Notes

Synthesis of Star-Shaped Block Copolymer of Tetrahydrofuran and Methyl Methacrylate

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Introduction

Block and grafted copolymers are often applied as a compatibilizer in polymer blends.[1] Usually, block and grafted copolymers are composed of plural polymer segments which compatibilize the blend components. Not only the molecular weights and segment ratio but also molecular architectures influence their properties. Thus, synthesis of block and grafted copolymers with various architectures is of importance to control their characters.[2]

Recently we reported that samarium enolates obtained by reduction of 2-bromoisobutyric esters with SmI_2 work as useful initiators for the living polymerization of methyl methacrylate (MMA) (Scheme 1).[3] This polymerization system is readily applied to the transformation from cationic to anionic polymerization. Namely, the cationic growing center of the living poly(tetrahydrofuran) [poly(THF)] can be quantitatively transformed into a terminal samarium enolate by the end-capping of the living end with sodium 2-bromoisobutyrate followed by reduction with SmI_2. The sequential polymerization of MMA with the terminal samarium enolate gives block copolymers of THF and MMA with well-controlled structures. The most characteristic point of this polymerization system is that the initiation species for the polymerization of methacrylates, samarium enolate, is potentially preparable in situ from various compounds having 2-bromoisobutyrate units. Therefore, multifunctional initiators effective for the living polymerization of MMA might be readily obtained from the compounds having plural 2-bromoisobutyrate moieties.[4] In the present study, this unique feature was demonstrated by the synthesis of star-shaped block copolymers consisting of plural polymer segments with different polymerization mechanisms. That is, the propagation centers of a star-shaped living poly(THF) were transformed into samarium enolates which were employed as multifunctional initiators for MMA (Scheme 2).

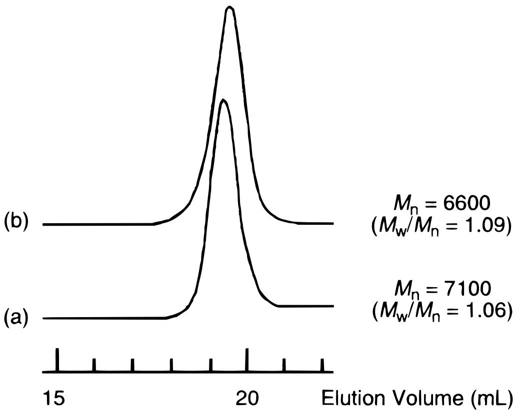

Figure 1. GPC profiles of **2b** (a) and **5b** (b).

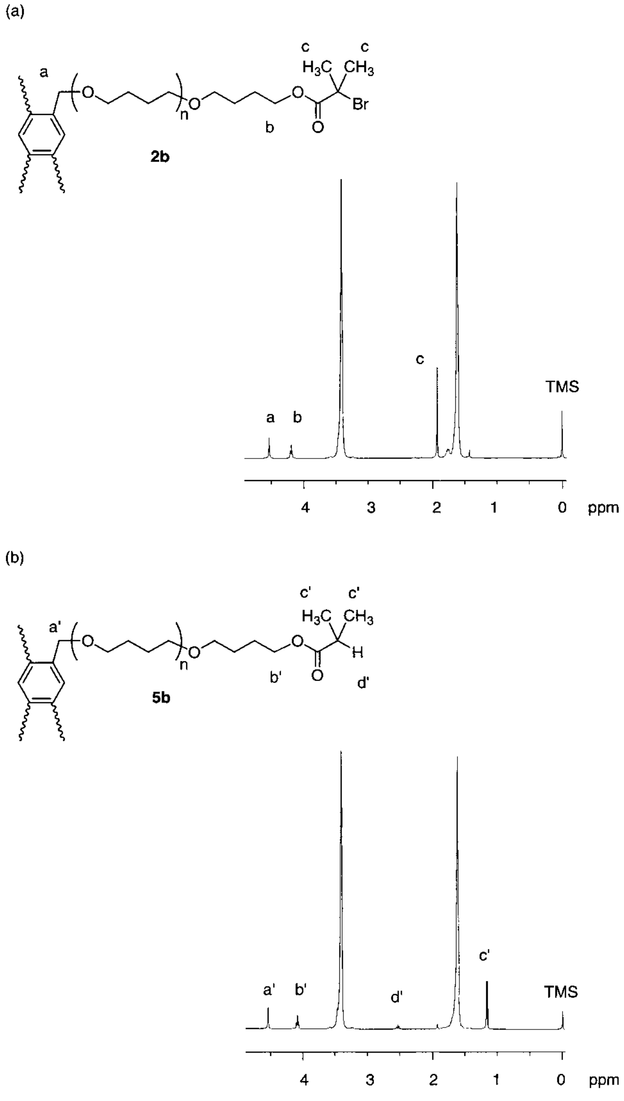

Figure 2. ^1H NMR spectra of **2b** (a) and **5b** (b) ($CDCl_3$, room temperature).

