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Living polymerization of methyl methacrylate by novel samarium-based trifunctional initiator

Mamiko Narita[1], Ryoji Nomurat[2], Ikuyoshi Tomita[3], and Takeshi Endo[4*]**

[1] Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta,
Midori-ku, Yokohama 226-8503, Japan
[2] Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Kyoto 606-8501, Japan
[3] Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology,
Yokohama 226-8502, Japan

[*] Present address: Department of Polymer Science and Engineering, Faculty of Engineering,
Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

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Summary

A novel trifunctional samarium enolate, prepared in situ by the reduction of 1,3,5-tris(2-bromoisobutyroyloxymethyl)benzene with SmI_2, has proven to initiate the polymerization of methyl methacrylate (MMA). Characterization of the polymer by ^1H NMR and GPC clearly supported the formation of a star-shaped tri-armed poly(MMA). The resulting star-shaped poly(MMA) possessed narrow molecular weight distribution, and its molecular weight agreed well with the theoretical value, which reveals the quantitative initiation efficiency.

Introduction

Star-shaped polymers have attracted much interest due to their characteristics such as a lower viscosity of their solution as compared with that of the corresponding linear polymers having similar compositions (1). Recent development of the controlled polymerization technique has allowed to prepare star-shaped polymers with well-defined structures (number and length of arms). The preparative methods of star-shaped polymers can be divided into two categories. One is based on the reaction of the propagating end of linear polymers with appropriate terminators or crosslinking agents. The other is by the polymerization starting from multifunctional initiators. The advantage of the former method is the simplicity to form star-shaped polymers with a large number of arms. Nevertheless, the method is not suited for the synthesis of star-shaped polymers with a well-defined number of arms because the reaction with multifunctional terminators does not permit the quantitative modification or the number of arms is statistically determined in the case of crosslinking process. On the other hand, the method using multifunctional initiators is more promising to give star polymers with well-defined number of arms.

Although this advantage has stimulated the synthesis of many kinds of multifunctional initiators (2), it is unfortunate that the polymerization methods suitable for the multifunctional initiation are limited so far. That is, the well-defined synthesis of star polymers via the multifunctional initiation has been limited in the living cationic polymerization of vinyl ethers and in the recently developed controlled radical polymerization of (meth)acrylates. Especially, only few example has been reported for the multifunctional initiation with transition-metal catalysts. This is because of the difficulty to synthesize the multifunctional organometallic compounds as well as their unsatisfactory solubility and stability.

Recently, we have reported that a new organolanthanide initiator, samarium enolates, nicely induces the living polymerization of MMA (3). The samarium enolate

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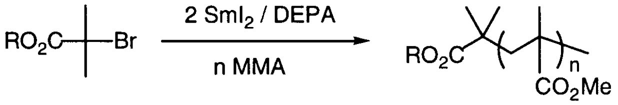
[**] Corresponding author

which is formed in situ by the reduction of 2-bromoisobutyric esters with samarium(II) iodide (SmI_2) can initiate the polymerization of MMA in quantitative initiation efficiency to give polymers with narrow molecular distributions (Scheme 1). The characteristic points of this method are that the initiation species are readily available without isolation and that the precursors for the initiator, 2-bromoisobutyrates, are stable and their structures are easily modified. Thus, appropriately designed multifunctional 2-bromoisobutyric esters will function as multifunctional initiators for the living polymerization of methacrylates to give star-shaped polymers (4). In this paper, we report the preparation of a novel lanthanide-based trifunctional initiator for MMA and its application to the synthesis of star-shaped poly(MMA).

Scheme 1



(DEPA = *N,N*-diethylpivalamide)

Experimental

Measurements. ^{1}H and ^{13}C-NMR spectra were recorded with a JEOL JNM-EX-400 spectrometer. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) on a Tosoh HLC-8020 (TSK gel G2500HXL and G3000HXL, THF as eluent) after calibration with standard poly(methyl methacrylate) samples. Purification by HPLC was carried out on a JAI LC-908 instrument.

Materials. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen prior to use. 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 0.1M THF solution of SmI_2 was prepared according to the reported manner (5). Trimethylolpropane was purchased and used after recrystallization from ethyl acetate. 1,3,5-Benzenetrimethanol was synthesized according to the previous report (6).

