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# Synthesis of poly(tetrahydrofuran-*b*-$\epsilon$-caprolactone) macromonomer *via* the $SmI_2$-induced transformation

**Ryoji Nomura, Takeshi Endo***

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan

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## Summary

A novel well-defined macromonomer consisting of different types of monomers in polymerization mechanisms was synthesized for the first time through the $SmI_2$-induced transformation. The macromonomer, ω-methacryloylpoly-(tetrahydrofuran-*b*-ε-caprolactone), was prepared by the reaction of methacryloyl chloride with living poly(tetrahydrofuran-*b*-ε-caprolactone) [poly(THF-*b*-CL)] which was obtained by the two-electron reduction of the cationic growing center of poly(THF) by samarium iodide ($SmI_2$) followed by the polymerization of CL. $^1H$ NMR analysis indicated the quantitative introduction of the methacryloyl group onto the polymer end. The molecular weight distribution of the macromonomer was relatively narrow, and the unit ratio of THF to CL could be controlled by both polymerization time of THF and the amount of CL, resulting from the living nature of both CL- and THF-polymerizations. Radical copolymerization of the produced macromonomers with methyl methacrylate in the presence of AIBN resulted in a polymethacrylate backbone grafted with poly(THF-*b*-CL) block copolymers.

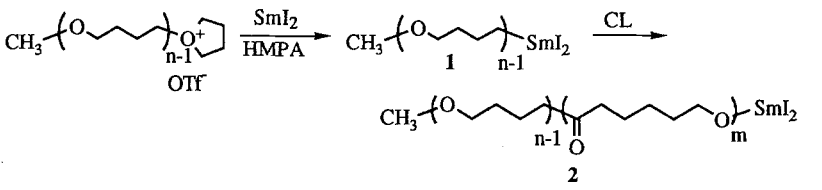
## Introduction

In recent years, many attempts have been made to synthesize and polymerize diblock macromonomers which contain polymerizable functional groups at terminus or centers of block copolymers [1]. The interest in these products arises from their ability to polymerize and copolymerize with various monomers, giving graft and star-block copolymers with many potential applications such as coating, adhesives, compatibilizers, emulsifiers, biomaterials, synthetic membranes and so on. The recent progress in the living polymerization technique which can offer well-defined polymers with living reactive ends has allowed production of diblock macromonomers with controlled structure and molecular weight.

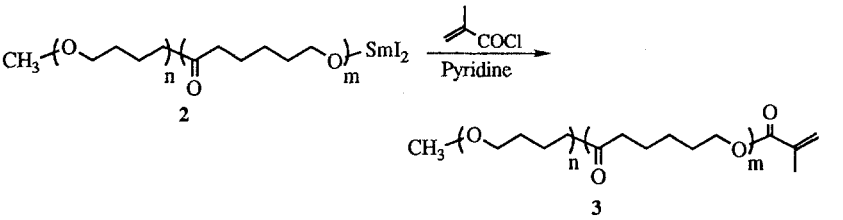
However, almost all efforts of the preparation of diblock macromonomers have been focused on chain polymerization by a single propagating mechanism, usually either cationic or anionic. Therefore, the number of attainable monomers and the kinds of resulting diblock macromonomers have been limited. These restrictions can be reduced by the transformation reactions which are theoretically possible to offer block copolymers consisting of different types of monomers in polymerization mechanism [2]. The transformation of active centers, however, has not been employed in the preparation of diblock macromonomers. This is because the traditional transformations often resulted in low initiation efficiency of second monomers, leading to the formation of multimodal copolymers.

* Corresponding author

**Scheme 1**



**Scheme 2**



Recently, we have reported the novel transformation from cationic polymerization into anionic one utilizing the excellent reducing ability of divalent samarium [3]. For instance, the cationic growing center of poly(tetrahydrofuran) [poly(THF)] was quantitatively converted into a terminal nucleophile by 2 equiv of $SmI_2$ in the presence of hexamethylphosphoramide (HMPA) [3a]. The transformed poly(THF) macroanion was active for the living polymerization of ε-caprolactone (CL) [3e] to give the unimodal block copolymer of THF with CL with controlled structure and narrow molecular weight distribution (Scheme 1). This paper is concerned with the potentialities of the $SmI_2$-induced transformation in the synthesis of diblock macromonomers consisting of different types of monomers in polymerization mechanism. The approach, we have employed, relies upon the reaction of the samarium alkoxide at the terminal of **2** with methacryloyl chloride (Scheme 2). We also describe the copolymerization of the diblock macromonomers (**3**) with methyl methacrylate (MMA) to provide a new graft copolymer, polymethacrylate backbone grafted with poly(THF-*b*-CL) diblock copolymers (Scheme 3).

