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Novel Transformation Reaction of a Cationic Propagating End into an Anionic One *via* Electron Transfer Induced by Samarium Iodide

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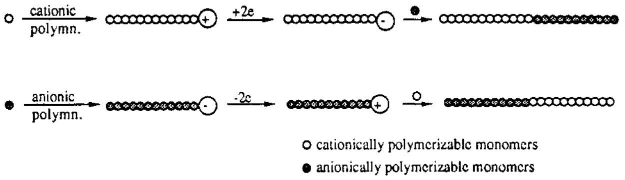
ABSTRACT: The cationic propagation end of poly(tetrahydrofuran)(polyTHF) was quantitatively reduced into an anionic one by using samarium(II) iodide in the presence of hexamethylphosphoramide (HMPA). Any side reactions such as dimerization or termination did not occur during the reduction. Transformed poly(THF) macroanion initiated the polymerization of *tert*-butyl methacrylate (TBMA), affording the block copolymer of THF with TBMA with narrow molecular weight distributions (1.07–1.22) without the formation of the respective homopolymer of THF or TBMA. The amount of HMPA was found to affect the molecular weight distribution of the copolymer. The unimodal copolymer was obtained by using 4.5 equiv of HMPA to SmI_2. The unit ratio of THF and TBMA and molecular weight of the copolymer could be facilely controlled by both the polymerization time of THF and the amount of TBMA.

Introduction

Block copolymers have been of interest because of their unique and characteristic properties in solution and in the solid state.[1] Introduction of the concept of living polymerization by Szwarc and co-workers stimulated the preparation of block copolymers by sequential addition processes. Many kinds of block copolymers can be obtained by the living polymerization technique if the monomers are properly selected. However, almost all of the synthetic effort has been focused on chain polymerization by a single propagating mechanism, usually cationic or anionic. Therefore, there are many limitations of the number of monomers which can be copolymerized. This restriction can be reduced by the transformation of the mechanism after polymerization of the first monomer to one suitable to the polymerization of the second. The transformation of active centers, i.e., polarity inversion, requires two-electron oxidation or reduction to take place during the transformation of ions, theoretically (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. Complicated multistep paths have been used to transform the polarity of the growing center.[2] For example, Rechards' methods for the transformation of anionic polymerization of styrene into a cationic one of THF involves (1) termination of the growing center of living polystyrene with excess 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 a 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 initiation efficiency of the second one is low. Thus, the obtained copolymers often show multimodal molecular weight distributions.

In recent years, much attention has been paid to lanthanide elements. Especially, divalent lanthanide complexes such as Sm(II), Eu(II), and Yb(II) are known

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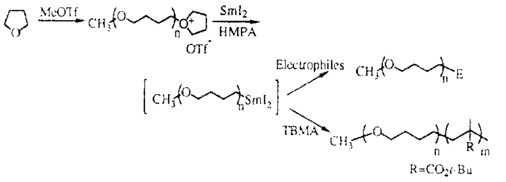
Scheme 2



as versatile and mild one-electron reducing agents. Many efficient electron transfer reductions have been reported to proceed under mild reaction conditions by using these complexes.[3] One of the most characteristics of the electron transfer reaction is the easy polarity inversion.[4] Namely, nucleophiles can be converted into species which gain electrophilicity by removal of an electron. Similarly, two-electron transfer to electrophiles can change its nucleophilic character. Application of this mild and powerful reducing ability of divalent lanthanide complexes is expected to accomplish the direct transformation of a growing center *via* electron transfer.

Previously, we have succeeded in the transformation of the polarity of a cationic active species of poly(tetrahydrofuran) [poly(THF)] into an anionic one *via* electron transfer following the SmI_2/HMPA system.[5a] The transformed poly(THF) macroanion reacted with a variety of electrophiles including aldehydes, ketones, and isocyanates.[5a] Furthermore, a recent paper from our laboratory outlined the polymerization of *tert*-butyl methacrylate (TBMA) with the poly(THF) macroanion, leading to the block copolymer of THF with TBMA (Scheme 2).[5b] In this paper, we present the full details of this block copolymerization, especially the effect of the amount of hexamethylphosphoramide (HMPA).

