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Two-Electron Reduction of the Cationic Propagating End of Poly(tetrahydrofuran) into Terminating Nucleophiles by Samarium Iodide

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ABSTRACT: Quantitative double electron reduction of the cationic propagation end of poly(tetrahydrofuran) into a terminating nucleophile was achieved by using samarium(II) iodide in the presence of hexamethylphosphoramide. Termination of the resulting organosamarium group at the terminus of the poly(THF) was attempted by using a variety of typical electrophiles such as aldehydes, ketones, isocyanates, and alkyl halides. The functionality of the obtained poly(THF)s was 0.64–1.10 when aldehydes, ketones, or isocyanates were used as electrophiles, indicating that the reaction of the terminating nucleophile with electrophiles successively proceeded. In the case of using allyl bromide or benzyl bromide as a terminating agent, the functionality of the poly(THF)s decreased (0.11–0.20).

Introduction

Reaction of growing centers with appropriate terminators makes it possible to introduce functional groups into the polymer ends in the chain polymerization. Functional polymers such as block polymers, graft polymers, macromonomers, star-shaped polymers, and so on are facilely obtained by this methodology. However, there are significant restrictions on terminators which react with growing centers of polymers. For instance, only nucleophiles terminate cationic propagation ends. Similarly, the terminators which react with anionic propagation ends are limited to electrophiles. The range of attainable terminators is greatly extended if the transformation of the growing center, so called polarity inversion, is easily achieved. Two-electron oxidation or reduction offers the possibility to change the polarity of active centers (Scheme 1). In practice, polarity inversion of growing centers requires complicated multistep paths,[1] and the two-electron transfer to or from propagation ends has not been achieved so far.

In recent decades, much attention has been paid to the characteristic properties of lanthanide elements. In particular, divalent lanthanide complexes such as Sm(II), Yb(II), and Eu(II) have been established as excellent one-electron reducing agents in the field of organic synthesis.[2] Among these complexes, Sm(II) exhibits the strongest reducing ability (−1.55 V vs SCE). Many efficient electron transfer reductions have been reported to proceed under mild reaction conditions by using Sm(II).[3] Thus, the application of this powerful and versatile reducing ability of Sm(II) is expected to enable cationic propagation ends to be transformed into anionic ones. In this paper, we report for the first time the reduction of cationic growing centers to terminating the nucleophiles *via* electron transfer induced by SmI_2. This method would provide new routes in the field of polymer architecture.

Tetrahydrofuran (THF) was chosen as a monomer that undergoes cationic polymerization because of the following reasons: (1) The polymerization of THF gives a living polymer when the initiators are properly selected.[4] (2) The growing center (oxonium cation) of the poly(THF) is stable in solution. (3) The polymerization of THF proceeds relatively slowly even at room temperature, and the molecular weights of the polymer can be easily controlled by reaction time, initiator concentration, polymerization temperature, and amount of added solvent. We also attempted the reaction of the transformed macroanion of poly(THF) with a variety of electrophiles.

Results and Discussion

Reduction of the Cationic Propagation End of poly(THF) by SmI_2. THF was polymerized at room temperature using methyl trifluoromethanesulfonate (MeOTf) as an initiator to afford the living THF polymer (1). The reduction was performed by adding hexamethylphosphoramide (HMPA, 8–9 equiv to SmI_2) and a 0.1 M solution of SmI_2 in THF (2 equiv to the initiator) into the

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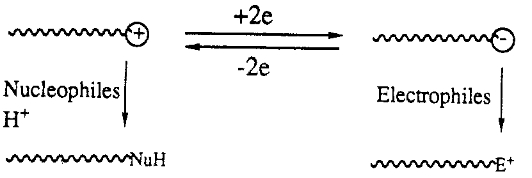
Scheme 1



solution of 1 (Scheme 2). The color of the reaction mixture changed from purple to yellow-brown within 30 min, indicating the completion of the reduction.

