Block and Star-Block Copolymers by Mechanism Transformation. 3. S-(PTHF-PSt)$_4$ and S-(PTHF-PSt-PMMA)$_4$ from Living CROP to ATRP

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ABSTRACT: Star-shaped poly(tetrahydrofuran) tetrols were prepared by living cationic ring-opening polymerization of tetrahydrofuran and esterified with bromoacetyl and bromoisobutyryl chloride. The intermediate produced was used as macroinitiator to initiate the atom transfer radical polymerization (ATRP) of styrene and subsequently atom transfer radical polymerization of methyl methacrylate at 80−110 °C with CuBr/2,2′-bipyridine as catalyst. Kinetic studies and GPC analyses provided the evidences of "living" polymerization: constant concentration of active species, narrow molecular weight distribution, and well control of molecular weight. The NMR spectra and GPC analyses demonstrated the formations of four-armed star polymer and copolymers: S-(PTHF)$_4$, S-(PTHF-PSt)$_4$, and S-(PTHF-PSt-PMMA)$_4$. For S-(PTHF-PSt)$_4$, this conclusion was further confirmed by GPC analysis of the PSt obtained from hydrolysis of the copolymer.

Introduction

Branched polymers with controlled architecture have been designed and prepared in order to better understand the relationship between their topologies and their unique solution and bulk properties, especially in comparison to the corresponding linear polymers. Among branched polymers, star polymers represent the most elementary way of arranging the subchains since they contain only one branching point. Star polymers are used as models for experimentally evaluating theories about the solution properties and rheological behavior of branched polymers.[1] Star polymers have been used as rheology modifiers or pressure sensitive adhesives.[2] Compared to linear block copolymer, such as polystyrene-*b*-polybutadiene (PS-*b*-PBD) and polystyrene-*b*-polyisobutylene (PSt-*b*-PIB), the corresponding star-block copolymers with similar molecular weight have lower melt and solution viscosities, are more processable, have superior mechanical properties, and are less sensitive to the methods of sample preparation.[3−5] The morphology of star-block copolymers have regularly arranged domains of uniform sizes.[3,4]

Among the variety of methods reported, living polymerization is the most suited for the synthesis of multiarmed polymers with controlled structure. Generally, the following three methods have been used for preparing star polymers: (1) living polymerization with a multifunctional initiator, (2) coupling reaction of linear living polymers with a multifunctional coupling agent, and (3) linking reaction of linear living polymers with a divinyl compound. Among these, methods 1 and 2 can afford a predetermined numbers of arms per molecule. All three approaches have been used successfully in various living polymerizations including anionic,[6,7] cationic,[8−10] and metathesis.[11,12]

The recent development of controlled/"living" radical polymerizations has opened a new and potentially general route to synthesize well-defined macromolecules.[13−17] These living and/or controlled systems can be achieved, in general, either by nitroxide-mediated stable free radical polymerization (SFRP)[18,19] or by atom transfer radical polymerization (ATRP).[20,21] These controlled polymerizations have been applied to the syntheses of well-defined block, graft copolymers, and hyperbranched polymers, either by sequential monomer addition or by mechanism transformations.[22−31] Both SFRP and ATRP have been used to prepare well-defined star polymers and star-block copolymers.[28,32−36] However, there are no reports of the synthesis of star-block copolymers by a combination of polymerization mechanisms.

In designing a research program for preparing star-shaped thermoplastic elastomers, we have synthesized a series of poly(tetrahydrofuran) (PTHF) and polyacetal polyols.[37−43] Since THF undergoes chain transfer reactions during cationic ring-opening polymerization,[44] it is impossible to prepare well-defined star-shaped PTHF polyols with a multifunctional initiator.[45] Recently, we have synthesized tri- and tetraarmed PTHF polyols with controlled molecular weights and narrow MWDs using tri- and tetraacyl chloride/silver perchlorate initiators, respectively, at low temperatures such as −15 °C.[42,43] Because of the incompatibility of PTHF with PSt and/or PMMA, linear block copolymers of PTHF with PSt or PMMA microphase segregate and behave as thermoplastic elastomers.[24,46] Thus, the star block copolymer S-(PTHF-PSt)$_4$[47] and especially the star-shaped S-(PTHF-PSt-PMMA)$_4$ triblock should show interesting microphase structure and mechanical properties. In this paper, we use the modified four-armed PTHFs as macroinitiators to prepare star-block copolymers with four-armed PTHF as core. To the best of our knowledge, this is the first report of the synthesis and characterization of four-armed star-block and triblock S-(PTHF-PSt)$_4$ and S-(PTHF-PSt-PMMA)$_4$ by a mechanism transformation from living cationic ring-opening polymerization to ATRP.