## Results and Discussion

*Preparation of the macromonomer.* The living block copolymer of THF with CL (**2**) was prepared as previously reported [3e]: the propagation center of the living poly(THF) was reduced by $SmI_2$ in the presence of HMPA, followed by the polymerization of CL at 0°C for 4h. The GPC and $^1H$ NMR analyses supported the successful formation of the block copolymer (**2**) with relatively narrow molecular weight distribution. The macromonomer (**3**), ω-methacryloylpoly(tetrahydrofuran-*b*-ε-caprolactone), was prepared by the reaction of **2** with methacryloyl chloride in the presence of pyridine (Scheme 2). $^1H$ and $^{13}C$ NMR spectra of **2a** (hydrolyzed product of **2**) and **3** are illustrated in Figures 1 and 2, respectively. The triplet signal (i) at 3.62 ppm could be assigned as the terminal methylene protons as illustrated in Figure 1a. On the other hand, after the reaction with methacryloyl chloride, this peak (i) completely disappeared, whereas the new olefin signals at 5.53 (k') and 6.07 (k") were formed as observed in Figure 1b. The triplet peak at 4.14 ppm was also assignable as the methylene protons (i'). In the similar way, the peak at 62.5 ppm corresponding to the a-hydroxylmethylene carbon (i) accordingly shifted to lower field (64.0 ppm), and extra signals observed at 124.8 and 136.5 ppm (k and l) could be assigned to the methacrylic unsaturation as shown in Figure 2. The functionality of the

macromonomer calculated from the integrated intensity of the terminal methyl group (3.31 ppm) and olefin protons was very close to unity. These results support the idea that the reaction of **2** with methacryloyl chloride successively occurred without any serious side reactions [4].

The results of the preparation of **3** under various conditions are summarized in Table 1. In all cases, unimodal macromonomers could be obtained without the formation of homopolymer of CL or THF. The functionality was very close to the theoretical value in each experiment. Additionally, the unit ratio of THF to CL was facilely controlled by both the polymerization time of THF and the amount of CL.