^{1}H NMR and IR spectra of the resulting polymers 3 ($\bar{M}_n$ = 3100, $\bar{M}_w/\bar{M}_n$ = 1.15, GPC, PSt standards) which was obtained by termination of 2 with water are shown in Figures 1 and 2, respectively. The characteristic triplet peak at 0.84 ppm (d) was observed together with a singlet peak at 3.26 ppm (a) attributed to the terminal *O*-methyl group in the ^{1}H NMR spectrum of 3. Because the integrated ratio of these two peaks (a and d) was almost 1:1, the peak (d) was assigned as one of the terminal methyl protons. The IR spectrum of 3 showed no characteristic absorption due to the terminal hydroxyl group which was observed in the spectrum of poly(THF) obtained after the termination of 1 by water. The structure of 3 was also confirmed by its ^{13}C NMR spectrum, as illustrated in Figure 3. These results strongly support that the cationic propagation end of poly(THF) was reduced almost quantitatively, yielding hydrogen-terminated poly(THF) 3. During the reduction, disproportion was negligible because no olefin proton was observed in the ^{1}H NMR spectrum of 3. Furthermore, no significant difference in the GPC profiles between 1 and 3 indicates that the coupling reaction of 1 with 2 may not take place (Figure 4).

Reaction of 2 with Electrophiles. The aliphatic primary halides are rapidly reduced by SmI_2 in the presence of HMPA, affording organosamarium intermediates.[3i] The organosamarium reagents have moderate stability in solution, and they react with various electrophiles.[3a,b] It is expected that electrophiles can be introduced into the polymer end by the reaction of the terminal organosamarium moiety of 2 with appropriate electrophiles. For the preliminary experiment, the reaction of benzaldehyde (4a) with 2 was examined (Scheme 3).

The reaction was performed by addition of 4a to the reaction mixture of 2 at room temperature. The peaks in GPC of the obtained polymer were detected by both UV and RI, whereas poly(THF) having a hydroxyl group at the terminus shows no UV absorption, which indicates the introduction of an aromatic group onto 2. ^{1}H NMR and ^{13}C NMR spectra of the resulting polymer (5a) are shown in Figures 5 and 6, respectively. The triplet peak at 0.82 ppm that was observed in the ^{1}H NMR spectrum of 3 disappeared approximately, and signals at 7.02–7.30 and 4.50 ppm were assignable as aromatic protons and the methyne proton (d), respectively. The proton ratio of *O*-methyl (a) and aromatic proton agreed well with the values of the structure 5a. ^{13}C NMR spectrum of 5a shows the peaks derived from 4a, but no signal due to the terminal methyl carbon at 12.9 ppm was detected. Additionally, the characteristic absorption due to the OH group was observed in the IR spectrum of 5a. From these results, it can be concluded that the C–C bond formation between the terminal organosamarium moiety and 4a successively occurred.

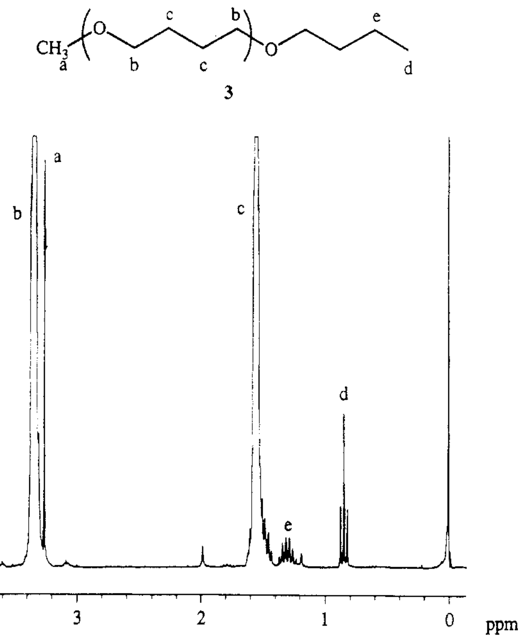


Figure 1. ^{1}H NMR spectrum of 3 (in $CDCl_3$).