Experimental Section

1. Materials. Styrene (St, Aldrich, 99%) and methyl methacrylate (MMA, Aldrich, 99%) were stirred over CaH_2 overnight and distilled under vacuum prior to use. CuBr (AR, Shanghai No. 1 Chemical Reagent Factory, 98%) was purified by stirring with glacial acetic acid, washing with ethanol, and then drying in a vacuum at 70 °C. 2,2′-Bipyridine (bpy) (Aldrich, 99%) was recrystallized from *n*-hexane. All the

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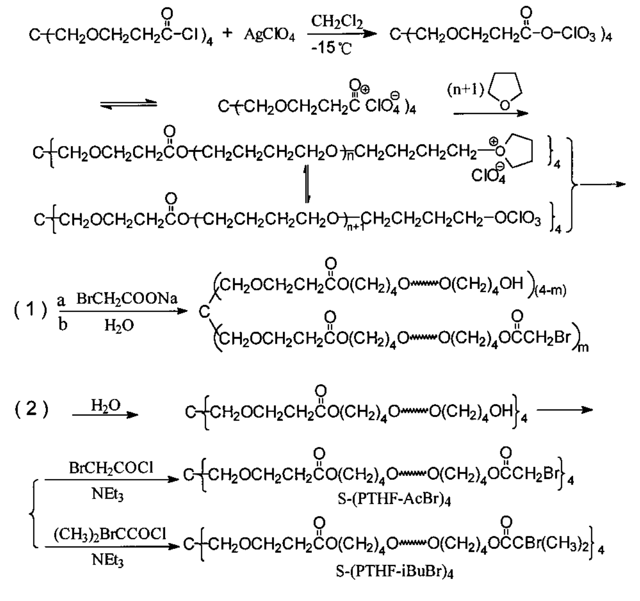
Scheme 1. Strategy for the Syntheses of Tetrafunctional Macroinitiators



reagents used for preparing four-armed PTHF were prepared and/or purified as described before.[42] Bromoacetyl and bromoisobutyryl chlorides were prepared by the reaction of the corresponding acid with thionyl chloride followed by distillation under reduced pressure.[48] Sodium bromoacetate was synthesized by the reaction of bromoacetic acid with aqueous sodium hydroxide.

2. Characterization. ^{1}H NMR spectra were obtained using a Bruker AC250 or DMX500 NMR spectrometer. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) as internal standard. The molecular weight distribution was determined on a Waters 150C-gel permeation chromatograph (GPC) equipped with microstyragel columns (500, 10^3, and 10^4 Å) using polystyrene standards and THF as eluent at a flow rate of 1.0 mL/min. The THF conversion was determined using a 102G gas chromatograph (GC) (Shanghai Analysis Instrument Co.):[42] column (3 m long) equipped with 101 white support coated by 15 wt % OV-17. The temperatures of injection, column, and identification were 120, 60, and 100 °C, respectively. The flow rate of hydrogen was 60 mL/min.

3. Syntheses of the Macroinitiators. Four-armed, living S-$(PTHF)_4$ was prepared according to the reported procedure.[42] At definite monomer conversion, macroinitiators were synthesized by two ways (see Scheme 1):

Route 1. A solution of sodium bromoacetate (2.6 g, 16 mmol, 10 M equivalent of sodium bromoacetate to the living species) in THF (100 mL) was added into the reaction mixture under nitrogen. After 2 h, the reaction temperature was allowed to rise to room temperature and kept stirring for another 24 h. The mixture was filtered to remove AgCl, dissolved in methylene chloride after removal of the unreacted THF in a vacuum, and then washed with distilled water until neutralization. After methylene chloride was removed, the PTHF-AcBr was dissolved in THF and precipitated from cold water. The "macroinitiator" obtained was finally dried at 40 °C/1 Torr for 24 h over P_2O_5; yield 51%, $M_n = 1.44 \times 10^4$ (by NMR), and MWD is 1.22.

^{1}H NMR (δ, $CDCl_3$): 4.20 (t, $-C\mathbf{H}_2OOCCH_2Br$), 4.09 (t, $-COOC\mathbf{H}_2-$), 3.82 (s, $-CH_2OOCC\mathbf{H}_2Br$), 3.65−3.30 (m, $-CC\mathbf{H}_2OC\mathbf{H}_2C-$), 2.55 (t, $-CH_2C\mathbf{H}_2COOCH_2-$), 1.9−1.5 ppm (m, $-CH_2C\mathbf{H}_2C\mathbf{H}_2CH_2-$).

Route 2. The polymerization was stopped by adding a small amount of distilled water; the product was purified and dried as before.[42] The end-capping procedure was as follows: under nitrogen, a solution of bromoisobutyryl chloride (0.37 g, 2 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of rigorously dried S-$(PTHF)_4$ tetrol (1.7 g, 0.1 mmol) and triethylamine (60 μL, 0.4 mmol) in CH_2Cl_2 (20 mL) for 1 h at 0 °C while stirring; subsequently, the temperature was allowed to rise to room temperature. The reaction was continued for 24 h. The solution was filtered, half of the solvent was evaporated, and the PTHF macroinitiator was precipitated in cold methanol. After filtration, the solid was dissolved in CH_2Cl_2 and washed with distilled water until neutral, and then the macroinitiator was precipitated and dried as in route 1; 1.71 g of product (yield: 99.7%) was obtained with $M_n = 1.7 \times 10^4$ (by NMR) and MWD = 1.25. The NMR spectrum is shown in Figure 5a.

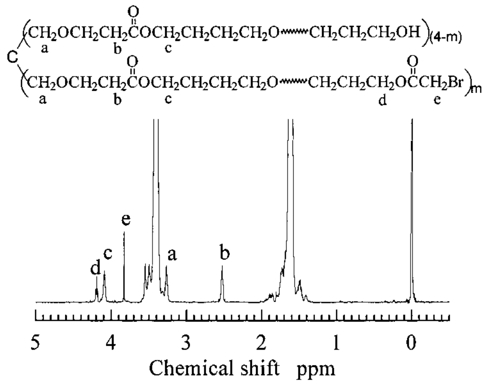


Figure 1. ^{1}H NMR spectrum of the "macroinitiator" prepared by route 1 in Scheme 1.