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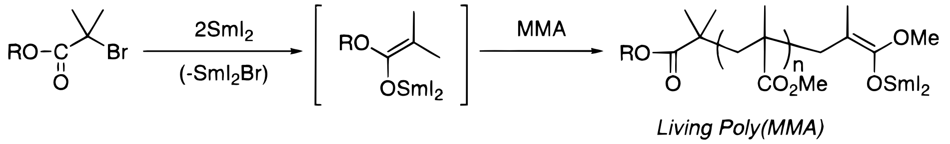
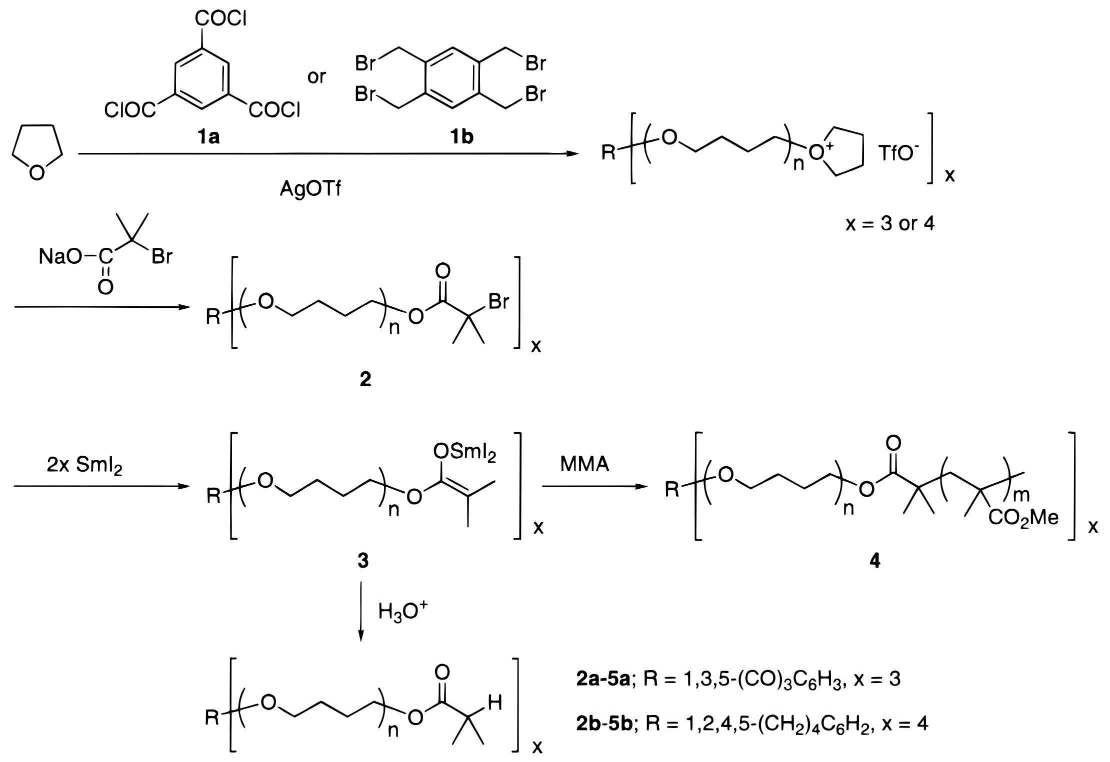
Scheme 1



Scheme 2



2

3

4

5

2a-**5a**; R = 1,3,5-(CO)$_3$C$_6$H$_3$, x = 3

2b-**5b**; R = 1,2,4,5-(CH$_2$)$_4$C$_6$H$_2$, x = 4

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL JNM-EX-400 spectrometer (400 and 100 MHz, respectively). Number-averaged molecular weights (M_n) and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography on a Tosoh HLC-8020 (TSK gel G2500HXL and G3000HXL tandem columns, THF as eluent) system after calibration with standard poly(styrene) samples.

