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Polarity Inversion of Cationic Growing Centers into Anionic Ones by Samarium Iodide. Synthesis of Poly(*tert*-butyl methacrylate-*b*-tetrahydrofuran-*b*-*tert*-butyl methacrylate) Triblock Copolymer

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ABSTRACT: The cationic propagation ends of telechelic living poly(tetrahydrofuran) (polyTHF) were reduced into anionic ones by 4 equiv of samarium(II) iodide in the presence of hexamethylphosphoramide (HMPA). NMR analyses indicated the quantitative reduction of poly(THF) into the telechelic poly(THF) macroanion without any serious side reaction. The transformed telechelic poly(THF) macroanion initiated the polymerization of *tert*-butyl methacrylate (TBMA) with quantitative initiator efficiency resulting in the production of ABA-type triblock copolymer of TBMA and THF with a narrow molecular weight distributions (<1.19). Any homopolymer of THF or TBMA was not detected. The unit ratio of THF and TBMA could be facilely controlled by both the poly(THF) macroanion and the amount of TBMA.

Introduction

Block copolymers have been widely applied to various functional materials such as thermoplastic elastomers, polymer surfactants, and polymer liquid crystals because they exhibit unique and useful properties in solution and in the solid state.[1] One of the most convenient methods for the preparation of block copolymers is a sequential addition process in chain polymerization. Many kinds of block copolymers have been synthesized by this methodology. Especially, block copolymers having well-defined structure can be obtained by the living polymerization technique. However, almost all synthetic effort has been confined to chain polymerization by a single propagating mechanism, usually cationic and anionic. Therefore, the number of monomers which can be copolymerized is limited. This restriction can be reduced by the transformation of the mechanism after polymerization of the first monomer to one suitable for the polymerization of the second monomer.[2] The transformation of active centers, polarity inversion, requires two-electron oxidation or reduction to take place during the transformation of ions, theoretically (Scheme 1). Although many efforts have been made to switch the mechanism of polymerization, direct reduction or oxidation of the growing centers has not been achieved so far. To transform the growing center in polarity complicated multistep paths have been used, in which resulting block copolymers often show multimodal molecular weight distributions.[3]

Previously, we have succeeded in the transformation of polarity of the cationic active species of poly(tetrahydrofuran) (polyTHF) into a terminating nucleophile via electron transfer under the SmI_2/HMPA system (Scheme 2).[4] The transformed poly(THF) macroanion (**2a**) reacted with a variety of electrophiles including aldehydes, ketones, and isocyanates, quantitatively.[4a] **2a** also initiated the polymerization of *tert*-butyl methacrylate (TBMA), leading to the unimodal block copolymer of THF and TBMA with a narrow molecular weight distribution.[4b] The initiation efficiency of the polymerization with the poly(THF) macroanion was almost quantitative.

It has been known that polymerization of THF with trifluoromethanesulfonic anhydride (Tf_2O) gives telechelic poly(THF) (**1b**) and that the polymerization proceeds in living fashion at the initial stage of the polymerization.[5] The transformation of the telechelic living poly(THF) under the SmI_2/HMPA system and subsequent addition of TBMA are expected to provide the novel ABA-type triblock copolymer of TBMA with THF. In this paper, we report the two-electron reduction of the living telechelic poly(THF) by SmI_2 into the corresponding macroanion together with the copolymerization of TBMA with the telechelic macroanion (Scheme 3).

Experimental Section

Materials. THF solution of SmI_2 was prepared according to the reported manner.[6] THF was distilled prior to use from sodium/benzophenone under nitrogen. TBMA and HMPA were distilled from CaH_2 under reduced pressure. Methyl trifluoromethanesulfonate and trifluoromethanesulfonic anhydride were distilled from P_2O_5 under a nitrogen atmosphere.

Measurements. NMR spectra were recorded with JEOL JNM-EX-90 and JNM-GX-270 spectrometers. FT-IR spectra were recorded with Jasco FT/IR-3 spectrometers. Gel permeation chromatographic analysis was carried out on a Toyo Soda (CCP&8000 (TSK gel G3000, THF) after calibration with standard polystyrenes. GC analyses were performed on a Shimazu gel chromatograph GC-8AP.