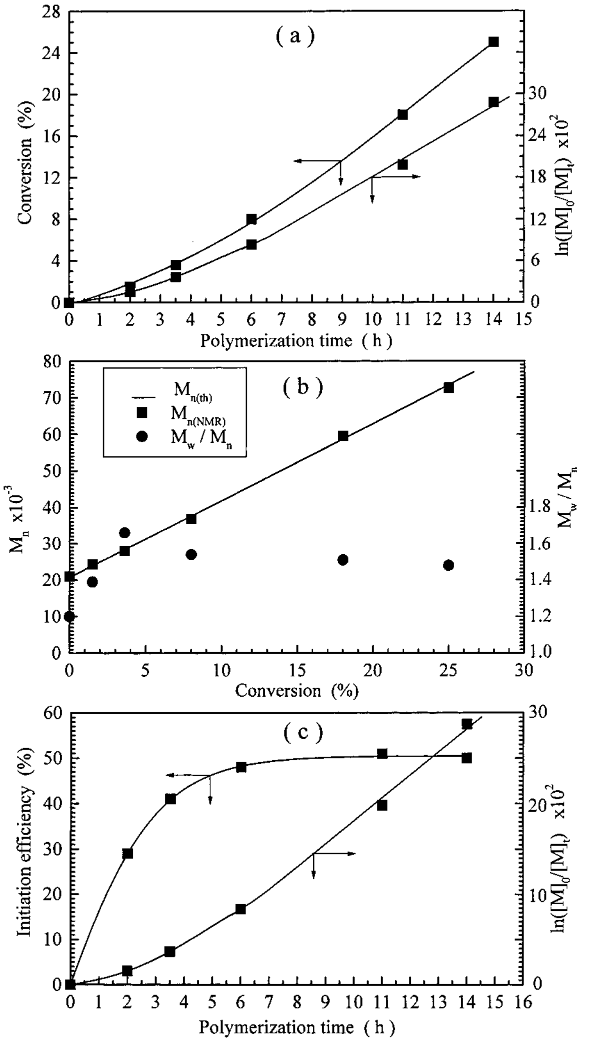


Figure 2. Kinetic curves for the bulk ATRP of St initiated by S-(PTHF-AcBr)$_4$ in the presence of CuBr/bpy. The polymerization conditions are given in Table 2.

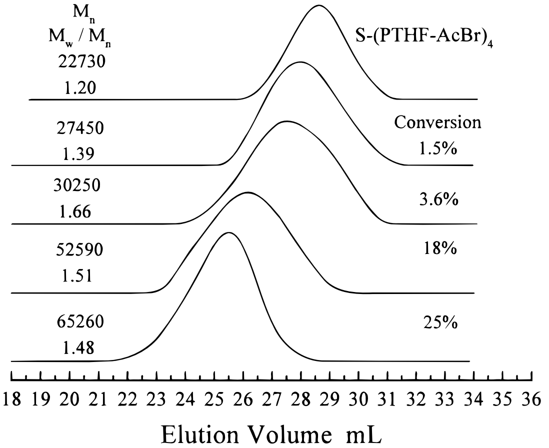


Figure 3. GPC curves of macroinitiator S-(PTHF-AcBr)$_4$ and its block copolymers at different monomer conversion. The polymerization conditions are given in Table 2.

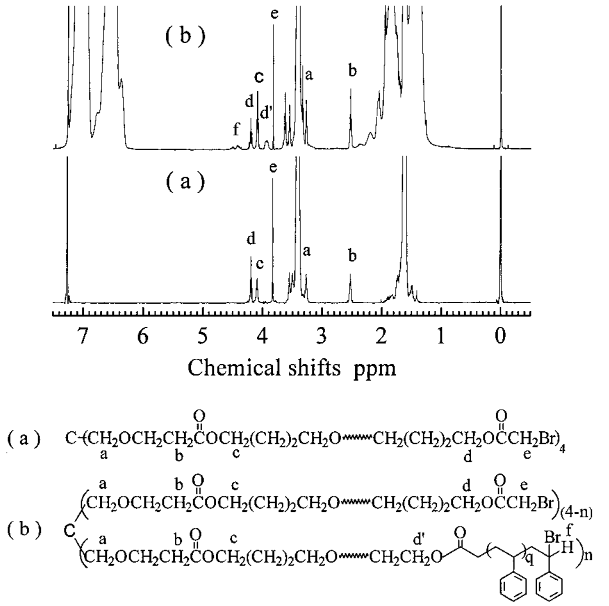


Figure 4. ^{1}H NMR spectra of (a) S-(PTHF-AcBr)$_4$ and (b) S-(PTHF-PSt)$_4$ (sample 4 in Table 2).

^{1}H NMR (δ, CDCl$_3$): 4.19 (t, $-$C**H**$_2$OOC(CH$_3$)$_2$Br), 4.10 (t, $-$COOC**H**$_2$$-$), 3.65$-$3.30 (m, $-$CCH$_2$OC**H**$_2$C$-$), 2.55 (t, $-$CH$_2$-C**H**$_2$COOCH$_2$$-$), 1.94 (s, $-$CH$_2$OOCC(C**H**$_3$)$_2$Br), 1.9$-$1.5 ppm (m, $-$CH$_2$C**H**$_2$C**H**$_2$CH$_2$$-$).