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 on CaH_2 under reduced pressure. Methyl trifluoromethanesulfonate was distilled on P_2O_5 under a nitrogen atmosphere.

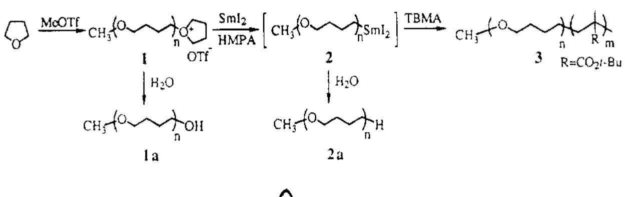
Measurements. NMR spectra were recorded with JEOL JNM-EX-90 and JNM-GX-270 spectrometers. Molecular weights and their distribution (M_w/M_n) were determined by gel permeation chromatography on a Toyo Soda CCP&8000 (TSK gel G3000, THF) after calibration with standard polystyrenes. HPLC analysis was carried out on a Nihon Bunseki Kokgy Model LC80.

Synthesis of a Block Copolymer of THF with TBMA. Methyl trifluoromethanesulfonate (0.16 mmol) was added to dry THF (5 mL), and the solution was stirred for 5 or 10 min at room temperature. After charging HMPA (240 mL), a 0.1 M THF solution of SmI_2 (3.2 mL, 0.32 mmol) 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). Into the reaction mixture was added TBMA, and the reaction mixture was stirred for 24 h. After addition of a 3% HCl solution, the reaction mixture was extracted with toluene, and the organic extract was washed with brine several times. The organic layer was dried over $MgSO_4$, filtered, and concentrated to give the copolymer.

Results and Discussion

THF and TBMA were chosen as the first and second monomers, respectively, for the following reasons: (1) The polymerization of THF gives living polymer without termination nor chain-transfer reaction at the initial stage of the polymerization when the initiators are properly selected.[7] (2) The growing center of poly(THF) is stable in solution. (3) TBMA is easily polymerized by typical anionic initiators, affording living poly(TBMA) even above room temperature.[8] THF was polymerized at room temperature using methyl trifluoromethanesulfonate (MeOTf) as an initiator to yield the living poly(THF) 1. The reduction was carried out at low THF conversion intentionally (within 3–5%), far before the equilibrium monomer concentration. The reversible propagation and chain transfer to the polymer can be avoided under these conditions, resulting in the formation of poly(THF) with a narrow molecular weight distribution. The reduction was performed by adding HMPA and 0.1 M solution of SmI_2 in THF (2 equiv to the initiator) into the solution of 1. After a complete change of the color of the reaction mixture (from purple to yellow–brown),[9] TBMA was added to the reaction mixture at room temperature (Scheme 3). The addition of HMPA is indispensable for the reduction of the growing center of 1,[10] and the amount of HMPA was found to affect the molecular weight distribution of the resulting block copolymer. The GPC chromatograms of the resulting copolymers using various amounts of HMPA are illustrated in Figure 1.

Scheme 3



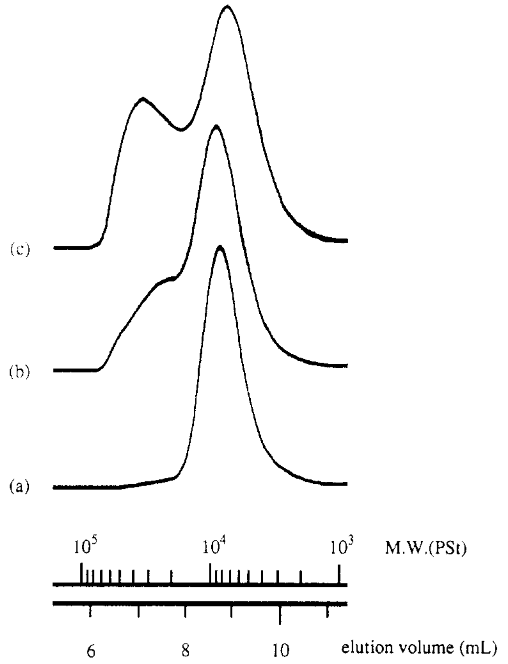


Figure 1. GPC profiles of block copolymerization using various amounts of HMPA: (a) 4.5 equiv (to SmI_2); (b) 6 equiv; (c) 12 equiv.