Synthesis of ABA−type Triblock Copolymer of TBMA and THF (3b). The general procedure is as follows: Tf_2O (16.9 mg, 0.06 mmol) was added to dry THF (5 mL), and the solution was stirred at room temperature for 5 min. After the solution was charged with HMPA (180 μL), 0.1 M THF solution of SmI_2 (2.4 mL, 0.24 mmol), was added. The reaction mixture was stirred at room temperature for 30 min (until the color of the solution changed to yellow-brown). Into the reaction mixture was added TBMA (648.3 mg, 4.6 mmol), and the reaction mixture was stirred at room temperature for 24 h. After addition of a 3% HCl solution, the reaction mixture was extracted with toluene, and the organic extract was washed with an aqueous sodium thiosulfate solution and then with brine several times. The organic layer was dried over $MgSO_4$, filtered, and concentrated to give **3b** (687.7 mg).

Results and Discussion

Reduction of Telechelic Living Poly(THF) with SmI_2. THF was polymerized at room temperature

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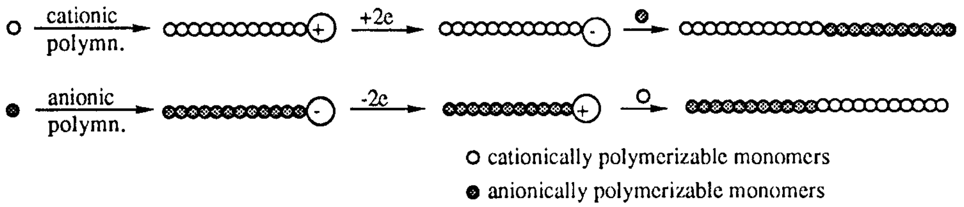
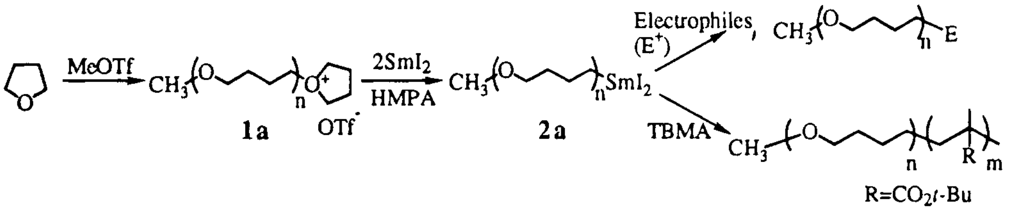
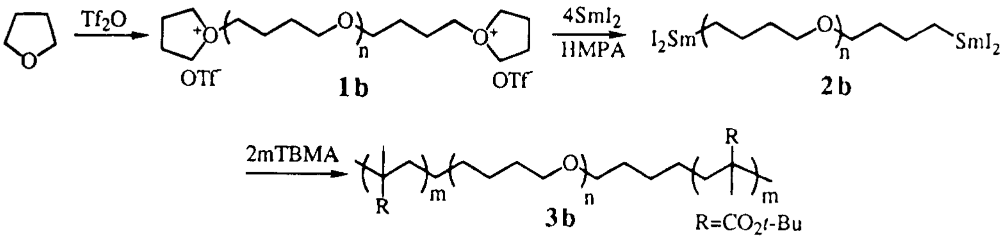
Scheme 1



