Block Copolymerization of Tetrahydrofuran and *tert*-Butyl Methacrylate. Polarity Inversion of Cationic Propagation Ends into Anionic Ones *via* Two-Electron Reduction by Samarium Iodide

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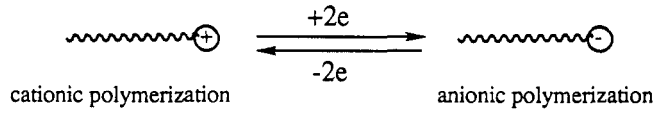
Transformation of the polarity of active centers in the ionic polymerization is of interest from the standpoint of attaining to novel polymerization methods. The polymerization initiated by transformed growing centers provides block copolymers that cannot be obtained by the usual manners. The transformation of active centers, polarity inversion, requires two-electron oxidation or reduction to take place during the transformation of ions (Scheme 1). Although several complicated multistep paths leading to the transformation of macroanions have been reported,[1] direct oxidation or reduction by electron transfer has not been achieved so far.

Recently, we have succeeded in the reduction of the cationic propagating end of poly(THF) to the anionic one by using the SmI_2/HMPA system.[2] The two-electron reduction of the growing center of poly(THF) proceeded quantitatively to give poly(THF) bearing the organosamarium moiety at the polymer end. The transformed anionic species reacted with electrophiles such as aldehydes and ketones, leading to poly(THFs) end-capped with electrophiles (Scheme 2). It is expected that polymerization of anionically polymerizable monomers by the transformed center of poly(THF) offers novel block copolymers of cationically and anionically polymerizable monomers in one pot. In this paper, we report a convenient and simple synthetic method for the preparation of block copolymers of THF and alkyl methacrylates *via* two-electron transfer induced by SmI_2[3] (Scheme 3).

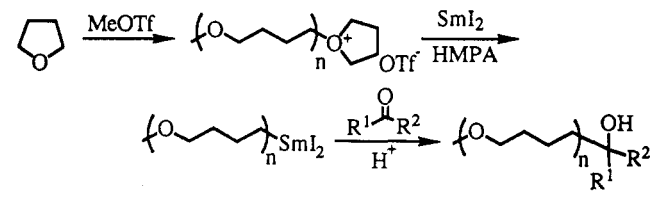
tert-Butyl methacrylate (TBMA) was selected as the second monomer because the polymerization of TBMA by typical anionic initiators gives living poly(TBMA) without serious side reactions even at above room temperature.[4] THF was polymerized at room temperature using methyl trifluoromethanesulfonate (MeOTf) as an initiator to afford the living poly(THF) **1**. The reduction was performed by adding HMPA and a 0.1 M solution of SmI_2 in THF (2 equiv to the initiator) into the solution of **1** (Scheme 3). The color of the reaction mixture changed from purple to yellow–brown within 30 min, indicating the completion of the reduction. TBMA was then added to the reaction mixture, and the reaction mixture was stirred for 24 h at room temperature. GPC profiles of the prepolymer (**1**), double-electron-reduced poly(THF) (**2a**), and the resulting copolymer (**3**) are shown in Figure 1.

The GPC curve of **1** showed the formation of living poly(THF) with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.20), which is inconsistent with the previous result of ring-opening polymerization of THF initiated by MeOTf.[5] No significant difference in the GPC profiles between **1** and **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. Any GPC trace attributed to the poly(THF) macroanion **2** was not observed. Figure 2 illustrates the ^1H NMR spectrum of **3** together with that of **2a**. A terminal methyl proton of **2a** (a) was observed as a triplet peak at 0.8 ppm in the ^1H NMR spectrum of **2a**. The integral ratio of this peak and the other terminal methyl peak at 3.26 ppm (b) was almost 1:1, which means that the reduction of **1** to **2** proceeded

Scheme 1



Scheme 2



Scheme 3

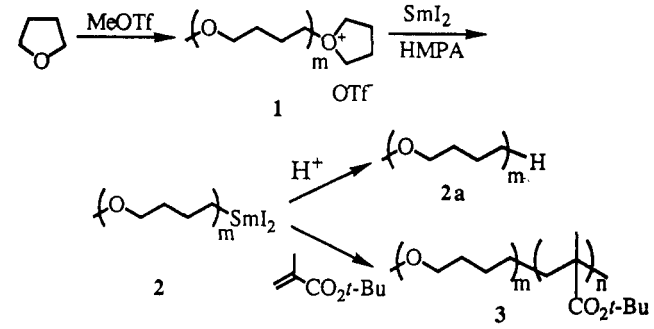


Table 1. Results of the Block Copolymerization of THF and TBMA

	polymerization of THF[a]		block copolymerization[b]				
run	MeOTf (mmol)	time (min)	TBMA (mmol)	polym (mg)[c]	M_n[c,d]	M_w/M_n[c,d]	*m*:*n*[e]
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

[a] Polymerization conditions: THF 5 mL, rt. [b] Carried out at rt for 24 h. [c] 3% HCl(aq)-insoluble parts. [d] Estimated by GPC (THF, PSt standards). [e] Determined by ^1H NMR spectra.

