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One-Pot Transformation of Living Cationic Polymerization into a Living Anionic One by Samarium(II) Iodide. Synthesis of Poly(tetrahydrofuran-*b*-ϵ-caprolactone) Block Copolymer

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ABSTRACT: The first example for the transformation of living cationic polymerization into a living anionic one was described. The cationic propagation ends of living poly(tetrahydrofuran) (poly(THF)) were quantitatively reduced into anionic ones by 2 equiv of samarium(II) iodide in the presence of hexamethylphosphoramide (HMPA). The transformed poly(THF) macroanion initiated the polymerization of ϵ-caprolactone (CL) quantitatively, resulting in the formation of the block copolymer of THF with CL with narrow molecular weight distributions (<1.21). The formation of a homopolymer of THF or CL could not be observed. The polymerization of CL with the poly(THF) macroanion proceeded in living fashion without termination and backbiting reactions. The unit ratio of THF and CL could be facilely controlled by both the polymerization time of THF and the amount of CL.

Introduction

Transformation of propagating centers can supply block copolymers consisting of several types of monomers with different polymerization mechanisms.[1] Copolymers obtained through the transformation process are expected to show unique properties which are not attainable by the usual methods. The change of character of the active center can be theoretically achieved by one- or two-electron oxidation or reduction (Scheme 1).

Scheme 1

Although many efforts have been made to switch the mechanism of polymerization, direct reduction or oxidation of the growing centers by electron transfer has not been achieved so far. In the traditional way, complicated multistep paths have been required for the achievement of the transformation.[2] For example, Richards' methods for the transformation of anionic polymerization of styrene into a cationic one of tetrahydrofuran (THF) involves (1) termination of the growing center of living polystyrene with an excess of bromine, (2) isolation of the bromine-terminated polystyrene, and (3) subsequent reaction of the polymer with a silver salt in the presence of THF.[2g−i,k] Another approach has been reported by Tseng et al. for the synthesis of the ABA-type block copolymer by a cation to anion transformation process which includes (1) termination of living telechelic poly(THF) by primary amine, (2) isolation of the amine-terminated polymer, (3) deprotonation of the polymer ends to the polymeric anion, and (4) the reaction of the polymeric dianion with methacrylates.[2e] Although these several methods supply block copolymers of both an anionically polymerizable monomer and a cationically polymerizable one, the initiator efficiency of the second one is low. Thus, the obtained copolymers often show multimodal molecular weight distributions.

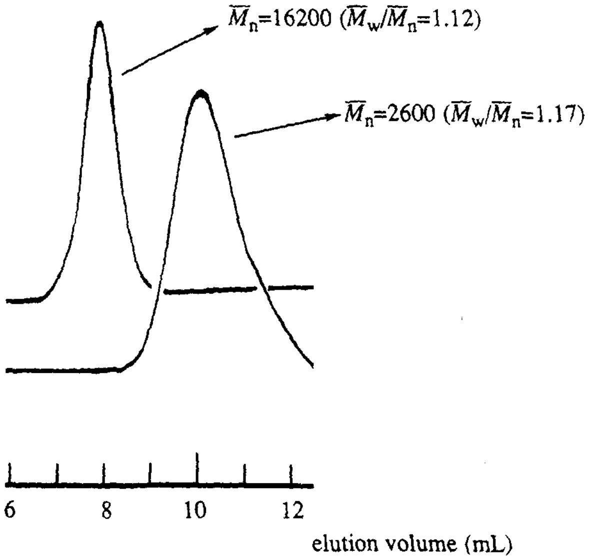

Figure 1. GPC traces of **2** and **3**.