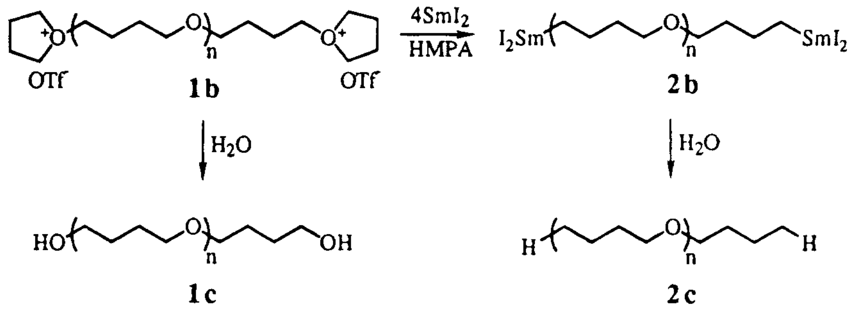
Scheme 2



Scheme 3



Scheme 4



using Tf_2O as an initiator to afford the telechelic living poly(THF) (**1b**). The reduction was performed by adding HMPA and 0.1 M solution of SmI_2 in THF (4 equiv to the initiator) into the solution of **1b**. We have already shown that the addition of HMPA is indispensable for the reduction of the growing center of poly(THF) (**1a**) and that the amount of HMPA is found to affect the molecular weight distribution of the copolymer.[4c] In this experiment, 4.5 equiv of HMPA to SmI_2 was employed, in which the best result has been obtained for the preparation of AB-type block copolymer of THF with TBMA. The typical color of SmI_2 (purple) turned to yellow within 30 min, which indicated the completion of the reduction.[7] Treatment of **1b** with water gives telechelic poly(THF) having hydroxyl groups at both polymer ends (**1c**). On the other hand, quenching of the polymer with water is expected to produce proton-terminated poly(THF) (**2c**) after the reduction (Scheme 4). The ^1H NMR and ^{13}C NMR spectra of **1c** and **2c** are shown in Figures 1 and 2, respectively.

The signals at 3.6 and 2.5 ppm in the ^1H NMR spectrum of **1c** could be assigned as methylene protons adjacent to the terminal hydroxyl groups and the terminal hydroxyl proton, respectively. On the other hand, these signals almost completely disappeared in the ^1H NMR spectrum of **2c**, and the triplet signal attributed to the terminal both methyl groups of **2b** was observed at 0.8 ppm. Similarly, the signals due to the terminal carbons of **1c** were assignable as shown in Figure 2, while these peaks approximately disappeared in the ^{13}C NMR spectrum of **2c**. The peaks at 14.0, 19.5, and 31.9 ppm were assignable as the end group in the structure **2c**. These results support the idea that both propagating centers of **1b** were almost quantitatively reduced into the poly(THF) having organosamarium moieties at both polymer ends. The GPC curves of **1c** and **2c** are illustrated in Figure 3. There was no significant difference in the GPC profiles between **1b** and **2b**, which indicates that the coupling reaction of **1b** with **2b** did not take place during the reduction.

Triblock Copolymerization of TBMA and THF. The preparation of triblock copolymer was carried out by the addition of TBMA into the reaction mixture of **2b** at room temperature. GPC traces of **2b** and the resulting polymer (**3b**) are illustrated in Figure 4. The GPC curves of **2b** showed the formation of living poly(THF) with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.19$), which was consistent with the previous result of ring-opening polymerization of THF initiated by Tf_2O.[5] After charging TBMA to the reaction mixture of **2b**, the GPC curve shifted to the high molecular weight region while maintaining the narrow

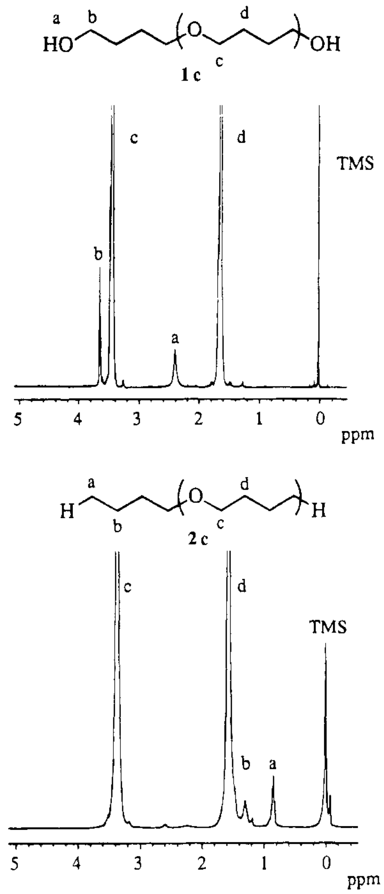


Figure 1. ^1H NMR spectra of **1c** and **2c** (28 °C, in $CDCl_3$).

