equipped with microstyragel columns (500, 10^3 and 10^4 Å) using PSt standards, and THF as eluent at a flow rate of 1.0 ml min^{-1}. ^{1}H NMR spectra were recorded on a Bruker DMX-500 NMR spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard. IR spectra were recorded on a vector-22 FTIR instrument. The conversion measurements of THF were carried out on 102G gas chromatography (Shanghai Analysis Instrument Co.) equipped with 3 m long column in which 101 white support coated with 15 wt% OV-17.

3. Results and discussion

3.1. CROP of THF initiated by DBSDC in combination silver perchlorate

The basic outline for the synthesis of DBSDC, $(PTHF)_2Br_2$ and PSt/PTHF A_2B_2 miktoarm star copolymer is shown in Scheme 1. The CROP of THF initiated by diacylium ions formed in situ by the reaction of DBSDC with $AgClO_4$ was performed. The conditions and results are listed in Table 1.

It was very important to know whether the bromine of the initiator reacted with $AgClO_4$ during the formation of oxocarbenium perchlorate, although accurate molar ratio of $AgClO_4$/DBSDC (2:1) was added into polymerization system. Therefore, ^{1}H NMR spectra of the polymers were measured. A typical spectrum is shown in Fig. 1b.

The protons of four methylene groups in the middle of the initiator appear at 1.36–1.52 ppm. The peak at 1.98–2.09 ppm is ascribed to the protons of methylene group next to methine group, and the signal at 4.18–4.25 ppm corresponds to the methylene protons adjacent the oxygen of the ester group and the methine proton connected with the bromine. The ratio of integral values of the signals at 4.18–4.25, 1.98–2.09 and 1.36–1.52 ppm is

Table 1
Results and conditions of CROP of THF initiated by DBSDC/$AgClO_4$ (the polymerization were performed at −15°C; $[THF]_0 = 8.0$ mol l^{-1})

No.[a]	$[I]_0$ (mmol l^{-1})	$[AgClO_4]$ (mmol l^{-1})	Time (h)	Conv[b] (%)	M_n			M_w/M_n (GPC)
					NMR[c]	GPC	th[d]	
1	9.61	19.22	16	26	18360	17990	15960	1.26
2[e]					8810	9190	7800[f]	1.30
3	14.4	28.8	4	11.5	6030	5810	4970	1.22
4	14.4	28.8	9	22	11470	11090	9160	1.28
5	28.8	57.6	5	19	3980	3710	4160	1.43
6	28.8	57.6	9	31	6720	6210	6560	1.41
7	28.8	57.6	15	41	8830	8940	8560	1.44
8	28.8	57.6	20	47	9470	9290	9760	1.40
9	28.8	57.6	26	52	10250	8970	10760	1.38

[a] The samples of Nos. 1, 3 and 4 were precipitated from excess of methanol at −30°C one time. The samples of Nos. 5–9 were obtained after evaporation of THF in vacuum.

[b] Determined by GC.

[c] Calculated by Eq. (1).

[d] Calculated by Eq. (2).

[e] The hydrolyzed product of sample 1.

[f] Theoretical molecular weight of each branch of $(PTHF)_2(Br)_2$, $M_{n,HPTHF}$(th), according to $M_{n,PHTHF}(th) = [M_{n,PTHF}(th) - 396 + 35.5 \times 2 - 17 \times 2]/2$, where $M_{n,PTHF}$(th), 396,35.5, 17 and 2 have the same meaning in Eq. (2).

3.00:2.09:3.89, which is about 3:2:4 within ±5% of experiment error. This demonstrates that the reaction of bromine with $AgClO_4$ could be negligible.

If –CHBr group participated in the CROP of THF, the signal at 1.98–2.09 ppm should be shifted to up field. The molecular weight calculated based on the integral value of this signal should have bigger difference with the corresponding theoretical one. Based on the integral values of the peaks at 1.98–2.09 ppm ($I_{2.0}$) and 3.41–3.77 ppm ($I_{3.4}$) corresponding to methylene group next to ether oxygen, the number-average molecular weight of $(PTHF)_2Br_2$, $M_{n,PTHF}$(NMR), can be calculated by Eq. (1):

$$M_{n,PTHF}(NMR) = (I_{3.4}/I_{2.0}) \times 72 + 396 - 35.5 \times 2 + 17 \times 2 \quad (1)$$

where 72, 396, 35.5 and 17 are the molecular weights of THF, DBSDC, Cl and OH, respectively.