Recently, we have demonstrated the first example for the quantitative two-electron reduction of the cationic growing center of living poly(THF) into an anionic one by using samarium(II) iodide in the presence of hexamethylphosphoramide (HMPA).[3] The reduction proceeded quantitatively at room temperature without serious side reactions such as dimerization or disproportionation. The transformed macroanion underwent the reactions with aldehydes, ketones, and isocyanates quantitatively.[3a] We have also shown that the poly(THF) macroanion initiated the anionic polymerization of *tert*-butyl methacrylate (TBMA) with quantitative initiator efficiency. The block copolymers of THF with TBMA having narrow molecular weight distributions were obtained by this methodology (Scheme 2).[3b,c]

Our previous study has shown that organosamariums derived from the two-electron reduction of alkyl halides with SmI_2 were active for the polymerization of ϵ-caprolactone (CL).[3d] The polymerization of CL with the poly(THF) macroanion is, therefore, expected to produce the block copolymer of THF with CL. In this paper, as a part of our recent investigation of polarity inversion of growing centers using SmI_2-induced electron-transfer reactions, the polymerization of CL by the poly(THF) macroanion is described (Scheme 3).

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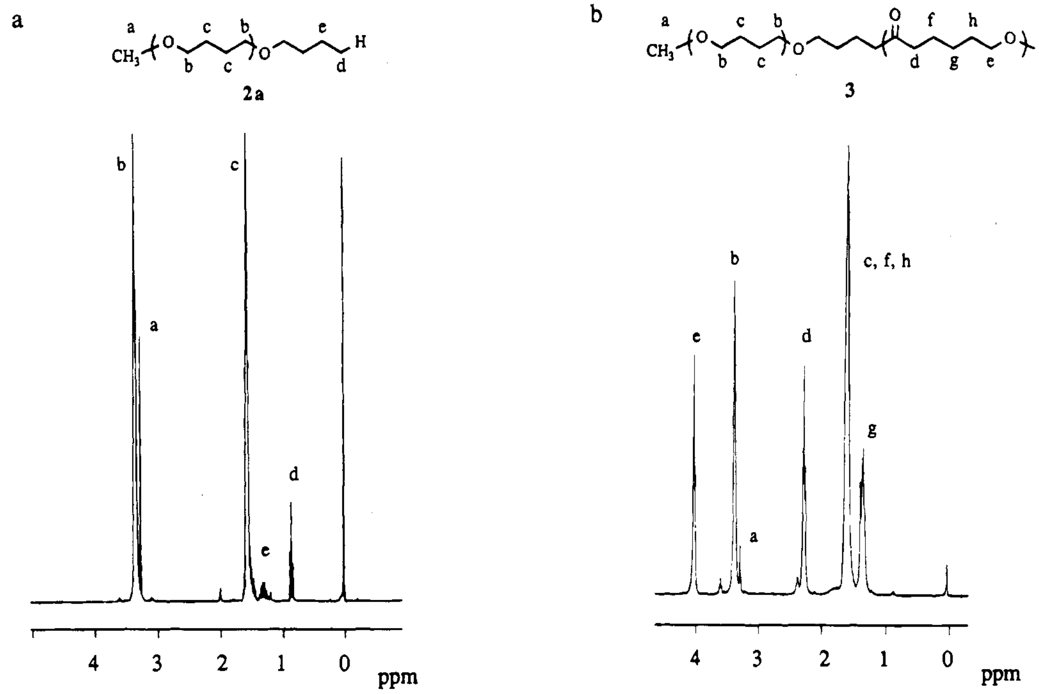
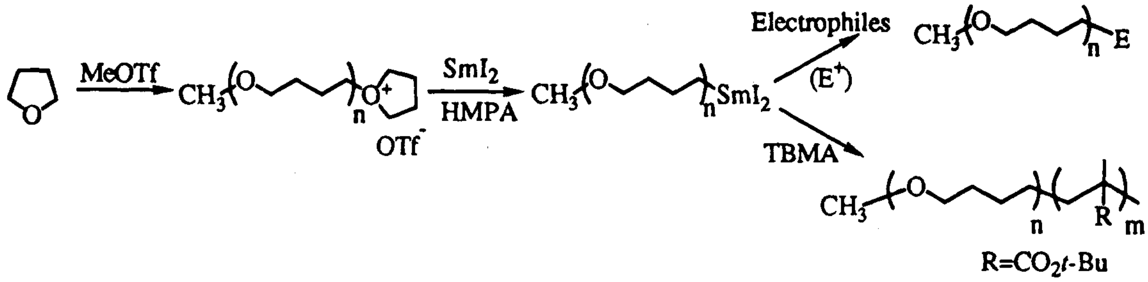
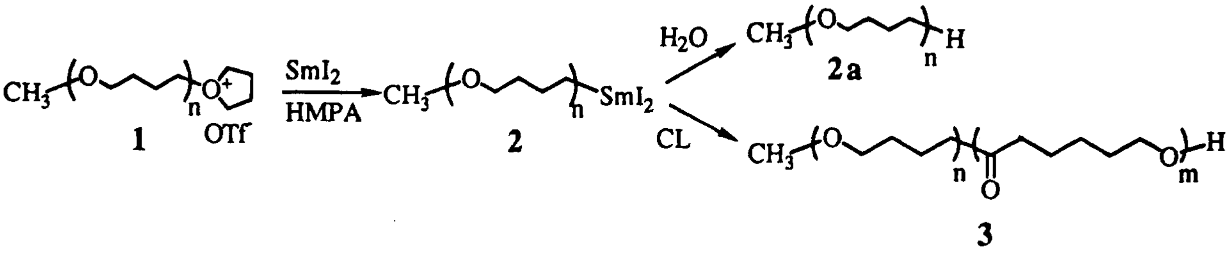