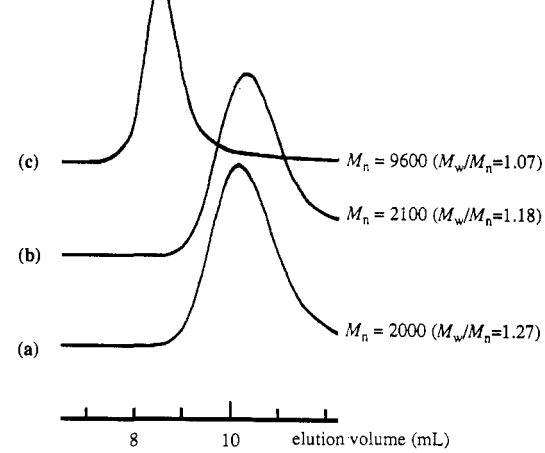


Figure 1. GPC profiles of (a) **1**, (b) **2a**, and (c) **3**.

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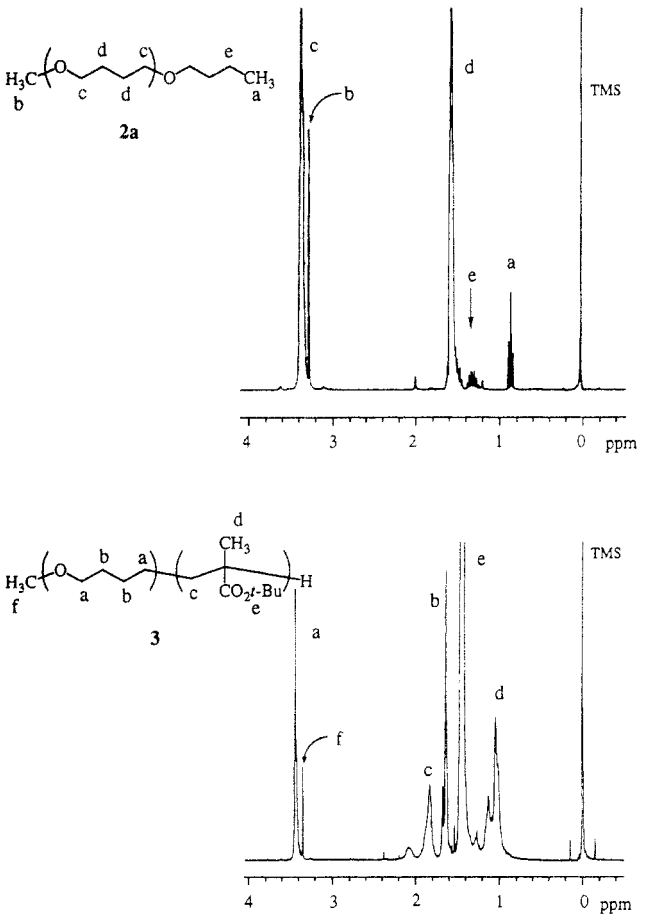

Figure 2. ^{1}H NMR spectrum of **2a** and **3** (60 °C, in $CDCl_3$).

quantitatively without serious side reaction. On the other hand, the peak of **2a** at 0.8 ppm approximately disappeared, and signals attributed to both THF and TBMA units were observed in the ^{1}H NMR spectrum of **3**. These results strongly support that the transformed macroanion (**2**) initiated the polymerization of TBMA quantitatively to give the copolymer of THF and TBMA.

The results of block copolymerization of THF and TBMA under various reaction conditions are summarized in Table 1. In all runs, transformation of the propagating end of poly(THF) into the anionic one successively proceeded, leading to the block copolymers of THF and TBMA. The GPC measurements showed that the molecular weight distribution of the copolymers was unimodal and narrow (<1.22) in each experiment. Additionally, the peaks attributed to both poly(THF) and poly(TBMA) were detected in the ^{1}H NMR spectra of the resulting copolymers in all cases. The unit ratio (m:n) was evaluated by the integrated ratio of the each unit in the ^{1}H NMR spectra. The unit ratio was facilely controlled by both the polymerization time of THF and the amount of TBMA as shown in Table 1.

In conclusion, we have demonstrated, for the first time, the two-electron reduction of cationic growing centers of poly(THF) by the SmI_2/HMPA system and consequent block copolymerization of TBMA. This method is one of the most convenient and simplest manners for the quantitative transformation of growing ends.

References and Notes

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