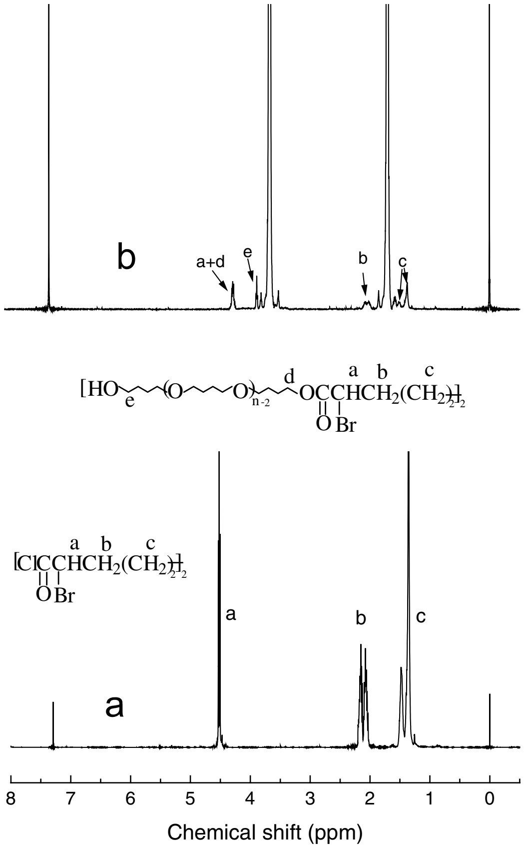


Fig. 1. (a) ^1H NMR spectra of DBSDC; and (b) $(PTHF)_2Br_2$ (No. 3 in Table 1).

Assuming that all of the initiator molecules participate in the initiation, and no intramolecular chain transfer reaction occurs, the theoretical molecular weight, $M_{n,PTHF}$(th), was calculated by Eq. (2):

$$M_{n,PTHF}(th) = ([M]_0/[I]_0) \times Conv. \times 72 + 396 - 35.5 \times 2 + 17 \times 2 \quad (2)$$

where $[M]_0$ and $[I]_0$ are the initial molar concentrations of the monomer and initiator, respectively. The results are calculated based on Eqs. (1) and (2), and listed in Table 1. The agreement of $M_{n,PTHF}$(NMR) and $M_{n,PTHF}$(th) (see Nos. 5–9 in Table 1) supports further that the amount of CHBr group remains unchanged during the CROP of THF.

Another important condition of preparing well-defined A_2B_2 miktoarm star copolymers is the "living" character of the polymerization. It was reported that the polymerization of THF was living, and transfer of active cation species to polyester oxygen could be virtually eliminated when

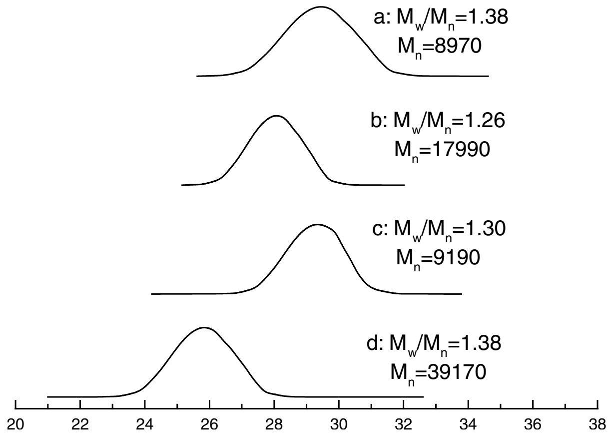


Fig. 2. GPC curves of: (a) $(PTHF)_2Br_2$ (No. 9); (b) No. 1 in Table 1]; (c) its hydrolyzed product (No. 2 in Table 1); and (d) $(PSt)_2(PTHF)_2$ (PT_2PS_1 in Table 2).