4. Synthesis of Star-Block S-(PTHF-PStBr)$_4$. S-(PTHF-PStBr)$_4$ star-block copolymer was synthesized by bulk polymerization. A typical bulk polymerization was as follows. A glass tube with a magnetic bar was charged with S-(PTHF-AcBr)$_4$ macroinitiator (0.5 g, 0.024 mmol), CuBr (14 mg, 0.095 mmol), and bpy (45 mg, 0.29 mmol). Then styrene (5.5 mL, 48 mmol) was added, and 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. After 11 h, the polymerization was stopped by cooling the tube to room temperature rapidly, and then the tube was opened. Conversion was determined by ^{1}H NMR and gravimetric methods; both gave comparable results: 18% and 17.8%, respectively. The mixture was dissolved in THF, and the solution was then passed through a neutral alumina column to remove the copper complexes. After several precipitations from THF into methanol, the solid was collected by filtration. After dried at 40 °C in a vacuum overnight, 1.39 g of block copolymer ($M_n = 5.96 \times 10^4$, MWD = 1.51, Table 2) was obtained; the NMR spectrum is shown in Figure 4b.

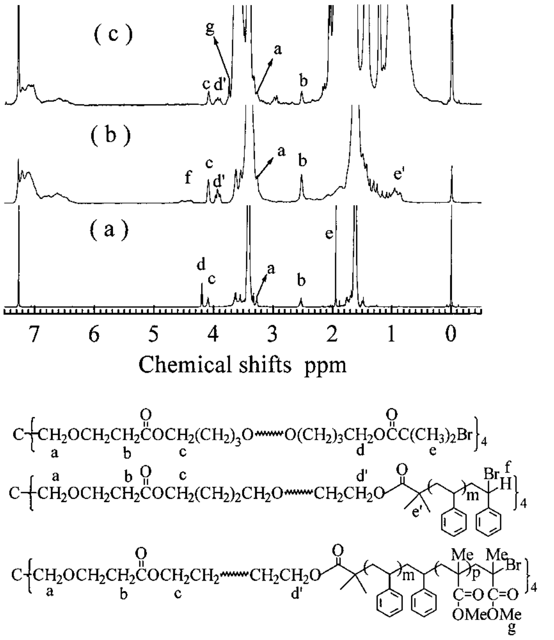


Figure 5. ^{1}H NMR spectra of (a) S-(PTHF-^{i}BuBr)$_4$, (b) four-armed star-block S-(PTHF-PSt-Br)$_4$ (no. 1 in Table 3), and (c) the four-armed triblock S-(PTHF-PSt-PMMA-Br)$_4$.

Table 1. Results of Macroinitiators Prepared by Living Cationic Ring-Opening Polymerization of THF and Subsequent Esterification with Bromoacetyl and Bromoisobutyryl Chloride[a]

polymer[b]	B[c]	ED (%)[d]	$M_{n(NMR)}$[e] $\times 10^{-4}$	$M_{n(GPC)}$[f] $\times 10^{-4}$	M_w/M_n[f]
S-(PTHF-AcBr)$_4$	3.98	98.5	2.10	2.273	1.20
S-(PTHF-^{i}BuBr)$_4$	3.99	99	1.70	1.909	1.25

[a] The cationic ring-opening polymerizaiton of THF was performed at -15 °C according to the same procedure as in ref 42. The esterification reactions were conducted as described in the Experimental Section. [b] S-(PTHF-AcBr)$_4$ means that the macroinitiator is end-capped with bromoacetate group and S-(PTHF-^{i}BuBr)$_4$ with bromoisobutyrate group. [c] The numbers of the branch chain of each polyTHF macromolecule were determined by the equation $B = 4I_{4.1}/I_{2.55}$, where $I_{4.1}$ and $I_{2.55}$ are the integral values of the peaks centered at 4.1 and 2.55 ppm, respectively.[42] [d] Calculated by eq 1: ED = $I_{4.20}/I_{4.10}$. [e] Estimated by ^{1}H NMR based on the intensity ratio of methylene protons at 3.41 ppm to the methylene protons at 2.55 ppm. [f] Determined by GPC relative to polystyrene.

5. Synthesis of Star-Shaped Triblock S-(PTHF-PSt-PMMABr)$_4$. The star-shaped triblock S-(PTHF-PSt-PMMA-Br)$_4$ was prepared in 70.8% yield in 3 h at 80 °C by the same method as for the preparation of S-(PTHF-PStBr)$_4$ using S-(PTHF-PStBr)$_4$ as the macroinitiator instead of S-(PTHF-Br)$_4$. Its NMR spectrum and the GPC curve are shown in Figure 5c and Figure 7, respectively.

6. Hydrolysis of the Star-Shaped Block Copolymers. The star-block copolymer (0.3 g, sample 5 in Table 3) was dissolved in THF (30 mL) in a 100 mL round-bottomed flask fitted. Then 1 M KOH in ethanol (10 mL) was added, and the charges were refluxed for 72 h. After evaporation of the solvent, the residue was dissolved in CH$_2$Cl$_2$ and washed with distilled water until neutral, and then precipitated by adding methylene chloride solution of the crude product into ethanol two times. The precipitate was collected, and after drying at 40 °C under reduced pressure overnight, 0.25 g of PSt (yield, 98.5%) was obtained. The PTHF segments were soluble in ethanol. ^{1}H NMR analysis confirmed that the obtained precipitate was pure PSt. The GPC data are listed in Table 3 and shown in Figure 7.