Table 1. Results of the Triblock Copolymerization of THF and TBMA

	polymerization of THF[a]		triblock copolymerization[b]				
run	Tf_2O (mmol)	time (min)	TBMA (mmol)	polym[c] (mg)	$\bar{M}_n$[c,d]	$\bar{M}_w/\bar{M}_n$[c,d]	*m*:*n*[e] (pTHF:pTBMA)
1	0.06	5	1.0	135	9300	1.18	63:37
2	0.06	5	1.6	280	11000	1.14	41:59
3	0.06	5	3.0	491	15000	1.12	30:70
4	0.06	5	4.6	613	20000	1.03	20:80
5	0.06	2.5	3.1	413	14000	1.19	17:83
6	0.07	7.5	3.1	508	16000	1.16	43:57
7	0.06	10	3.0	522	16000	1.18	44:56

[a] Polymerization conditions: THF 5 mL, room temperature. [b] Carried out at room temperature for 24 h. [c] Extracted with toluene. [d] Estimated by GPC (THF, PSt standards). [e] Determined by ^1H NMR spectra.

molecular weight distribution. Any GPC trace attributed to the prepolymer **2b** was not detected. Moreover, the triplet signal at 0.8 ppm (the terminal methyl group of **2c**) completely disappeared, while the signals attributed to both THF and TBMA units were observed in the ^1H NMR spectrum of **3b** as shown in Figure 5. From these results, it can be concluded that the transformed macroanion initiated the polymerization of TBMA with quantitative initiation efficiency.

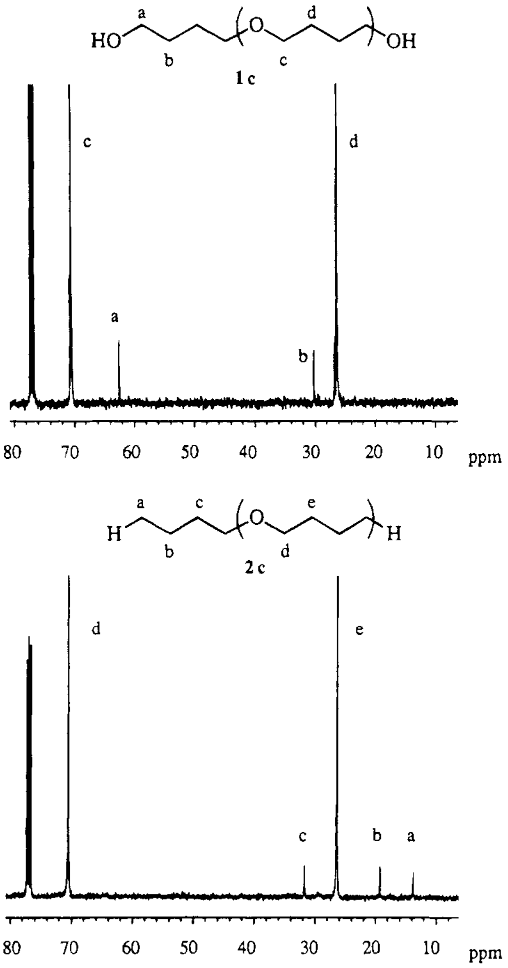


Figure 2. ^{13}C NMR spectra of **1c** and **2c** (28 °C, in $CDCl_3$).

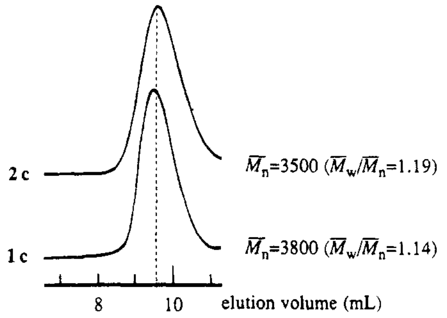


Figure 3. GPC profiles of **1c** and **2c**.

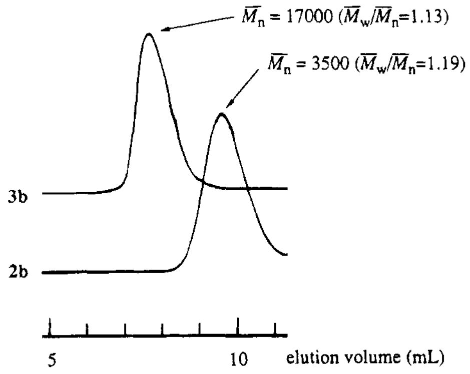


Figure 4. GPC profiles of **2b** and **3b**.