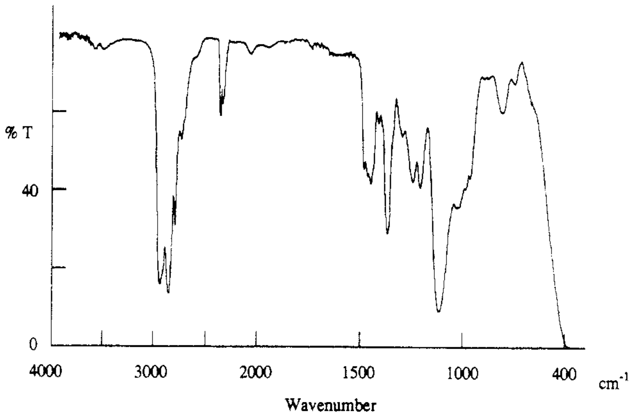
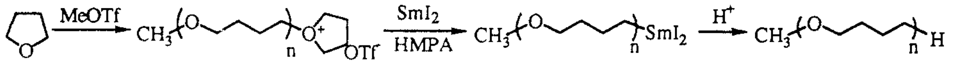


Figure 2. IR spectrum of 3.

The GPC chart of 5a showed the formation of a polymer with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.19), which is inconsistent with the previous result of the ring-opening polymerization of THF initiated by CH_3OTf.[4a]

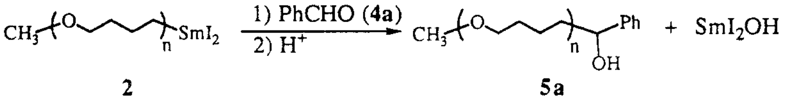
Reaction of 2 with Various Electrophiles. The results of the reaction of 2 with a variety of electrophiles

Scheme 2



1 2 3

Scheme 3



2 5a

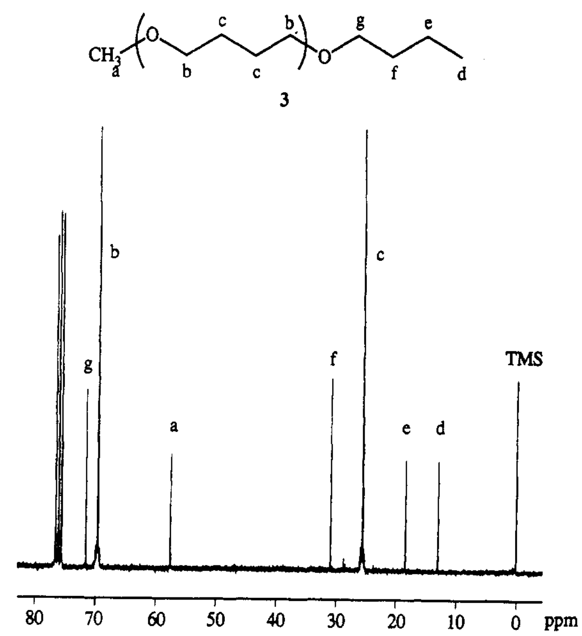


Figure 3. ^{13}C NMR spectrum of 3 (in $CDCl_3$).

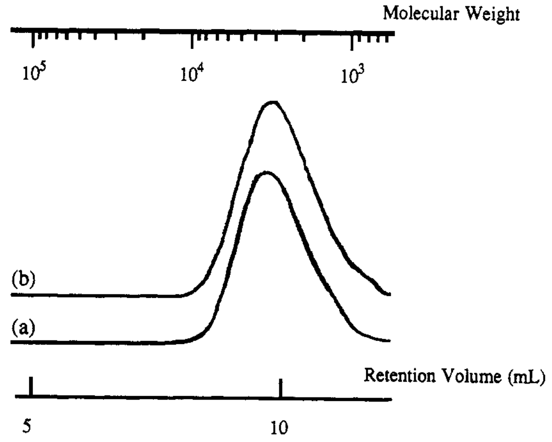


Figure 4. GPC traces of poly(THF)s: (a) terminated with water; (b) terminated by water after addition of HMPA and a THF solution of SmI_2.

are summarized in Table 1. In all experiments, 3 was generated by addition of HMPA (8–9 equiv to SmI_2) and SmI_2 in THF (2 equiv to MeOTf) at room temperature. The functionality of the resulting poly(THF)s was estimated by the proton ratio of the terminal *O*-methyl group and protons due to the electrophiles. When aldehydes or aromatic ketones were used as electrophiles, the functionality of the polymers was close to 1.0, which indicates that the reaction of 2 with electrophiles proceeded successively without serious side reactions. However, the functionality was low in the reaction of 2 with the aliphatic ketone. Reaction of phenyl isocyanate with 2 effectively gave a poly(THF) having an amide group at the polymer end. On the other hand, the functionality of the polymers decreased in the reaction with alkyl halides such as benzyl bromide or allyl bromide.