Results and Discussion

1. Syntheses of Macroinitiators. The procedures for the synthesis of initiator and the living cationic ring-

Table 2. Conditions and Results of the Bulk ATRP of Styrene Initiated with S-(PTHF-AcBr)$_4$ in the Presence of CuBr/Bpy[a]

sample no.	time (h)	conv (%)		$M_n \times 10^{-4}$			M_w/M_n[f]	EI (%)[g]
		b	*c*	th[d]	NMR[e]	GPC[f]		
1	2	1.5	1.4	2.41	2.43	2.75	1.39	29
2	3.5	3.6	3.5	2.85	2.80	3.03	1.66	41
3	6	8	7.8	3.76	3.68	3.66	1.54	48
4	11	18	17.8	5.84	5.96	5.26	1.51	51
5	14	25	25	7.30	7.27	6.53	1.48	50

[a] Polymerization was conducted at 110 °C, $[St]_0/[S\text{-}(PTHF\text{-}AcBr)_4]_0/[CuBr]/[bpy] = 2000/1/4/12$ (molar ratio), $[St]_0 = 8.0$ moL/L (bulk). [b] Monomer conversion determined by ^{1}H NMR. [c] Monomer conversion determined by gravimetric method. [d] $M_{n(th)} = ([St]_0/[S\text{-}(PTHF\text{-}AcBr)_4]_0) \times \text{conv} \times 104 + 21000$, where 104 and 21000 are the molecular weights of St and the macroinitiator, respectively, monomer conversion was that determined by ^{1}H NMR. [e] Calculated by eq 2: $M_{n(NMR)} = [\{(I_{2.0} - I_{3.4})((MW)_{MI} - 424) \times 104\}/(I_{3.4} \times 54)] + (MW)_{MI}$. [f] Determined by GPC relative to polystyrene. [g] The initiation efficiency, EI, was obtained by eq 3: EI (%) $= (1 - I_{4.2}/I_{4.1}) \times 100$.

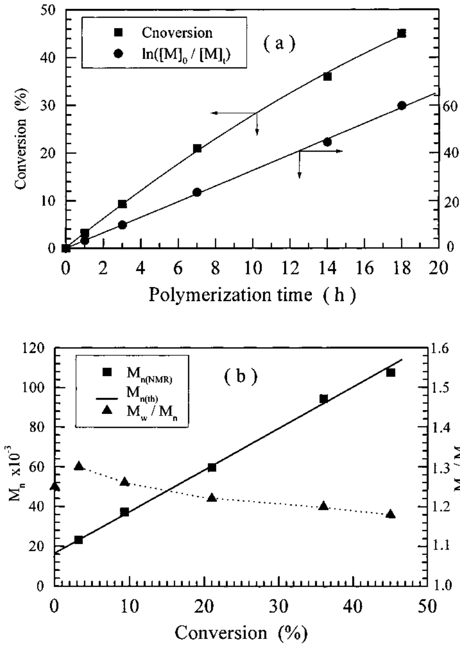


Figure 6. Kinetic curves for the bulk ATRP of St with S-(PTHF-^{i}BuBr)$_4$ as initiator and CuBr/bpy as catalyst. The polymerization conditions are given in Table 3.

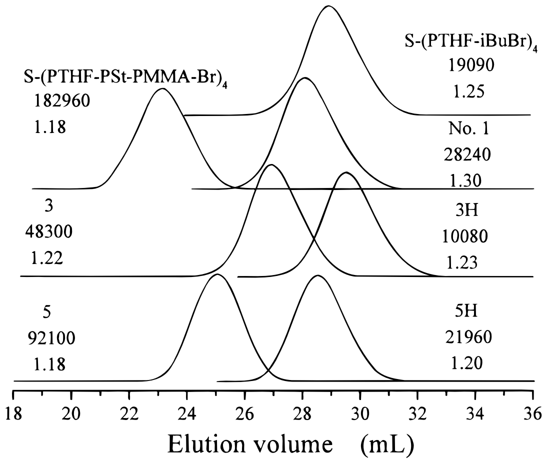


Figure 7. GPC curves and M_w/M_n's of the macroinitiator S-(PTHF-^{i}BuBr)$_4$, star-block copolymers and corresponding hydrolysis products (the sample numbers are the same as those in Table 3), and the star-shaped triblock S-(PTHF-PSt-PMMA)$_4$.

Table 3. Conditions and Results of the Bulk ATRP of St Using S-(PTHF-^{i}BuBr)$_4$ as Initiator in Conjunction with CuBr/Bpy[a]

sample no.	time (h)	conv (%)		$M_n \times 10^{-4}$			M_w/M_n[f]
		b	*c*	th[d]	NMR[e]	GPC[f]	
1	1	3.2	3.1	2.37	2.33	2.82	1.30
2	3	9.3	9.2	3.63	3.73	3.55	1.26
3	7	21	20.5	6.07	5.96	4.83	1.22
3H[g]				1.09		1.01	1.23
4	14	36	35.8	9.19	9.43	7.87	1.20
4H[g]				1.87		1.99	1.20
5	18	45	44.6	11.06	10.75	9.21	1.18
5H[g]				2.34		2.20	1.20

[a] Bulk ATRP of St was conducted at 105 °C, $[St]_0/[S\text{-}(PTHF\text{-}^iBuBr)_4]_0/[CuBr]/[bpy] = 2000/1/4/12$ (molar ratio), $[St]_0 = 8.0$ moL/L. [b] Estimated by ^{1}H NMR data. [c] Monomer conversion determined by gravimetric method. [d] Calculated according to the equation $M_{n(th)} = ([St]_0/[S\text{-}(PTHF\text{-}^iBuBr)_4]_0) \times \text{conv} \times 104 + 17000$, where 104 and 17000 are the molecular weights of St and the macroinitiator, respectively; monomer conversion was that determined by ^{1}H NMR. [e] Obtained by eq 2, where $(MW)_{MI}$ is 17 000. [f] Determined by means of GPC using standard polystyrene in calibration. [g] The suffix "H" means that the sample is the hydrolysis product of the sample to whose name it was attached.