Materials. THF was distilled prior to use from sodium/benzophenone ketyl under nitrogen. MMA was distilled over CaH$_2$ under reduced pressure. *N*,*N*-Diethylpivalamide (DEPA) was synthesized by the reaction of trimethylacetyl chloride with diethylamine and purified by distillation over CaH$_2$. A 0.1 M THF solution of SmI$_2$ was prepared according to the reported manner.[5] Sodium 2-bromoisobutyrate was prepared by the treatment of 2-bromoisobutyric acid with NaH in diethyl ether and washed with dry THF. 1,3,5-Benzenetricarbonyl trichloride (**1a**) and 1,2,4,5-tetrakis(bromomethyl)benzene (**1b**) were purified by distillation and recrystallization from chloroform, respectively. AgOTf was used as received. All other solvents were used without purification.

Synthesis of Star-Shaped Block Copolymers of THF and MMA. To a solution of AgOTf (60.6 mg, 0.24 mmol) in THF (5 mL) was added 1,2,4,5-tetrakis(bromomethyl)benzene (**1b**) (25.1 mg, 0.056 mmol) in THF (170 mg), and the resulting solution was stirred at room temperature for 5 min under a nitrogen atmosphere. After the addition of sodium 2-bromoisobutyrate (137 mg, 0.72 mmol), unreacted sodium 2-bromoisobutyrate was filtered off by using a glass filter (G4) under nitrogen. To the filtrate were added DEPA (306 mg, 1.95 mmol), MMA (693 mg, 6.92 mmol) and then a THF solution of SmI$_2$ (4.8 mL, 0.48 mmol) at −78 °C. After the reaction mixture was kept stirring at −78 °C for 12 h, an aqueous 3% HCl solution was added. THF was removed under reduced pressure and the product was dissolved into dichloromethane. The organic layer was washed with aqueous 3% HCl solution. After being dried over MgSO$_4$, the organic solution was filtered and concentrated to give a block copolymer. Further purification was carried out by the precipitation into hexane for several times. Yield: 721 mg. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.86, 1.03, 1.13 ($-\mathrm{CH_2C(C}\mathit{H}_3)-$, $-\mathrm{OCOC(C}\mathit{H}_3)_2-$), 1.62 ($-\mathrm{OCH_2C}\mathit{H}_2-$), 1.82 ($-\mathrm{C}\mathit{H}_2\mathrm{C}-$), 3.41 ($-\mathrm{OC}\mathit{H}_2\mathrm{CH_2}-$), 3.60 ($-\mathrm{CO_2C}\mathit{H}_3$), 4.08 ($-\mathrm{C}\mathit{H}_2\mathrm{OCO}-$), 4.54 ($\mathrm{C_6H_2C}\mathit{H}_2\mathrm{O}-$) 7.37 ($-\mathrm{C_6}\mathit{H}_2$) ppm.

Results and Discussion

On the basis of the previous reports on the synthesis of star-shaped poly(THF), a multifunctional initiator consisting of **1a**/AgOTf was employed for the polymerization of THF (Scheme 2).[6] By the addition of **1a** to the solution of AgOTf in THF, a three-armed poly(THF) was readily obtained whose molecular weight distribution was relatively narrow (M_w/M_n = 1.24), which is consistent with the previous results.[6] The end-capping of the three-armed living poly(THF) was carried out by adding sodium 2-bromoisobutyrate under nitrogen. A quantitative end-capping proceeded, which was confirmed by the ^{1}H NMR spectrum of the resulting polymer (**2a**). Reduction of the terminal C−Br bonds in **2a** with SmI$_2$ was performed in the presence of DEPA at −78 °C according to our previous report,[3] which, however, provided an insoluble precipitate. This is most probably caused by the nucleophilic attack of the terminal samarium enolates toward the ester groups at