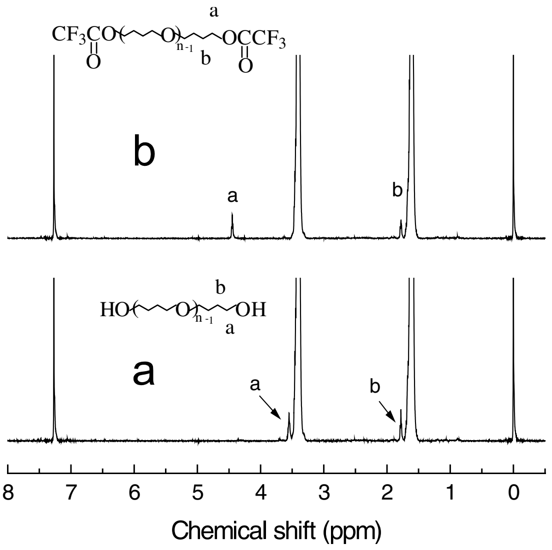


Fig. 3. ^{1}H NMR spectra of hydrolyzed product of $(PTHF)_2(Br)_2$ (No. 2 in Table 1): (a) before; and (b) after esterification with $(CF_3CO)_2O$.

oxocarbenium perchlorate was used as initiator at −10°C or at much lower temperature [35,36]. Typical GPC curves of the $(PTHF)_2Br_2$ is shown in Fig. 2a. Symmetric peak indicates that no detectable cyclics were formed, which means that no detectable intramolecular chain transfer reaction took place during the polymerization.

In order to get more information on the structure, MW and MWDs of the branch chain in $(PTHF)_2Br_2$ obtained, hydrolysis of the polyether was investigated. The results are listed in Table 1. ^{1}H NMR spectra of the hydrolyzed product, HPTHF, recorded before and after esterification with trifluoroacetic anhydride (TFA) are shown in Fig. 3. Complete hydrolysis was supported by the absence of signals originating from the initiator comparison with Fig. 1. GPC of HPTHF shows the expected decrease in molecular weight, almost half of MW of $(PTHF)_2Br_2$ (see Fig. 2c).

As we know, each molecule of the hydrolyzed product contains two end-standing hydroxyl groups: one is original; the other is the result of hydrolysis of the ester group. After esterification with TFA, the peak at 3.55 ppm in Fig. 3a corresponding to the methylene protons next to the end-standing hydroxyl group shifted to 4.32–4.48 ppm (see Fig. 3b). If the amount of cyclic oligomers is negligible, the molecular weight of HPTHF, $M_{n,HPTHF}$(NMR) can be calculated according to Eq. (3):

$$M_{n,HPTHF}(NMR) = (I_{3.4}/I_{4.4}) \times 72 + 18 \quad (3)$$

where $I_{4.4}$ is the integral value of the peak at 4.32–4.48 ppm, 72 and 18 are the molar masses of THF and H_2O,

Table 2

Results and conditions of ATRP of St initiated with $(PTHF)_2(Br)_2$/CuBr/bpy (the polymerization was performed at 110°C; St: 3.64 g; $[St]_0:[PT_1]:[CuBr]:[bpy] = 1000:1:2:6$ (molar ratio))

No.	Time (h)	Conv.[a] (%)	PSt segment		Star copolymer				DP$_n$ THF/St (NMR)
			M_n (NMR)[b]	M_n (th)[c]	M_n (NMR)[d]	M_n (GPC)	M_n (th)[e]	M_w/M_n (GPC)	
PT_1[f]			11 470					1.28	77/0
PT_1PS_1	2	7	7170	7280	18 640	17 830	18 750	1.42	77/34
PT_1PS_2	4	13.5	14 250	14 040	25 720	24 110	25 510	1.44	77/69
PT_1PS_3	6	20	21 610	20 800	34 080	30 390	32 270	1.40	77/104
PT_1PS_4	8	25	24 880	26 000	36 350	34 900	37 470	1.37	77120
PT_1PS_5	10	31	33 590	32 310	45 060	41 050	43 480	1.37	77/161
PT_2[f]			18 310					1.26	126/0
PT_2PS_1[g]	8	19	24 650	23 710	42 960	39 170	42 020	1.38	126/119

[a] Determined by ^{1}H NMR data.

[b] Calculated by Eq. (4).

[c] Theoretical molecular weight of PSt segment was calculated according to $M_{n,PS}(th) = ([M]_0/[I]_0) \times \text{Conv.} \times 104$, where $[M]_0$ and $[I]_0$ are the initial molar concentrations of monomer and macrointiator, respectively; 104 is the molecular weight of St.