Figure 2. ^{1}H NMR spectra of **2a** and **3**.

Scheme 2



Scheme 3



Experimental Section

Materials. A THF solution of SmI_2 was prepared according to the reported manner.[4] THF was distilled prior to use from sodium benzophenone under nitrogen. HMPA and CL were distilled from CaH_2 under reduced pressure. Methyl triflate was distilled from P_2O_5 under a nitrogen atmosphere.

Measurements. NMR spectra were recorded with JEOL JNM-EX-90 and JNM-EX-400 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.

Preparation of a Block Copolymer of THF with CL. General Procedure. Methyl triflate (28.0 mg, 0.171 mmol) was added to dry THF (5 mL) at room temperature, and the solution was stirred for 5 min. After charging of HMPA (250 μL), a 0.1 M THF solution of SmI_2 (3.5 mL) was added to the solution. The reaction mixture was stirred at room temperature for 30 min (until the color of the solution changed to yellow−brown). CL (496 mg, 4.34 mmol) was added at 0 °C, and the reaction mixture was stirred at 0 °C for 3 h. After addition of a 3% HCl solution, the reaction mixture was extracted with toluene, and organic extract was washed with brine several times. The organic layer was dried over $MgSO_4$, filtered, and concentrated to give the block copolymer (596 mg, slightly viscous solid).

Results and Discussion

THF was polymerized using methyl trifluoromethanesulfonate (MeOTf) at room temperature to afford living poly(THF) (**1**).[5] The two-electron reduction of the growing center of poly(THF) was carried out by adding HMPA and then a 0.1 M THF solution of SmI_2. The typical color of divalent samarium (purple) turned into yellow[6] within 20 min, which indicated the complete reduction of the growing center of poly(THF). CL was then added to the reaction mixture at 0 °C, and the reaction mixture was stirred at 0 °C for 3 h (Scheme 3).