When the amount of HMPA was less than 3 equiv to SmI_2, the characteristic color of divalent samarium did not disappear completely, meaning the reduction did not completely proceed. More than 4.5 equiv of HMPA was required to accomplish the complete reduction.

When 4.5 equiv of HMPA was employed, the block copolymer of THF with TMBA having a narrow molecular weight distribution was obtained as illustrated in Figure 1. The GPC traces of poly(THF)s (**1a** and **2a**) and the resulting block copolymer **3** are shown in Figure 2. The GPC curve of 1 showed the formation of living poly(THF) with narrow molecular weight distribution ($M_w/M_n = 1.27$), which is inconsistent with the previous result of ring-opening polymerization of THF initiated by MeOTf.[7a] No significant difference in the GPC profiles between 1 and

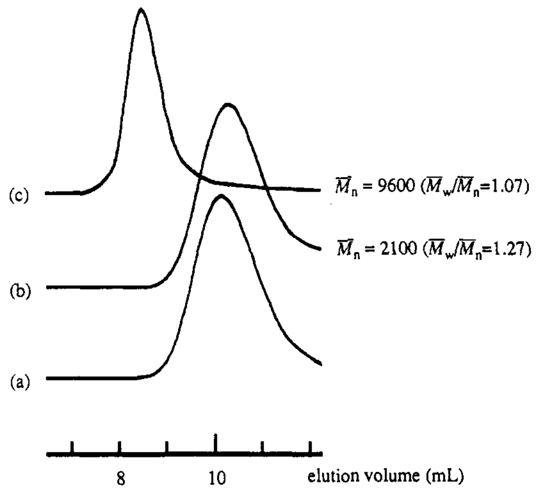


Figure 2. GPC profiles of (a) **1a**, (b) **2a**, and (c) **3**.

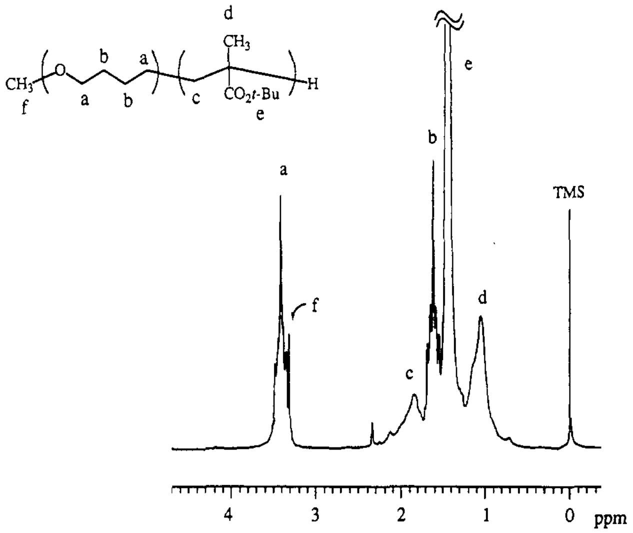


Figure 3. ^{1}H NMR spectrum of the resulting copolymer **3** (60 °C, in CDCl$_3$).

2 indicates that dimerization of 1 with 2 did not take place during the reduction. After charging TBMA to the reaction mixture of 2, the GPC curve shifted to the high molecular weight region while maintaining a narrow molecular weight distribution without any GPC trace attributed to the prepolymer 1. Moreover, signals attributed to both THF and TBMA units were observed in the ^{1}H NMR spectrum (Figure 3). These results strongly support that the transformation of a cationic propagation end to an anionic one proceeded quantitatively and that the transformed macroanion initiated the polymerization of TBMA with quantitative initiation efficiency.

In the case of using a large excess of HMPA (more than 6 equiv), the molecular weight distribution of the resulting polymer was bimodal. The high and low molecular weight polymers were separated by HPLC and found to be a homopolymer of TBMA and a block copolymer of THF with TBMA, respectively. Because the typical color of divalent samarium completely disappeared in this case, the reaction of SmI$_2$ with TBMA which gives homopolymer of TBMA[5c] might not occur. This reason could not be clarified in this experiment. Probably, the trivalent samarium complex may contribute to the homopolymerization of TBMA since TBMA was polymerized in the presence of SmI$_2$ and a large amount of HMPA even in a low yield.