*Synthesis of 1,1,1-tris(2-bromoisobutyryloxymethyl)propane (**1a**).* To a solution of 2-bromoisobutyric acid (2.06 g, 12.3 mmol) in dichloromethane (20 mL) were added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl) (2.37 g, 12.4 mmol), a solution of trimethylolpropane (0.495 g, 3.69 mmol) in dichloromethane (20 mL), and 4-dimethylaminopyridine (0.151 g, 1.23 mmol) at 0°C. The resulting mixture was stirred for 2 days at room temperature. The reaction mixture was washed with 1M HCl, saturated aqueous solution of $NaHCO_3$ and then brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography. Yield 0.494 g (23 %). Further purification was carried out on HPLC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (C**H**$_3$CH$_2$-, t, *J*=7.6Hz, 3H), 1.64 (CH$_3$C**H**$_2$-, q, *J*=7.6Hz, 2H), 1.94 (-C(C**H**$_3$)$_2$Br, s, 18H), 4.19 (-C**H**$_2$OCO-, s, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 7.4, 23.0, 30.6, 41.9, 55.4, 64.7, 171.1. IR (neat) 3003, 2975, 2932, 2363, 1740, 1464, 1391, 1372, 1273, 1159, 1109, 1051, 1013, 990, 930, 858, 783, 760, 644 cm^{-1}.

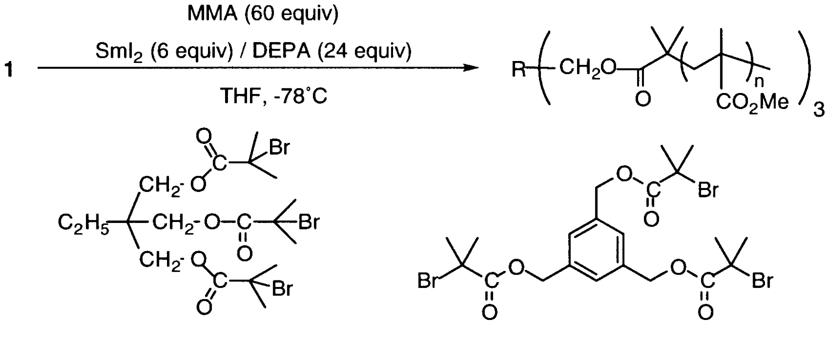
*Synthesis of 1,3,5-tri(2-bromoisobutyryloxymethyl)benzene (**1b**).* To a solution of 2-bromoisobutyric acid (5.00 g, 29.9 mmol) in dichloromethane (50 mL) were added EDC•HCl (5.67 g, 29.6 mmol), a solution of 1,3,5-benzenetrimethanol (1.34 g, 8.15 mmol) in dichloromethane (10 mL), and 4-dimethylaminopyridine (0.18 g, 1.48 mmol) at 0°C. The resulting mixture was stirred overnight at room temperature. The mixture was washed with 1M HCl, saturated aqueous solution of $NaHCO_3$ and then brine. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by column chromatography. Yield 3.79 g (77%). Further purification was carried out on HPLC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96 (-C(C**H**$_3$)$_2$Br, s, 18H), 5.23 (-C**H**$_2$OCO-, s, 6H), 7.37 (-C$_6$**H**$_3$-, s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 55.5, 66.9, 126.9, 136.4, 171.3. IR (neat) 3659, 3574, 3455, 3005, 2976, 2932, 1738, 1613, 1524, 1462, 1389, 1372, 1273, 1157, 1109, 1013, 914, 860, 820, 762, 733 cm^{-1}.

Synthesis of star-shaped poly(MMA). A typical procedure: A 0.1 M THF solution of SmI_2 (4.2 mL, 0.42 mmol) was added to a THF (2 mL) solution containing **1b** (40.1 mg, 0.0652 mmol) and DEPA (251 mg, 1.59 mmol) at -78°C. MMA (583 mg, 5.82 mmol) was added to the resulting suspension, and the reaction mixture was stirred at -78°C for 12h. After addition of an aqueous 3% HCl solution, the reaction mixture was extracted with dichloromethane, and the organic extract was washed several times with brine. The organic layer was dried over $MgSO_4$, filtered, concentrated, and precipitated several times into hexane to give poly(MMA).