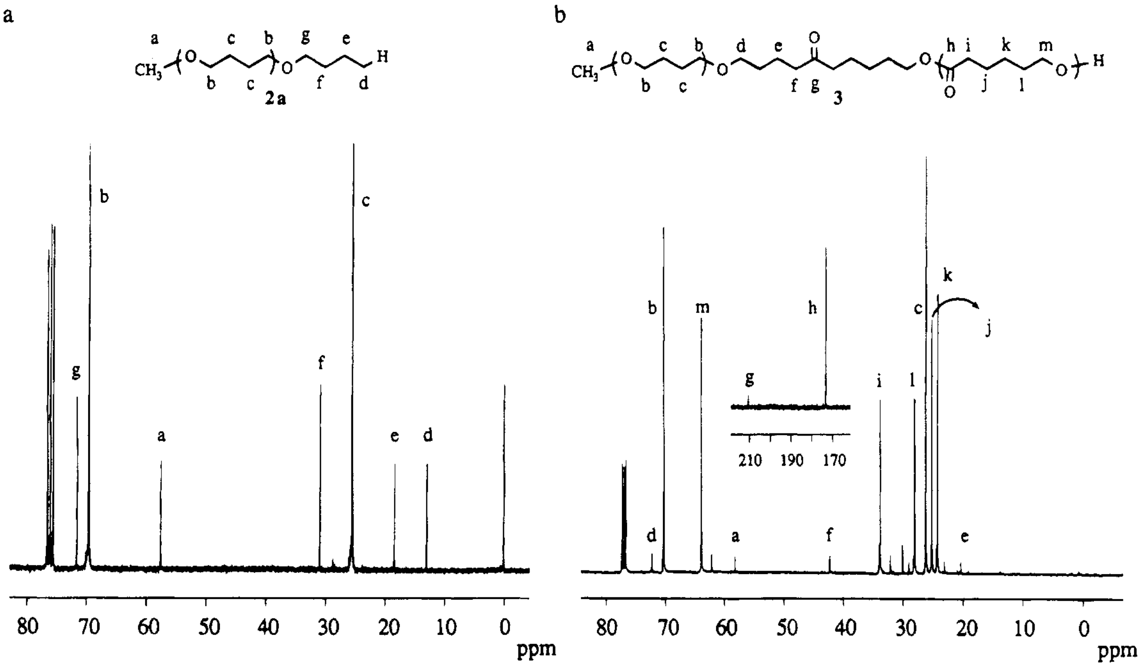


Figure 3. ^{13}C NMR spectra of **2a** and **3**.

GPC profiles of the two-electron-reduced poly(THF) (**2**) and the resulting copolymer (**3**) are shown in Figure 1.

After charging CL to the reaction mixture, the GPC curve shifted to the high molecular weight region while maintaining a narrow molecular weight distribution. No GPC trace attributed to **2** was detected. ^{1}H NMR and ^{13}C NMR spectra of **2a** obtained by hydrolysis of **2** and **3** are shown in Figures 2 and 3, respectively.

The singlet peak attributed to the terminal methyl group derived from the initiator could be observed at 3.3 ppm together with the other methyl group at 0.8 ppm as a triplet peak (Figure 2a). Because the integral ratio of these peaks was almost 1:1, the poly(THF) growing center was almost quantitatively reduced to the corresponding macroanion. The triplet peak of **2a** at 0.8 ppm almost disappeared, and the peaks due to both THF and CL units were observed in the ^{1}H NMR spectrum of **3**. Similarly, the signals attributed to the terminal groups of **2a** were completely consumed in the ^{13}C NMR spectrum of **3**. Furthermore, a signal due to the carbonyl group of the joint unit could be observed at 211 ppm. These GPC and NMR data suggested that the transformed poly(THF) macroanion polymerized CL with quantitative initiator efficiency.

In the case of polymerization of ϵ-caprolactone in THF, monomer is first converted to linear polymer, and subsequently the formation of cyclic oligomers is observed. This backbiting reaction results in a considerable decrease of the molecular weight of the polymer.[7] It should be noted that the backbiting reaction was negligible in the polymerization of CL with **2**. The GPC profiles of the block copolymers polymerized for 2.5 h and 2 days at 0 °C are shown in Figure 4. Although a small change in the molecular weight distribution was observed, no serious decrease of the molecular weight was detected. In order to demonstrate the living nature of the block copolymerization, a fresh feed of CL was added to the reaction mixture after the initial charge of the CL was almost consumed (at 94% conversion by a gas chromatograph analysis). The second-stage polymerization of CL quantitatively proceeded to give the block copolymer, which could be confirmed by GPC analysis (Figure 5). The molecular weight distribution of the block copolymer remained relatively narrow before and after the monomer addition. In other words, the polymerization of CL with the poly(THF) macroanion was found to proceed with living-like character.