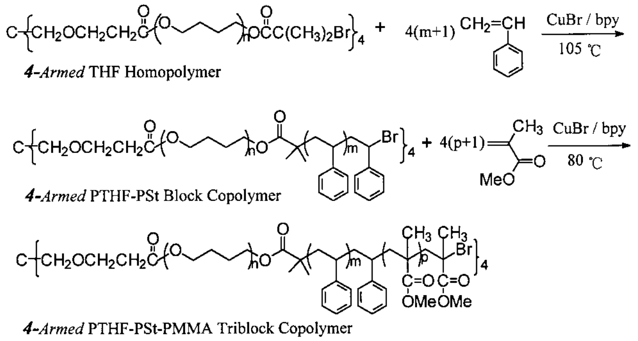
opening polymerization of THF were the same as those described before.[42] The macroinitiators used for the preparation of star-shaped block copolymers were synthesized according to Scheme 1. Matyjaszewski et al.[30] reported that, when THF underwent cationic ring-opening polymerization with triflic anhydride as initiator, it could be end-capped by terminating the living chain with a methanol solution of sodium bromopropionate. However, we found that the transformation of living PTHF end group into bromoacetate ester group (route 1 in Scheme 1) was far from complete. Figure 1 shows the ^{1}H NMR spectrum of the "macroinitiator" prepared by this method. The equal integral values of the peaks corresponding to the methylene protons next to the carbonyl group (2.55 ppm) and those adjacent to the oxygen of the carboxylate group at the center of star block copolymers (4.10 ppm) indicate that the four-armed PTHF was produced.[42] The single peak at 3.82 ppm is ascribed to the protons of the bromomethylene group ($-CH_2OOCC\mathbf{H}_2Br$). The resonance centered at 4.20 ppm is assigned to the ester methylene protons of the bromoacetate standing at the end of each branch chain. The end-capping degree (ED) was calculated by eq 1:

$$ED = I_{4.20}/I_{4.10} \tag{1}$$

where $I_{4.20}$ and $I_{4.10}$ are the integral values of the peaks centered at 4.20 and 4.10 ppm, respectively. The end-capping degree of all of the samples prepared by route 1 in Scheme 1 was lower than 45%. In our previous paper, we reported that, because of the high nucleophilicity of perchlorate group, ester/ion equilibrium existed, and it mainly shifted to the ester state during the polymerization (Scheme 1).[42] This may be the main reason for the low end-capping efficiency.

Figures 4a and 5a are the ^{1}H NMR spectra of the macroinitiators, S-(PTHF-AcBr)$_4$ and S-(PTHF-^{i}BuBr)$_4$, prepared by method 2, respectively (Scheme 1). The end-capping degrees calculated by eq 1 were higher than 98% for all the samples prepared by route 2 (Table 1). Thus, the two macroinitiators used in this paper were synthesized by route 2.

Scheme 2. Strategy for the Syntheses of Star-Shaped Block Copolymers



2. Syntheses of Star-Block S-(PTHF-PSt-Br)$_4$. Star-block S-(PTHF-PSt-Br)$_4$ was prepared (Scheme 2) by the bulk ATRP of St using S-(PTHF-AcBr)$_4$ or S-(PTHF-^{i}BuBr)$_4$ as macroinitiator and CuBr/bpy as catalyst at 110 or 105 °C. To ensure that bromine at the end of each macromolecule was not lost during the polymerization, the polymerization was generally stopped at low conversion.

2.1. Bulk ATRP of St Initiated with S-(PTHF-AcBr)$_4$ in the Presence of CuBr/bpy. The conditions and results of the bulk ATRP of styrene initiated with S-(PTHF-AcBr)$_4$ using CuBr/bpy as catalyst are listed in Table 2.

Figure 2a shows the conversion−time curve and ln([M]$_0$/[M]$_t$) vs time curve. A curved line at the beginning of the polymerization was observed in the latter curve of Figure 2a, indicating that the initiation reaction was slow, and the amount of propagation species increased with time. Because of the stabilizing capabilities, the tertiary alkyl halides are better initiators than the secondary ones, which are better than the primary alkyl halides.[49] Among the halides of the same structure, alkyl chloride is the least efficient initiator and alkyl iodide is the most efficient.[49,50] Höcker et al. reported that when the polymerization of styrene was initiated with a chloroacetate in the presence of CuCl/bpy, the initiation reaction was slow, resulting in the higher experimental values of molecular weight ($M_{n(GPC)}$) than the theoretical ones.[51] In our system with S-(PTHF-AcBr)$_4$ as the initiator, however, the $M_{n(NMR)}$'s agree well with the theoretical ones calculated by the molar ratio of the monomer consumed to the macroinitiator used based on the assumption that all the macroinitiators initiated the ATRP of styrene (Figure 2b). A probable reason is that in the initial period of polymerization not all the initiating sites of each macroinitiator, probably one or two or three participated in the initiation reaction, so the $M_{n(NMR)}$ (see calculation below) agrees well with $M_{n(th)}$. This is confirmed by the GPC curves of the polymers obtained at different monomer conversions shown in Figure 3. Compared with common ATRP of styrene, the MWD of these block copolymers are relatively broad (1.39−1.66). The shapes of the curves are somewhat asymmetric, with a small shoulder on the low MW side at low monomer conversion. The disappearance of the macroinitiator signal in the GPC curves suggests that all of the S-(PTHF-AcBr)$_4$ molecules initiated the atom transfer radical polymerization of styrene. The $M_{n(GPC)}$'s show some discrepancy from the $M_{n(th)}$'s (Table 2), which may be due to the different hydrodynamic volumes of the block (or "star-block") copolymers from that of the polystyrene standard.