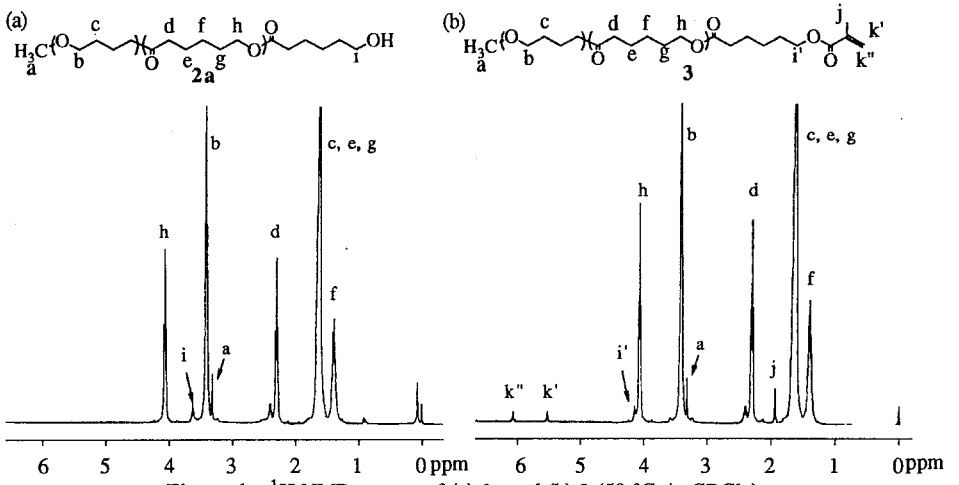



**Figure 1.** $^{1}H$ NMR spectra of (a) **2a** and (b) **3** (50 °C, in $CDCl_3$).

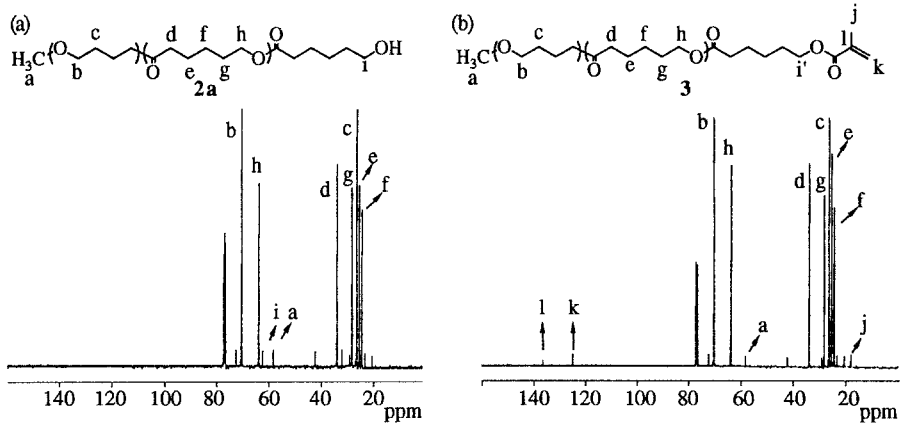


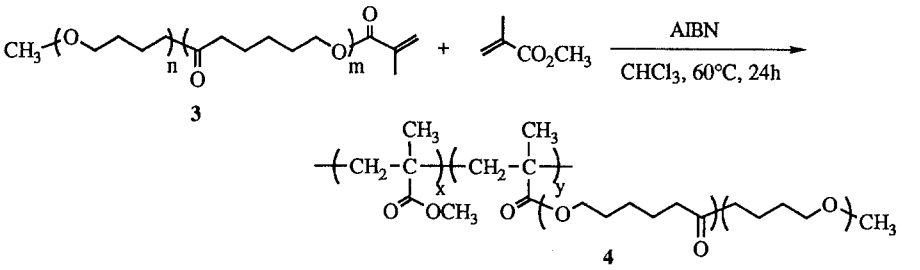

**Figure 2.** $^{13}C$ NMR spectra of (a) **2a** and (b) **3** (50 °C, in $CDCl_3$).

**Table 1. Preparation of the macromonomer**

| run | THF-Polymzn.[a] MeOTf (mmol) | Time (min) | Block Copolymerization[b] CL (mg) | Yield (mg) | CL-Conv. (%) | $\overline{M}_n$ (GPC) | $\overline{M}_n$ (NMR) | $\overline{M}_w/\overline{M}_n$[c] | CL : THF[d] | $f$[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.11 | 7.5 | 109 | 180 | 83 | 4100 | 4200 | 1.25 | 39 : 61 | 1.02 |
| 2 | 0.12 | 5 | 111 | 132 | 99 | 3400 | 2500 | 1.29 | 73 : 27 | 1.01 |
| 3 | 0.10 | 5 | 56 | 91 | 99 | 2800 | 1800 | 1.26 | 50 : 50 | 1.01 |
| 4 | 0.13 | 5 | 233 | 300 | 99 | 5000 | 6600 | 1.14 | 82 : 18 | 1.14 |

[a] Polymerization Conditions; THF (5 mL), rt. [b] Polymerization Conditions; 0°C, 4h. [c] Estimated by GPC (THF, PSt standards). [d] Determined by $^1$H NMR.

**Scheme 3**




3

4

*Copolymerization of the Macromonomer with MMA.* The copolymerization of **3** [-$M_n$ = 3800 ($^1$H NMR), 5500 (GPC), CL : THF = 47 : 53, $f$ = 1.04] with MMA was conducted in the presence of azo-2,2'-bis(isobutyronitrile) (AIBN) at 60 °C for 24 h (Scheme 3). $CHCl_3$ was employed as a solvent because of the high solubility of **3** as well as its low chain transfer constant.