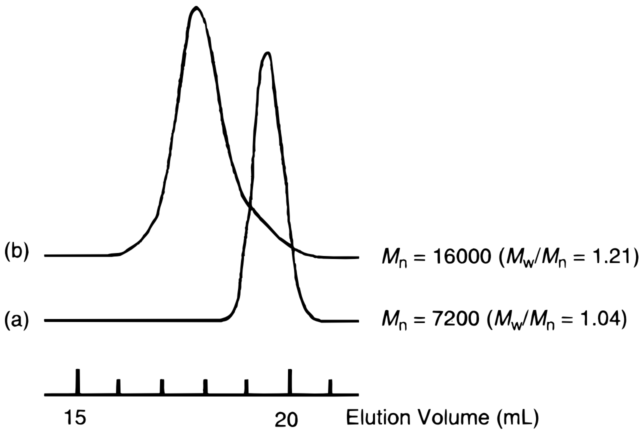
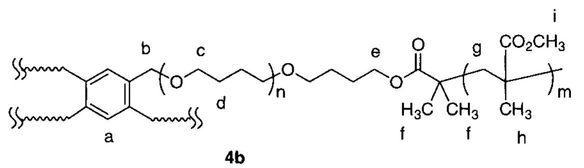


Figure 3. GPC profiles of **2b** (a) and **4b** (b).

the core of the star-shaped poly(THF), giving rise to a network structure. A substantial increase of the M_n of the soluble part obtained after reduction with SmI_2 may support this possibility (before the reduction; M_n = 10 400, after the reduction; M_n = 17 200).

To exclude this possibility for the cross-linking reaction, a multifunctional initiator consisting of **1b** and AgOTf, which is also reported to provide four-armed living poly(THF),[6c] was used for the present study because the resulting living poly(THF) does not contain electrophilic groups at its core. The propagating ends of the living poly(THF) starting from **1b**/AgOTf were likewise end-capped with an excess of sodium 2-bromoisobutyrate to give a four-armed poly(THF) having four 2-bromoisobutyrate ends (**2b**). Reduction of C−Br bonds in **2b** was also performed by the addition of DEPA and then SmI_2 at −78 °C to give a macroenolate (**3b**). GPC profiles of **2b** and **5b**, which was obtained by quenching **3b** with water, are shown in Figure 1. No significant difference in the GPC profile between **2b** and **5b** indicates that intermolecular cross-linking reaction does not take place during the transformation process. The quantitative conversion of the C−Br bonds to the samarium enolates was supported by the ^1H NMR analysis. As shown in Figure 2, the peak of the dimethyl protons in the 2-bromoisobutyrate moieties in **2b** (c, in Figure 2a) completely disappeared and the doublet signals at 1.2 ppm assignable to the isopropyl protons ([c′, in Figure 2b) and the septet signals of the methine proton (d′) in the end isobutyrate moieties were detected in the spectrum of **5b**. The integrated intensity ratio of the aromatic to the dimethyl protons was 2.0:23.8, which is very close to the theoretical value (2.0:24.0), supporting the theory that the transformation efficiency is quantitative.

Finally the synthesis of the star-shaped block copolymer of THF and MMA was examined. After the tetraenolate (**3b**) was generated from the living poly(THF) (**2b**), the unreacted excess sodium 2-bromoisobutyrate was removed by filtration under nitrogen, to which was added directly DEPA, MMA, and then a solution of SmI_2 in THF at −78 °C. As shown in Figure 3, the elution peak of the poly(THF)−prepolymer (**2b**) shifted toward a higher molecular weight region after the postpolymerization of MMA. Only a slight broadening of the molecular weight distribution was observed, which is indicative of a high block efficiency. The ^1H NMR spectrum of the resulting copolymer (**4b**) clearly showed peaks due to both poly(THF) (c,d) and poly(MMA) (g,h,i) segments (Figure 4). These results support the successful formation of a four-armed star-shaped block copolymer (**4b**).



4b

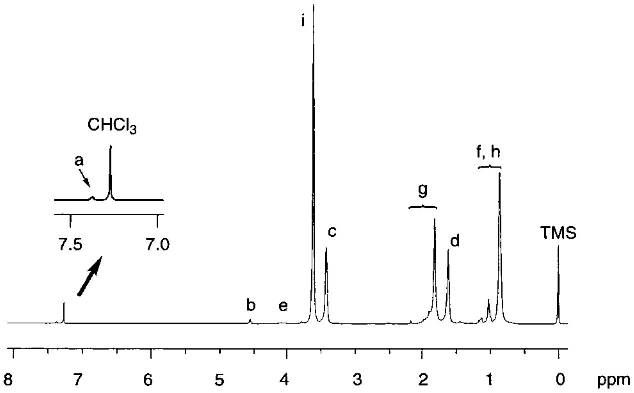


Figure 4. ^1H NMR spectrum of **4b** ($CDCl_3$, room temperature).

References and Notes

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