Results and discussion

As a precursor of trifunctional samarium enolates, we designed and synthesized trifunctional 2-bromoisobutyric esters (**1a** and **1b**). The former (**1a**) possesses a flexible chain between the ester groups, while the latter (**1b**) has ester groups separated by a rigid benzene ring. The trifunctional esters (**1a** and **1b**) were readily accessible by the condensation between 2-bromoisobutyric acid and trimethylolpropane or 1,3,5-benzenetrimethanol using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl) as a condensation agent.

Scheme 2



1a **1b**

As we described previously, a quantitative initiation efficiency was attainable in the samarium enolate-catalyzed polymerization, when the reduction of 2-bromoisobutyric esters was carried out in the presence of monomer (3). Thus, we first examined the polymerization of MMA by reducing **1** with SmI_2 in the presence of MMA (Scheme 2). *N*,*N*-Diethylpivalamide (DEPA) was used as an additive because this additive promotes the living polymerization of MMA by the samarium enolates (3). However, the GPC traces of the resulting polymers displayed bimodal elution peaks irrespective of the initiators. This result might be taken to mean the presence of plural propagation species. Because MMA is not reduced by SmI_2 under the examined conditions (3), the polymerization initiated by the dianion though the reductive homocoupling of MMA is negligible. Although ethyl 2-bromoisobutyrate is reduced to ethyl isobutyrate quantitatively by SmI_2, the possibility of side reactions in the reduction process or the initial stage of the polymerization cannot be ruled out in the case of **1a** or **1b**. Accordingly reduction of **1** was performed with a slightly excess amount of SmI_2 at -78°C in the absence of MMA. The reduction of **1a** gave a complex mixture, indicating that the initiation step involves unfavorable side reactions such as the intramolecular reaction between the samarium enolate and a neighboring unreduced bromoisobutyrate moiety that leads to initiating species with lower number of active sites. On the other hand, **1b** was transformed into the corresponding simply reduced product [i.e., 1,3,5-tris(isobutyryloxymethyl)benzene] quantitatively. Although the side reaction does not take place at the reduction stage, the unsatisfactory initiation efficiency of **1b** might occur by the intrarmolecular reaction between the unreacted bromoisobutyrate moiety and the growing end of poly(MMA) having samarium enolate structures. To avoid this possibility, it is preferable to carry out the reaction in a two step in which reduction of **1b** and the polymerization of MMA were performed separately.

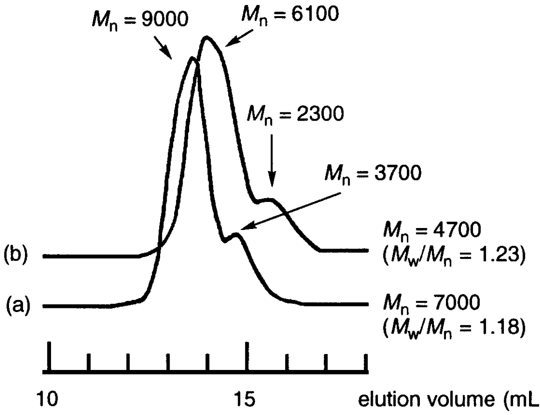
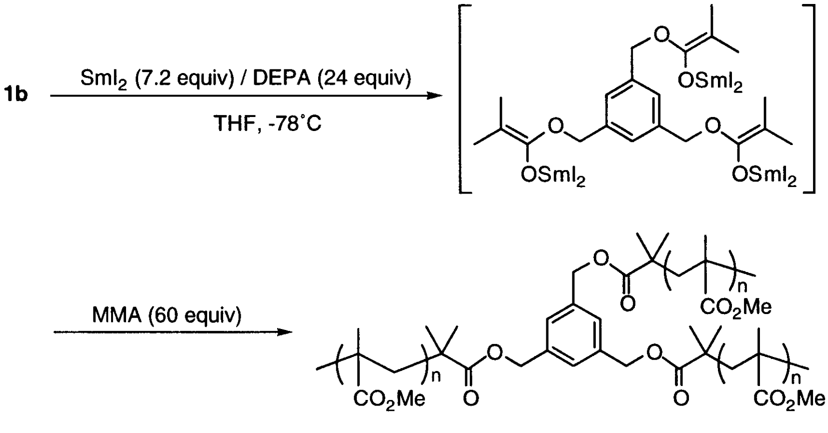


Figure 1. GPC profiles of the polymers produced by the route in Scheme 1. Polymers were prepared using (a) **1a** and (b) **1b**.