Scheme 4

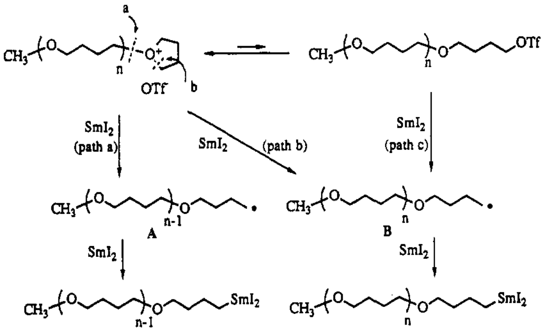


Table 1. Results of the Block Copolymerization of THF and TBMA

	polymn of THF^a		block copolymn^b				
run	MeOTf (mmol)	time (min)	TBMA (mmol)	polym (mg)	$\bar{M}_n{}^c$	$\bar{M}_w/\bar{M}_n{}^c$	m:n^d
1	0.15	10	0.8	234	4800	1.22	77:23
2	0.16	10	1.6	318	7700	1.13	51:49
3	0.16	10	3.1	469	7900	1.10	37:63
4	0.16	10	4.6	683	9600	1.07	25:75
5	0.16	5	0.8	119	3200	1.20	47:53
6	0.16	5	1.5	236	7400	1.08	32:68
7	0.17	5	3.2	454	9600	1.07	19:81
8	0.16	5	4.6	555	17000	1.07	13:87

^{a} Polymerization conditions: THF 5 mL; RT. ^{b} Carried out at RT for 24 h. ^{c} Estimated by GPC (THF, PSt standards). ^{d} Determined by ^{1}H NMR spectra.

The mechanism of the reduction is not clear at present. Considering the mechanism of the two-electron reduction of primary alkyl halides with SmI$_2$, a possible mechanism is proposed as outlined in Scheme 4. There are three pathways of the reduction mechanism (paths a–c). Path a involves the reductive cleavage of the C–O bond, leaving one molecule of THF, while the C–O bond of the THF ring at the polymer end is cleaved in path b. In path c, the reduction proceeds through the triflate ester. One-electron reduction of the oxonium cation or the triflate ester gives primary radicals (**A** or **B**) which rapidly undergo further one-electron reduction to produce the anionic species. Although no direct evidence could be provided, the main pathway may be path a or b because the high polarity of polymerization solution shifts the equilibrium toward the oxonium cation. The study on the reduction mechanism is now in progress.

The results of block copolymerizations of THF with TBMA using 4.5 equiv of HMPA to SmI$_2$ are summarized in Table 1. In all runs, any trace based on the prepolymer 1 was not observed in the GPC measurements. The GPC analyses also showed that molecular weight distribution of the copolymers weas unimodal and narrow (<1.2) in each experiment. Additionally, the peaks attributed to both poly(THF) and poly(TBMA) 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. The unit ratio (m:n) was calculated by the integrated ratio of signals of each unit in their ^{1}H NMR spectra. When the polymerization time of THF was fixed at 5 or 10 min, the molecular weight of the copolymer was increased with increasing the amount of TBMA as shown in Table 1. Similarly, the unit ratio of TBMA to THF was increased with increasing the amount of TBMA. 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 TBMA.

In summary, we have demonstrated the novel method for the transformation of the growing center of cationic polymerization into an anionic one *via* two-electron transfer utilizing the SmI_2/HMPA system and sequential block copolymerization of TBMA. The amount of HMPA was significant to produce unimodal block copolymers. The transformation reaction proceeded smoothly under mild reaction conditions without side reactions. The block copolymerization proceeded with quantitative initiators efficiency if the proper amount of HMPA was employed. This method is the first example for the transformation leading to the copolymer having a unimodal molecular weight distribution in one pot. This methodology is more convenient and simpler for the polarity inversion of cationic active centers to anionic ones compared to the other multistep methods reported previously. This method provides new routes in the field of polymer architecture.

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