To get detailed information on the initiation reaction, we followed the polymerization by NMR spectroscopy. The amplified ^{1}H NMR spectrum of sample 4 in Table 2 is shown in Figure 4b. In addition to the two main resonances centered at 3.41 and 1.62 ppm, corresponding to the protons of the methylene groups next to ether oxygen and in the middle of tetramethylene unit, respectively, another three groups of signals appear at 6.3−7.25 ppm and 1.44 and 1.85 ppm. The former is assigned to the aromatic protons, and the latter is ascribed to the methylene and methine protons of polystyrene, indicating that styrene was polymerized by the PTHF macroinitiator. Assuming that all of the macroinitiator sites participated in the initiation reaction, $M_{n(NMR)}$, the number-average molecular weights of the block copolymers are calculated by eq 2:

$$M_{n(NMR)} = [\{(I_{2.0} - I_{3.4})((MW)_{MI} - 424) \times 104\}/(I_{3.4} \times 54)] + (MW)_{MI} \qquad (2)$$

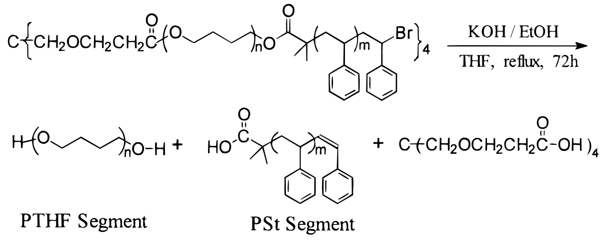
where $I_{2.0}$ and $I_{3.4}$ are the integral values of the resonances ranged from 1.2 to 2.5 ppm and the resonance centered at 3.41 ppm, respectively; (MW)$_{MI}$ and 424 are the molecular weights of the macroinitiator and the core initiator, tetracarboxylic acid, respectively; and 104 is the molecular weight of styrene. The results are listed in Table 2. As shown in the amplified spectrum in Figure 4b, the resonances centered at 4.2 and 3.82 ppm (−C**H**$_2$OOCCH$_2$Br and −CH$_2$OOCC**H**$_2$Br, respectively) are still detectable, indicating that initiation is slow and inefficient. Two new resonances appear at 4.3 to 4.6 ppm and at about 4.0 ppm. The former is attributed to the methine proton of polystyrene adjacent to the terminal bromine atom, and the latter is presumably due to the methylene protons of the ester group, −C**H**$_2$OOCCH$_2$Br, after initiation. This assignment was confirmed by the following facts. The ratio of the integrals at 4.0 and 4.3−4.6 ppm is two. The integral of the resonance at 4.1 ppm is equal to the sum of those at 4.2 and 4.0 ppm. The signal of the methylene group next to the carbonyl group originated from the bromoacetate group after initiation should appear at about 2.0−2.5 ppm, which was slightly overlapped with the methine protons of PolySt. The initiation efficiency, EI, was calculated on the basis of the integrals of the resonances at 4.2 ($I_{4.2}$) and 4.1 ppm ($I_{4.1}$) according to eq 3, and the results are listed in Table 2.

$$\text{EI (\%)} = (1 - I_{4.2}/I_{4.1}) \times 100 \qquad (3)$$

The changes of initiation efficiency and ln([M]$_0$/[M]$_t$) with polymerization time are shown in Figure 2c. Figure 2c shows that initiation efficiency and propagation species increased slowly during the first 5−6 h to reach a maximum initiation efficiency of 50%, and ln([M]$_0$/[M]$_t$) vs time became linear, indicating that the propagation species was constant. The slow initiation may be due to the primary structure of the bromoacetate. The maximum initiation efficiency of 50% may be due to the incompatibility between PTHF and PSt segments. After segregation of PSt segments from PTHF, the unreacted bromoacetate in PTHF phase does not continue to initiate St monomer.

2.2. Bulk ATRP of St Initiated with S-(PTHF-^{i}BuBr)$_4$ in Conjunction with CuBr/bpy. The conditions and procedure for the bulk ATRP of styrene with

Scheme 3. Hydrolysis of the Star-Block Copolymer S-(PTHF-PSt-Br)$_4$



S-(PTHF-^{i}BuBr)$_4$ as initiator were the same as those using S-(PTHF-AcBr)$_4$, except that the polymerization temperature was 105 °C. The results are listed in Table 3.

Figure 5a shows the ^{1}H NMR spectrum of the macroinitiator S-(PTHF-^{i}BuBr)$_4$. The equal integrals of the resonances at 2.55 and 4.1 ppm demonstrate that four-armed polyTHF was obtained. The resonance centered at 4.19 ppm is assigned to the methylene protons of the 2-bromoisobutyrate ester group. The geminal methyl protons of the bromoisobutyrate group appear at 1.94 ppm. The integral of the resonance at 4.19 ppm is almost equal to that at 4.10 ppm, indicating that the end-capping reaction is quantitative. The proton NMR spectrum of sample 1 in Table 3 is shown in Figure 5b. In addition to the large resonances belonging to the repeating units of PTHF and PSt, the resonance at 1.94 ppm in Figure 5a was shifted to about 1.0 ppm. The complete disappearance of the resonance at 4.19 ppm and the appearance of a new resonance at 4.3−4.6 ppm due to the methine protons of polySt next to the terminal bromine strongly suggest that all of the bromoisobutyrate groups initiated St. The new resonance centered at about 3.95 ppm is due to the ester methylene protons of the isobutyrate after initiation.