Accordingly we performed another method. Namely, after **1b** was completely transformed to the trifunctional samarium enolate with a slightly excess amount of SmI_2, MMA was then added to perform the polymerization (Scheme 3). The GPC traces of the polymer obtained by this modified method are illustrated in Figure 2. The resulting polymer revealed a unimodal elution peak and possessed a narrow molecular weight distribution. This polymer showed UV absorption at 254 nm, which means the presence of aromatic group. The observation of the peak due to the initiator at 7.4 ppm in the ^1H NMR spectrum of the polymer (Figure 3) also supports that the resulting polymer contains an aromatic core originated from the initiator. From these results, it can be concluded that the trifunctional samarium enolate formed in situ initiated the polymerization of MMA to give a tri-armed star-shaped polymer.

Figure 4 illustrates a plot of M_n versus the ratio of MMA to **1b**. As is clear from this figure, a good linear relationship exists between the molecular weight and the ratio of MMA to **1b**. In all runs, the molecular weight distributions were constantly narrow and the molecular weight agreed well with the theoretical value, although branched structures in polymers might cause underestimation of their molecular weight. This result clearly means the living nature of this polymerization system.

Scheme 3



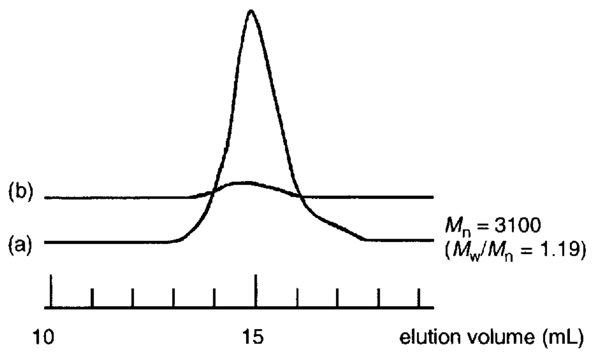


Figure 2. GPC profiles of the polymers prepared by the method in Scheme 2 using **1b**. GPC traces were detected by (a) RI and (b) UV detectors (254 nm).

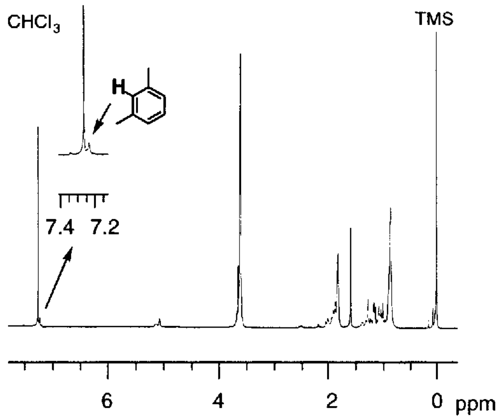


Figure 3. ^{1}H NMR spectrum of the polymer prepared by the route in Scheme 1 using **1b** (rt, in CDCl$_3$).

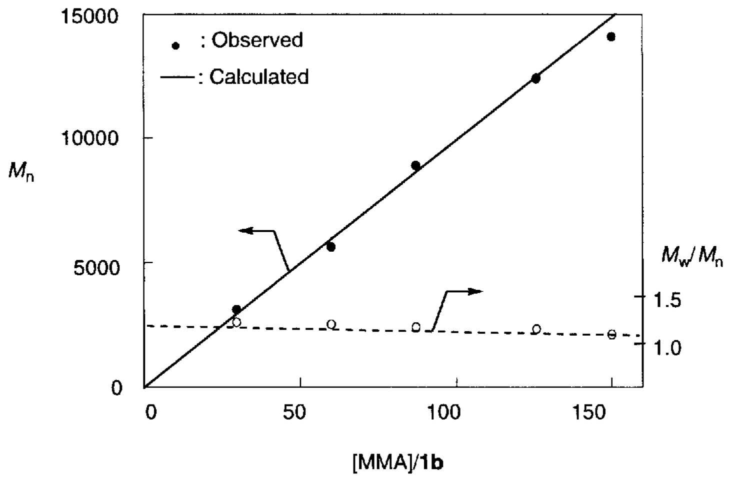


Figure 4. Plot of M_n and M_w/M_n versus the feed ratio of MMA to **1b**.

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