[d] $M_{n,PTPS}(NMR) = M_{n,PT}(NMR) + M_{n,PS}(NMR)$.

[e] $M_{n,PTPS}(th) = M_{n,PT}(NMR) + M_{n,PS}(th)$.

[f] PT_1: No. 4 in Table 1; PT_2: No. 1 in Table 1.

[g] $[St]_0:[PT_2]:[CuBr]:[bpy] = 1200:1:2:6$ (molar ratio).

respectively. The results listed in Table 1 show that $M_{n,HPTHF}$(NMR) is half of $M_{n,PTHF}$(NMR) of the original $(PTHF)_2Br_2$, and the molecular weight distribution of HPTHF is almost the same with $(PTHF)_2Br_2$, indicating that all acylium ions in the initiator took part in the initiation, and the propagation possibility of the two chains were almost the same. As a result, polyether with almost equal chain length of two arms was produced.

3.2. Preparation of PSt/PTHF A_2B_2 star copolymers by ATRP methods

The synthesized $(PTHF)_2Br_2$ was used in the preparation of PSt/PTHF miktoarm star copolymers. The conditions and results are summarized in Table 2. In comparison with the ATRP of St with $CH_3CH(PH)Br$ or other bromide compounds as initiators, the ATRP of St initiated by the $(PTHF)_2Br_2$ macroinitiator system seems slow, the reason probably is that low molar concentration of macroinitiator in St ($[St]_0:[(PTHF)_2Br_2]_0 = 1000:1$) decreased the concentration of free radical species.

It was reported that St could well undergo ATRP in the presence of an initiator with CHBr and hydroxyl groups [32]. In order to obtained the well-defined A_2B_2 miktoarm copolymers, it is necessary to know whether the ATRP of St using $(PTHF)_2Br_2$/CuBr/bpy as initiator system is of "living" character. Kinetic study shows linear relationship between $\ln[M]_0/[M]_t$ and polymerization time in Fig. 4a, suggesting that the concentration of the active species kept constant and the termination reaction was negligible at least during the early stage of the polymerization. From Fig. 4b, we can see that the MW of the PSt segment increased linearly and the MWD improved as the increase of monomer conversion, which are generally observed in ATRP process.

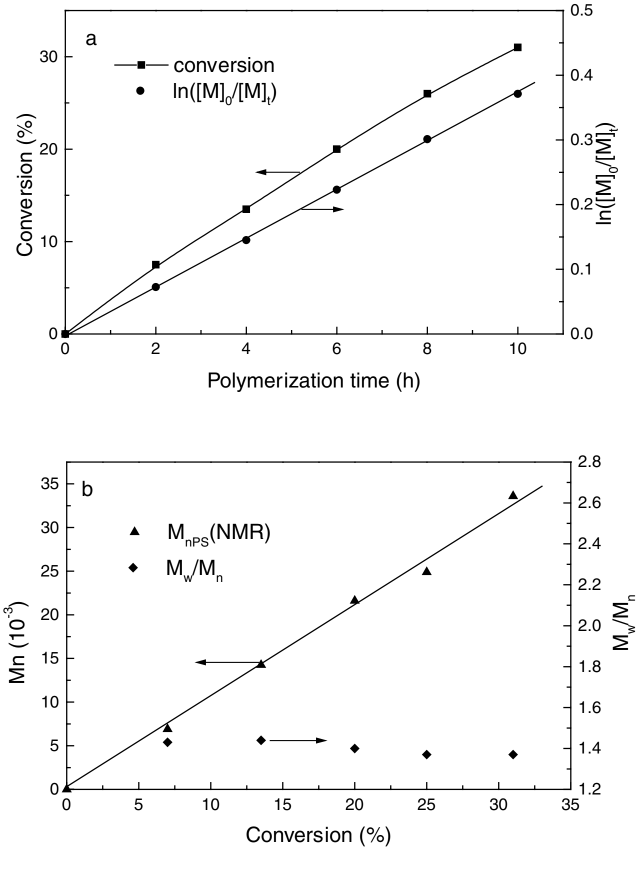


Fig. 4. (a) Conversion and $\ln([M]_0/[M]_t)$ — polymerization time curves; and (b) M_n and M_w/M_n — conversion curves for the bulk ATRP of St conducted at 110°C. [St]:[macroinitiator]:[CuBr]:[bpy] = 1000:1:2:6 (molar ratio).