Compared to S-(PTHF-AcBr)$_4$, bromoisobutyrate is an efficient initiator for the atom transfer radical polymerization of St; quantitative initiation was obtained within 1 h. The kinetic curves of the polymerization and the molecular weight and polydispersity dependence on monomer conversion are shown in Figure 6. The linearity of the plot of $\ln([M]_0/[M]_t)$ vs time suggests that initiation was fast and termination reactions were negligible. The number-average molecular weights determined by ^{1}H NMR, $M_{n(NMR)}$'s, agree well with the theoretical values corresponding to the molar ratio of the monomer consumed to the initiator used, indicating that all of the macroinitiators participated in the initiation reaction. The symmetrical GPC curves of the star-block copolymers and the absence of the shoulder of the macroinitiator (Figure 7) indicate that all of the macroinitiators initiated the atom transfer radical polymerization of St to generate block copolymers.

2.3. Hydrolysis of the Four-Armed Star-Block S-(PTHF-PSt-Br)$_4$. To determine whether all four of the initiating sites of one macroinitiator initiated the atom transfer radical polymerization of St, the block copolymers were hydrolyzed and analyzed by GPC. The hydrolysis reaction was performed by refluxing a mixture of the block copolymer and potassium hydroxide in THF and ethanol (Scheme 3). The molecular weight of the PSt block agrees well with the theoretical values and is $^1/_4$ of that before hydrolysis. This suggests that all the initiating sites of the macroinitiator S-(PTHF-^{i}BuBr)$_4$ took part in the initiation reaction. The narrow polydispersities of the PSt blocks and the symmetric GPC curves demonstrate that the block copolymerization was of “living” character.

3. Preparation of Star-Shaped Triblock S-(PTHF-PSt-PMMA-Br)$_4$. Four-armed triblock S-(PTHF-PSt-PMMA-Br)$_4$ copolymer was prepared by the bulk ATRP of MMA using the four-armed star-block S-(PTHF-PSt-Br)$_4$ as macroinitiator (sample 1 in Table 3) and CuBr/bpy as catalyst. The copolymerization was performed at 80 °C with $[MMA]_0/[I]_0/[CuBr]/[bpy] = 3200/1/4/12$. MMA polymerized smoothly, and as shown in Figure 7, the molecular weight determined by GPC increased from 2.82×10^4 to 1.83×10^5 and the polydispersity reduced from 1.30 to 1.18. The decrease in the molecular weight distribution demonstrates that the initiation rate of the macroinitiator S-(PTHF-PSt-Br)$_4$ was rapid, almost all of the initiating sites propagated at the same time, resulting in almost the same length of the PMMA block. With the increase of the molecular weight of the triblock copolymer, the molecular weight difference became smaller and thus the molecular weight distribution became narrower.

Figure 5c shows the proton NMR spectrum of the star-shaped triblock copolymer. The signals of the MMA repeat units are seen, in addition to those of THF and St units. The molecular weight obtained from the NMR data (2.54×10^5) agrees well with the theoretical value calculated from monomer conversion (2.43×10^5). Furthermore, the absence of the terminal methine protons (4.3−4.6 ppm) and the presence of the terminal methyl ester protons (3.75 ppm) adjacent to bromine indicate that the four-armed, star-shaped triblock S-(PTHF-PSt-PMMA-Br)$_4$ is generated. No signals at 5.5 and 6.2 ppm, which were characteristic of olefinic methylene protons, suggest that hydrogen bromide is not eliminated during the polymerization.[52] The symmetric GPC curve and low molecular weight distribution (1.18) demonstrate that intermolecular termination is negligible.

Conclusions

Four-armed PTHFs with bromoacetate and bromoisobutyrate terminal groups were prepared by two methods. ^{1}H NMR results showed that the direct end-capping of living PTHF chain with sodium bromoacetate was incomplete, whereas the reaction between PTHF tetraol and bromoacetyl or bromoisobutyryl chloride yielded the products with end-capping efficiency higher than 98%. When S-(PTHF-AcBr)$_4$ was used as the initiator for the bulk atom transfer radical polymerization of styrene, the initiation efficiency was low ($\leq$50%), resulting in ill-defined block copolymers. When S-(PTHF-^{i}BuBr)$_4$ was used in conjunction with CuBr/bpy, however, the initiation reaction was fast and efficient, and the molecular weight distributions of the resulting block copolymers were narrow. ^{1}H NMR results confirmed that all of the initiating sites participated in the block copolymerization. Kinetic studies showed that the active species remained constant during the polymerization process. GPC results of the hydrolyzed product demonstrated that the molecular weights of PSt blocks agreed well with the theoretical values, and their molecular weight distributions were narrow ($\leq$1.3). Four-armed triblock S-(PTHF-PSt-PMMA-Br)$_4$ copolymer was successfully prepared by the bulk atom transfer radical polymerization of MMA, using the four-armed star-block S-(PTHF-PSt-Br)$_4$ as macroinitiator and CuBr/bpy as catalyst.

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