GPC traces of **3** and the resulting polymer (**4**) are illustrated in Figure 3. The presence of a shoulder identified with **3** in the GPC curve of **4** indicates that the radical copolymerization provided the corresponding graft copolymer as the main constituent and several percents of the unpolymerized macromonomer. The formation of the copolymer was also confirmed in $^1$H NMR spectrum (Figure 4). The signals attributed to both **3** and poly(MMA) could be observed, while the ratio of integrated intensity of the olefin protons to terminal methyl protons decreased compared with that of **3**. Table 2 summarizes the results of the copolymerization varying the feed ratios of **3** to MMA. The conversion of **3** was calculated by comparing the integrated intensities of the olefin protons with that of the terminal methyl group. Relatively high conversions of both **3** and MMA were attainable in the range of the feed ratios as shown in Table 1. Although the contamination of a trace amount of **3** in the graft copolymers was observed, the unit ratio of MMA and **3** (x : y) was in relatively good agreement with the feed ratio of MMA and **3**.

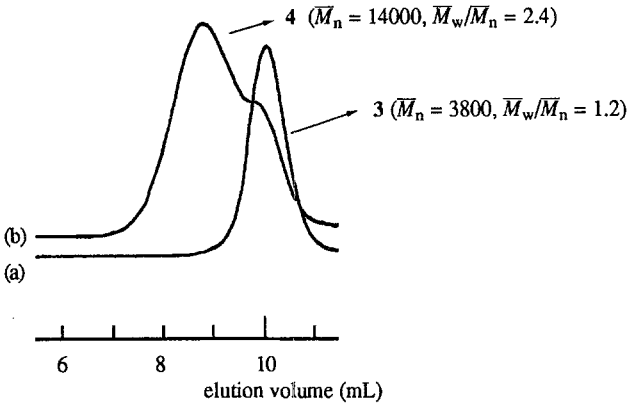



**Figure 3.** GPC profiles of (a) **3** and (b) **4**.

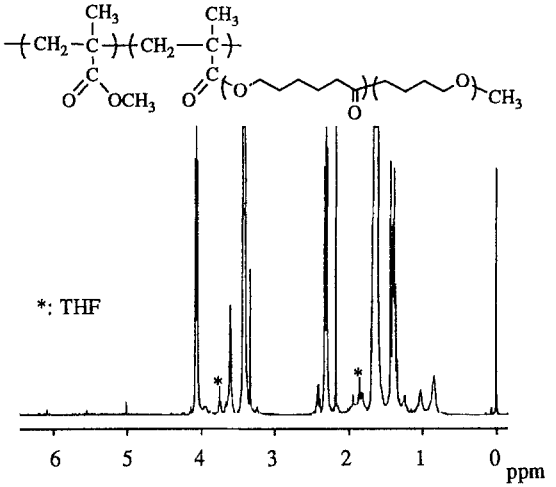



**Figure 4.** $^1$H NMR spectra of **4** (50 °C, in $CDCl_3$).

In summary, we have demonstrated the first example of the preparation of a novel diblock macromonomer consisted of different types of monomers in polymerization mechanisms. The diblock macromonomer, ω-methacryloylpoly(tetrahydrofuran-*b*-ε-caprolactone), with controlled structure and narrow molecular weight distribution could be obtained by the $SmI_2$-induced transformation. The copolymerization of the diblock macromonomer with MMA gave polymethacrylate backbone with poly(THF-*b*-CL) block copolymers as the side chains. This synthetic procedure would provide a new route in the field of polymer architecture.

## Experimental Section

*Materials.* A THF-solution of $SmI_2$ was prepared according to the reported manner [6]. THF was distilled prior to use from sodium benzophenone under nitrogen. CL and HMPA were distilled from $CaH_2$ under reduced pressure. Methyl trifluoromethanesulfonate and methacryloyl chloride were distilled from $P_2O_5$ under a nitrogen atmosphere. Pyridine was distilled from KOH under nitrogen.

**Table 2. Radical copolymerization of the macromonomer with MMA[a]**

| run | 3[b] (mmol) | MMA (mmol) | [MMA] / [3] | AIBN (mmol) | Conv. (%) 3[c] | Conv. (%) MMA | Yield (mg) | $\overline{M}_n$[d] | $\overline{M}_w/\overline{M}_n$[d] | x : y[c] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.077 | 0.43 | 5.6 | 0.041 | 91 | 81 | 326 | 14000 | 2.36 | 79 : 21 |
| 2 | 0.079 | 0.68 | 8.6 | 0.040 | 89 | 77 | 353 | 17000 | 2.28 | 90 : 10 |
| 3 | 0.040 | 1.49 | 37.3 | 0.074 | 96 | 93 | 289 | 9000 | 2.63 | 97 : 3 |
| 4 | 0.043 | 1.88 | 43.7 | 0.097 | 96 | 81 | 315 | 6300 | 2.81 | 97 : 3 |
| 5 | 0.040 | 2.50 | 62.5 | 0.087 | >98 | 83 | 361 | 7300 | 2.76 | 98 : 2 |