The GPC curve of star copolymer $(PTHF)_2(PSt)_2$ shown in Fig. 1d is unimodal and symmetric. The MWD listed in Table 2 is relatively low. All of the facts verify the living nature of the ATRP of St. Therefore, we could presume that the star copolymer obtained has the structure as shown in Scheme 1. A typical spectrum of the copolymer (PT_1PS_5 in Table 2) is shown in Fig. 5.

The peak at 0.97 ppm is assigned to the protons of six methylene groups from the initiator. The signal at 4.45 ppm is ascribed to the methine proton next to the end-standing bromine atom. The protons of the methylene group connected to the oxygen of the ester group from the macroinitiator $(PTHF)_2Br_2$ appear at 4.22 ppm. The ratio of integral values of the peaks at 4.45, 4.22 and 0.97 ppm is 1.00:2.02:5.83, supporting that all –CHBr group of $(PTHF)_2(Br)_2$ participated in the initiation of ATRP of St, and $(PTHF)_2(PSt)_2$ miktoarm star copolymer was formed, and the elimination of bromine was negligible probably due to low conversion of St.

From the integral values of aromatic protons (I_{Ar}) and methylene protons from initiator ($I_{0.97}$), the number-average molecular weight of PSt segment, $M_{n,PSt}$(NMR), can be

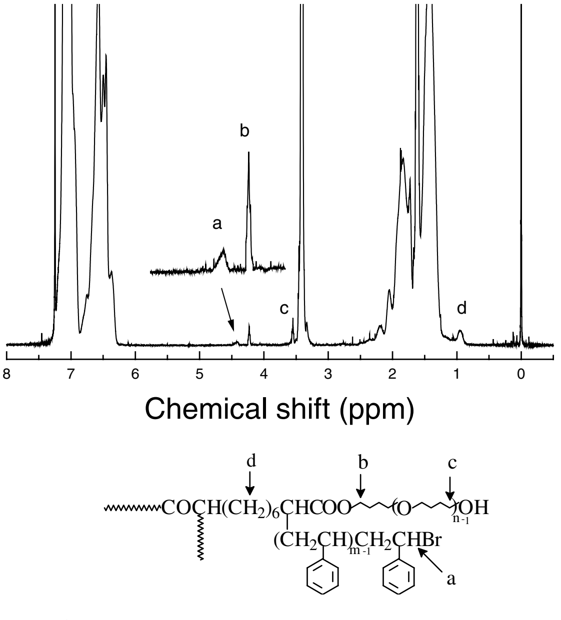


Fig. 5. ^1H NMR spectrum of $(PSt)_2(PTHF)_2$ (PT_1PS_5 in Table 2).

calculated by Eq. (4):

$$M_{n,PSt}(NMR) = 12/5 \times (I_{Ar}/I_{0.97}) \times 104 \qquad (4)$$

where 104 is the molecular weight of St. The results are listed in Table 2.

From Table 2, we can see that the M_w/M_n values of the obtained star copolymers approach to the value (1.28) of the originated $(PTHF)_2Br_2$, as the increase of monomer conversion. The $M_{n,PS}$(NMR) of the copolymer agrees well with $M_{n,PS}$(th). These facts are another evidences that all –CHBr group of the macroinitiator took part in the initiation; as a result, the miktoarm $(PTHF)_2(PSt)_2$ was virtually formed.

4. Conclusions

The miktoarm A_2B_2 star copolymer, $(PTHF)_2(PSt)_2$, could be prepared by a sequential two-step method without any modification of the initiating site, using transformation from CROP to ATRP. Two oxocarbenium perchlorate groups in each molecule of the initiator initiated polymerization of THF, and two-armed $(PTHF)_2Br_2$ with narrow MWD was formed. The MW of each arm is almost the same, and could be controlled by initial molar ratio of THF/DBSDC, and conversion. No CHBr group was lost during CROP. The macroinitiator, $(PTHF)_2Br_2$ is an effective initiator of ATRP of St, its two PTHF segments with two end-standing hydroxyl groups do not affect the living character of the ATRP process. A well-defined PSt/PTHF A_2B_2 miktoarm star copolymers was virtually produced.

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