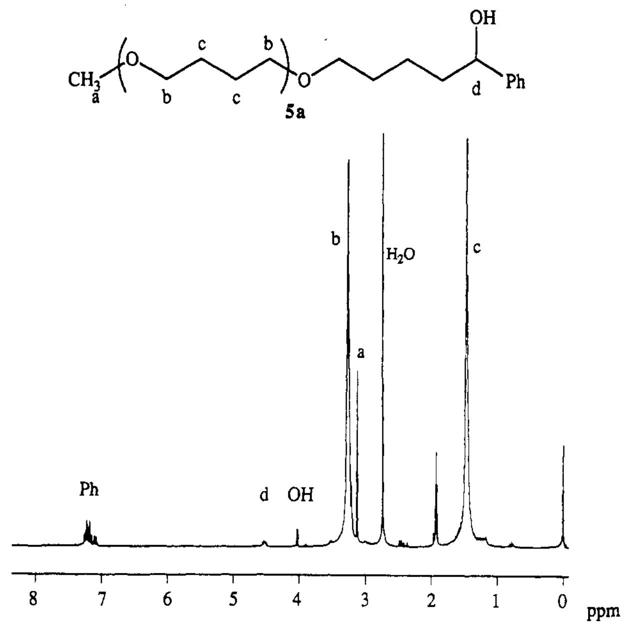


Figure 5. ^1H NMR spectrum of 5a (in CD_3COCD_3).

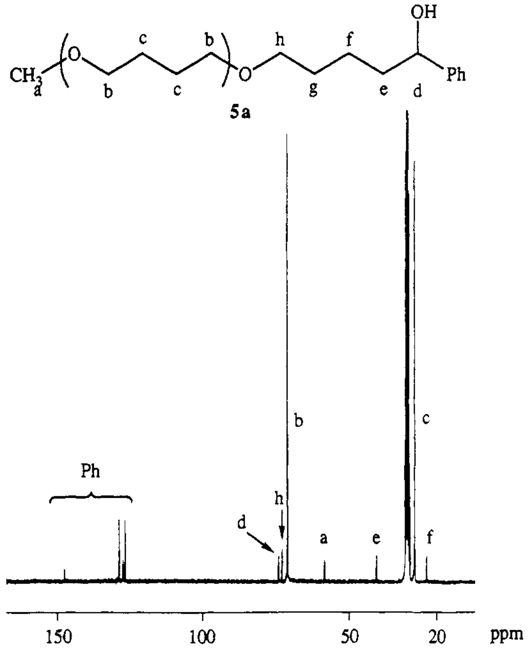


Figure 6. ^{13}C NMR spectrum of 5a (in CD_3COCD_3).

Table 1. Reaction of 2 with Various Electrophiles

run	amt of MeOTf (mmol)	electrophiles	polym [amt/(mg)]	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[a]	functionality[b]
1	0.184	PhCHO	**5a** (101)	2400 (1.19)	0.95
2	0.145	$PhCOCH_3$	**5b** (91.0)	2600 (1.20)	0.94
3	0.216	$PhCH_2CH_2CHO$	**5c** (158)	2500 (1.16)	1.10
4	0.179	$PhCH_2CH_2COCH_3$	**5d** (47.7)	2700 (1.19)	0.64
5	0.202	*p*-$CH_3C_6H_4NCO$	**5e** (140)	2500 (1.26)	1.10
6	0.230	$PhCH_2Br$	**5f** (70.1)	2600 (1.22)	0.11
7	0.191	$CH_2{=}CHCH_2Br$	**5g** (57.6)	2700 (1.21)	0.20

[a] Estimated by GPC (THF, PSt standards). [b] Calculated by ^1H NMR.

Conclusions

In this paper, we demonstrated the first example of the transformation of the cationic living propagation end of poly(THF) into a terminating nucleophile by double electron transfer. The SmI_2/HMPA system was found to be an excellent reducing agent for this polarity inversion of the active center. The reduction proceeded under mild conditions, and quantitative transformation to anionic centers was achieved. Poly(THF)s end-capped with electrophiles were obtained by the reaction of the transformed centers with carbonyl compounds in one pot. We believe that the reduction using the SmI_2/HMPA system is one of the most convenient and simplest procedures for the polarity inversion of growing centers among the other multistep methods reported previously.