[a] In $CHCl_3$ (2mL), 60°C, 24h. [b] $\overline{M}_n$ = 3800 (NMR), 5500 (GPC). [c] Calculated by $^1H$ NMR.
[d] Estimated by GPC (THF, PSt standards).

*Measurements.* NMR spectra were recorded with JEOL JNM-EX-400 spectrometer. Molecular weights and their distribution ($\overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography on a Toyo Soda CCP&8000 (TSK gel G3000, THF) after calibration with standard polystyrenes.

*Synthesis of ω-methacryloylpoly(tetrahydrofuran-b-ε-caprolactone) macromonomers (3).* A typical procedure was as follows. Methyl trifluoromethanesulfonate (0.11 mmol) was added to dry THF (5 mL), and the solution was stirred at room temperature for 7.5 min. After charging HMPA (130 mL), a 0.1 M THF solution of $SmI_2$ (2.2 mL, 0.22 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 CL (109 mg, 0.77 mmol) at 0°C. After 4h at 0 °C, pyridine (ca. 40mL) and then methacryloyl chloride (0.15 mmol) were added to the reaction mixture at 0°C. The reaction mixture was kept with stirring at room temperature for 4 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 macromonomer. Further purification was carried out by the reprecipitation with hexane.

*Copolymerization of 3 with MMA.* **3** (301 mg, 0.079 mmol), MMA (68.4 mg, 0.684 mmol), and AIBN (6.6 mg, 0.040 mmol) in $CHCl_3$ (2 mL) solution were stirred overnight (24 h) at 60°C. $CHCl_3$ was distilled off and the polymeric product was reprecipitated in hexane. It was collected, washed with hexane and dried under reduced pressure (352.9 mg).

## References and Notes


1) Recent examples for preparation of diblock macromonomers: (a) K. Ishizu, S. Yukimasa, R. Saito, *J. Polym. Sci., Polym. Chem.*, **31**, 3073 (1993). (b) K. Ishizu, K. Kuwahara, *J. Polym. Sci., Polym. Chem.*, **31**, 661 (1993). (c) K. Ishizu, *Polym.-Plast. Technol. Eng.*, **32**, 511 (1993). (d) I. V. Berlinova, I. M. Panayotov, *Makromol. Chem.*, **190**, 1515 (1989). (e) M. Niwa, N. Higashi, *Macromolecules*, **21**, 1191 (1988). (f) K. Ishizu, K. Shimomura, R. Saito, T. Fukutomi, *J. Polym. Sci., Polym. Chem.*, **29**, 607 (1991).
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3) (a) R. Nomura, T. Endo, *Macromolecules*, **27**, 5523 (1994). (b) R. Nomura, M. Narita, T. Endo, *Macromolecules*, **27**, 4853 (1994). (c) R. Nomura, M. Narita, T. Endo, *Macromolecules*, **27**, 7011 (1994). (d) R. Nomura, M. Narita, T. Endo, *Macromolecules*, **28**, 86 (1995). (e) R. Nomura, T. Endo, *Macromolecules*, **28**, 1754 (1995).

4) The homopolymerization of CL took place in the case of employing excess of $SmI_2$ to the initiator, which resulted in the contamination of telechelic poly(CL) having two polymerizable groups at both polymer ends. The run 4 in Table 1 showed larger functionality than the theoretical value, which might be because of the presence of excess of $SmI_2$. Evans et al. have reported that $SmI_2$ itself could not initiate the polymerization of CL in THF at ambient temperature [5]. However, the $SmI_2$ was active for CL-polymerization in the presence of HMPA.

5) W. J. Evans, H. Katsumata, *Macromolecules*, **27**, 2330 (1994).

6) P. Girard, J. L. Namy, H. B. Kagan, *J. Am. Chem. Soc.*, **102**, 2693 (1980).