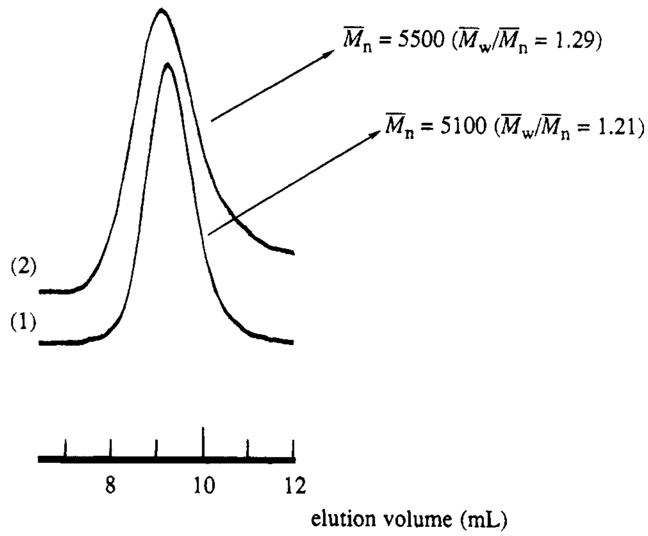


Figure 4. GPC profiles of the block copolymer: (1) polymerized for 2.5 h at 0 °C; (2) polymerized for 2 days at 0 °C.

The results of the block copolymerization of THF with CL under various conditions are summarized in Table 1. In all runs, no trace based on the prepolymer **1** was observed in the GPC measurements. The GPC analyses also showed that the molecular weight distribution of the copolymers was unimodal and narrow (<1.21) in each experiment. Additionally, the peaks attributed to both poly(THF) and poly(CL) were observed in the ^{1}H NMR spectra of the resulting copolymers in all cases. These results mean that the block copolymerization successively occurred without serious side reactions such as termination and chain-transfer reaction. The unit ratio (*m*:*n*) was calculated by the integrated ratio of signals of each unit in their ^{1}H NMR spectra. The molecular weights, yields of the copolymers, and unit ratio of CL to THF increased with increasing the

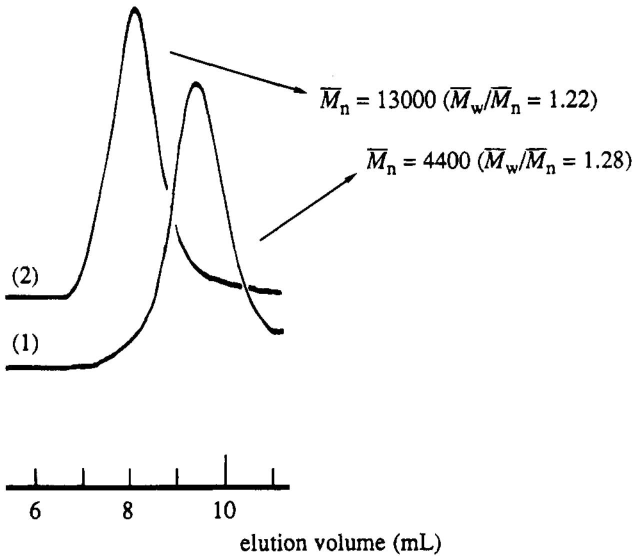


Figure 5. Monomer-addition experiments in the block copolymerization of THF and CL: (1) just before the initial charge of CL was consumed; (2) after the consumption of the second charge of CL.

Table 1. One-Pot Block Copolymerization of THF with CL

	polymerization of THF[a]		block copolymerization[b]					
run	MeOTf (mmol)	time (min)	CL (mg)	polym (mg)	conv of CL (%)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	$m:n$[d]
1	0.20	5	233	355	86	5400	1.21	45:55
2	0.19	5	347	423	82	6600	1.18	56:44
3	0.17	5	496	596	87	9500	1.16	62:38
4	0.21	2.5	255	289	97	4800	1.12	79:21
5	0.18	10	244	399	76	6000	1.21	35:65

[a] Polymerization conditions: THF 5 mL, room temperature. [b] Carried out for 2.5 h at 0 °C. [c] Estimated by GPC (THF, PSt standards). [d] Determined by ^{1}H NMR spectra.

amount of CL as shown in Table 1. Similarly, the unit ratio of THF to CL increased with increasing the polymerization time of THF. In other words, the molecular weight and unit ratio (*m*:*n*) were facilely controlled by both the polymerization time of THF and the amount of CL.

In summary, we have demonstrated the first example for the transformation of living cationic polymerization into a living anionic one *via* two-electron transfer utilizing the SmI_2/HMPA system. This method provides new routes in the field of polymer architecture.

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