Experimental Section

Materials. A THF solution of SmI_2 was prepared according to the reported manner.[5] THF was distilled prior to use from sodium/benzophenone under nitrogen. HMPA was distilled from CaH_2 under reduced pressure. Methyl triflate was distilled from P_2O_5 under a nitrogen atmosphere. All electrophiles were distilled under reduced pressure.

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.

Preparation of Poly(THF)s End-Capped with Electrophiles. General Procedure. Methyl triflate (30.2 mg, 0.184 mmol) was added to dry THF (5 mL) at room temperature, and the solution was stirred for 7 min. After charging with HMPA (570 μL), a 0.1 M THF solution of SmI_2 (3.9 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). Neat **4a** (33.8 mg, 0.334 mmol) was added (resulting in immediate color change to yellow), and the reaction mixture was stirred at room temperature for 12 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 **5a**. Purification was performed by using HPLC (eluent $CHCl_3$). **3** was obtained by acidic working up before the addition of **4a**. The spectral data were as follows.

3: ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J = 5.4 Hz), 1.22–1.34 (m), 1.42–1.63 (m), 3.26 (s), 3.29–3.42 (m); ^{13}C NMR ($CDCl_3$) δ 12.9, 18.4, 25.5, 30.9, 57.5, 69.6, 71.6; IR (neat) 2942, 2857, 2797, 1368, 1113 cm^{-1}.

5a: ^{1}H NMR (CD_3COCD_3) δ 1.18–1.77 (m), 3.12 (s), 3.15–3.5 (m), 4.02 (d, J = 5.4 Hz), 4.46–4.68 (m), 7.04–7.32 (m); ^{13}C NMR (CD_3COCD_3) δ 23.4, 27.4, 40.4, 58.4, 71.1, 73.0, 74.1, 126.7, 127.5, 128.8, 147.3; IR (neat) 3447, 2940, 2857, 2797, 1113 cm^{-1}.

5b: ^{1}H NMR (CD_3COCD_3) δ 1.17–1.81 (m), 2.47–2.73 (m), 3.13 (s), 3.17–3.60 (m), 6.98–7.11 (m); ^{13}C NMR (CD_3COCD_3) δ 21.8, 31.4, 36.9, 39.0, 57.1, 69.7, 69.9, 71.6, 124.9, 127.7, 127.8, 142.3; IR (neat) 3464, 2963, 2855, 1262, 1110, 1020 cm^{-1}.

5c: ^{1}H NMR (CD_3COCD_3) δ 0.96–1.10 (m), 1.21–1.35 (m), 1.37 (s), 1.39–1.55 (m), 1.61–1.74 (m), 3.12 (s), 3.13–3.33 (m), 7.00–7.19 (m); ^{13}C NMR (CD_3COCD_3) δ 20.1, 26.0, 28.3, 29.7, 41.2, 43.6, 57.0, 69.7, 69.8, 70.5, 124.9, 127.7, 142.8; IR (neat) 3484, 2855, 2857, 2797, 1111 cm^{-1}.

5d: ^{1}H NMR (CD_3COCD_3) δ 1.38 (s), 1.40–1.53 (m), 1.55–1.64 (m), 2.52–2.61 (m), 3.12 (s), 3.14–3.36 (m), 6.98–7.10 (m); ^{13}C NMR (CD_3COCD_3) δ 20.1, 26.0, 29.3, 29.6, 43.8, 57.0, 69.7, 71.6, 72.8, 124.4, 125.2, 127.1, 148.7; IR (neat) 3467, 2961, 2857, 2797, 1109 cm^{-1}.

5e: ^{1}H NMR (CD_3COCD_3) δ 1.10–1.71 (m), 2.04–2.28 (m), 2.28 (s), 3.12 (s), 3.15–3.5 (m), 6.87–7.26 (m), 8.85 (s); ^{13}C NMR (CD_3COCD_3) δ 19.5, 20.9, 21.8, 26.0, 28.2, 36.0, 57.0, 69.7, 71.6, 119.1, 128.6, 135.4, 136.6, 170.1; IR (neat) 3300, 2941, 2857, 2797, 1693, 1111 cm^{-1}.

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