To determine whether both organosamarium moieties in **2b** are independent chain-propagating centers, the rate of polymerization of TBMA was studied using both **2b** and the monofunctional poly(THF) macroanion (**2a**). The rate of disappearance of TBMA was measured by GC analysis at identical initial monomer concentrations for both **2a** and **2b**. From the slope of a linear plot of $[TMBA]_0 - [TBMA]$ versus time, pseudo-zero-order rate constants were determined for the polymerization of TBMA by **2a** and **2b**. First-order rate constants for **2a** and **2b** were then obtained from linear plots of these pseudo-zero-order rate constants versus catalyst con-

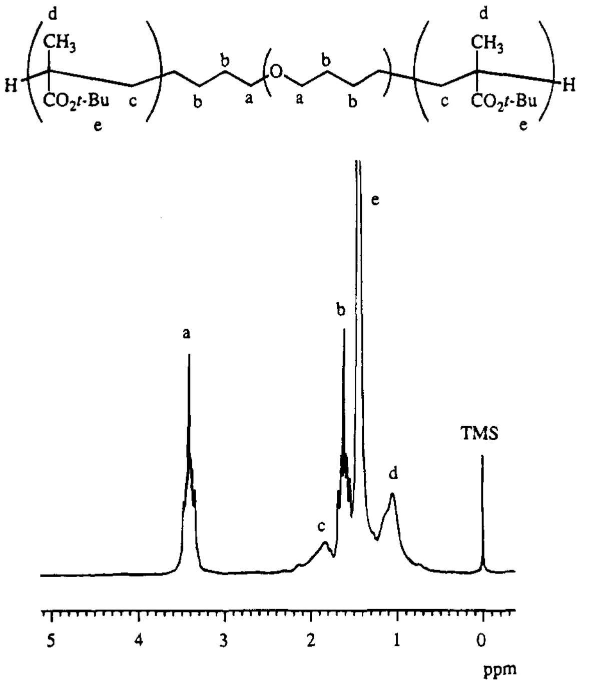


Figure 5. ^{1}H NMR spectrum of **3b** (28 °C, in CDCl$_3$).

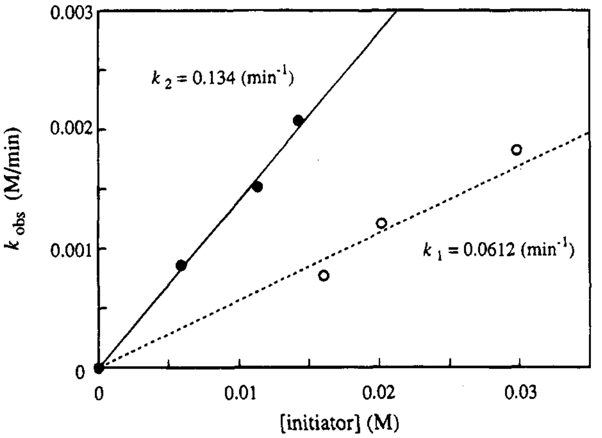


Figure 6. Pseudo-zero-order rate constants, k_{obs}, versus initiator concentration for the polymerization of TBMA by **2a** and **2b** ([TBMA] = 0.33 M).

centration (Figure 6). The first-order rate constant for the telechelic poly(THF) (**2b**), k_2 = 0.134 min^{-1}, was found to be almost twice as large as that for the monofunctional poly(THF) (**2a**), k_4 = 0.0612 min^{-1}. These results indicate that both samarium centers in **2b** are active independently. In other words, ABA-type triblock copolymer was undoubtedly obtained by this procedure.

The results of block copolymerizations of THF and TBMA under various conditions are summarized in Table 1. The GPC measurements showed that molecular weight distribution of the copolymers was unimodal and narrow ($\bar{M}_w/\bar{M}_n$ <1.19). The peaks attributed to both poly(THF) and polyTBMA were detected in the ^{1}H NMR spectra of the resulting copolymers in all cases. Namely, quantitative transformation of the propagating ends of telechelic poly(THF) into the anionic ones was achieved, and the block copolymerization proceeded with almost quantitative initiation efficiency. The unit ratio was calculated by the integrated ratio of signals of each unit in the ^{1}H NMR spectra of **3b**. When the polymerization time of THF was fixed, molecular weight, yield, and the unit ratio of TBMA to THF increased with increasing amounts of TBMA (runs 1–4). Similarly, the unit ratio of THF to TBMA was increased with an increase in the polymerization time of THF (runs 3 and 5–8). In other words, the unit ratios (*m*:*n*) were facilely controlled by both the poly(THF) macroanion and the amount of TBMA.

References and Notes

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