Living Polymerization of *tert*-Butyl 4-Vinylbenzoate by the SmI_2/SmI_3 System

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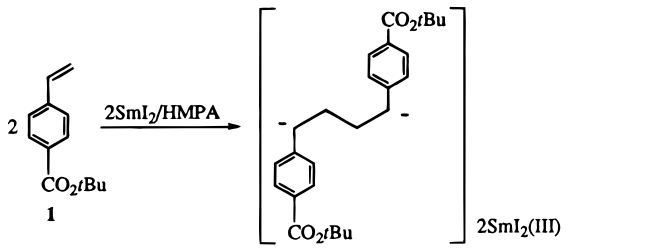
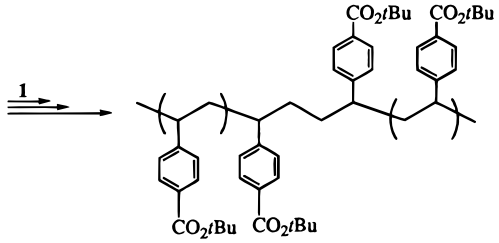
One of the recent remarkable strides in polymer synthesis represents the application of lanthanide complexes as initiators.[1] The most characteristic point of lanthanide-based catalysts involves their high ability to initiate and control the polymerization of a wide range of monomers. Unfortunately, the precise polymerization of styrene and its derivatives with lanthanide catalysts has not been achieved so far.[2] Here we report the preliminary results on the lanthanide-catalyzed polymerization of *tert*-butyl 4-vinylbenzoate (**1**),[3] a styrene derivative having an ester moiety at its *para* position (Scheme 1).[4] The first example for the living polymerization of a styrene derivative was accomplished by the use of divalent samarium(II) iodide (SmI_2) as an electron-transfer agent.[5]

The polymerization of **1** was conducted at −40 °C for 24 h by the addition of **1** into a THF solution of SmI_2 and HMPA, from which a complete conversion of **1** was not achieved and a polymer was obtained in 75% yield.[6] The molecular weight distribution of the obtained polymer was rather broad (1.36) under the conditions (Figure 1a). Many attempts to optimize the conditions (e.g., reaction temperature, reaction time, and the concentration of HMPA) with the motivation of providing living polymer failed. For example, reaction runs at various amounts of hexamethylphosphoramide (HMPA, 0−10 equiv with respect to SmI_2), which remarkably influence the polymerization behavior of alkyl methacrylates by SmI_2,[7] resulted in the formation of the polymers with rather broad molecular weight distributions (1.36−1.54) in moderate yields (60−86%). By these attempts, we could not exclude the possible side reactions such as termination by the attack of the propagation center with the pendant ester groups.

On the other hand, it should be noted that the addition of SmI_3 as a common cationic ion has proven to drastically enhance the living nature of the polymerization.[8] That is, the addition of SmI_3 led to the quantitative formation of the polymer with a quite narrow molecular weight distribution.[9] GPC measurements of the produced polymer gave a sharp contrast, which indicates a large difference in polymerization behavior between in the absence and presence of SmI_3 (Figure 1a,b, respectiviely). Figure 2 shows the molecular weight of the polymer obtained under the SmI_2/

Scheme 1





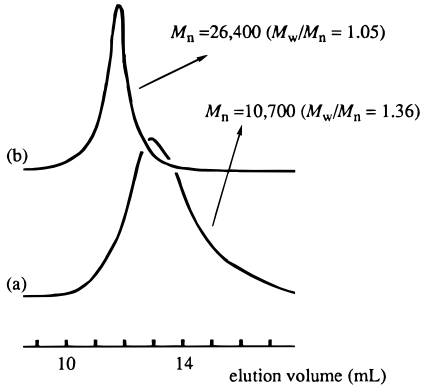


Figure 1. GPC chromatograms of poly(**1**) obtained by the reaction at −40 °C for 24 h ([**1**]/[SmI_2] = 7.5): (a) without SmI_3; (b) with SmI_3 ([SmI_2]/[SmI_3] = 9.0).

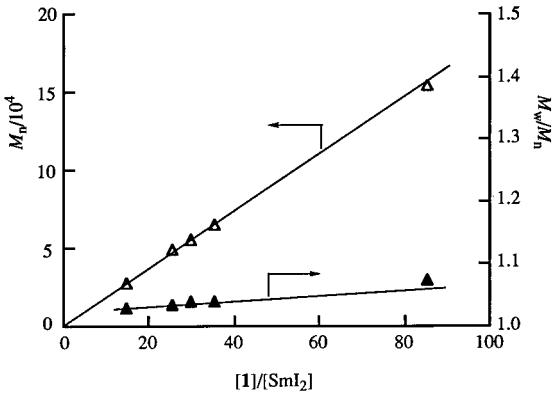


Figure 2. Plots of M_n versus the monomer/initiator ratio for the polymerization of **1** using 6.0 equiv of HMPA to SmI_2 at −40 °C. [SmI_2]/[SmI_3] = 9.0.

SmI_3/HMPA system at various feed ratios of **1** to SmI_2. A linear relationship between the molecular weight and the feed ratio was observed clearly, and the polydispersity was quite low in every case. In the postpolymerization experiments, the GPC signal of the prepolymer shifted toward the high molecular weight region after the fresh feed of the monomer, while maintaining its narrow molecular weight distribution (Figure 3). Thus the polymerization of **1** with the common salt (SmI_3)

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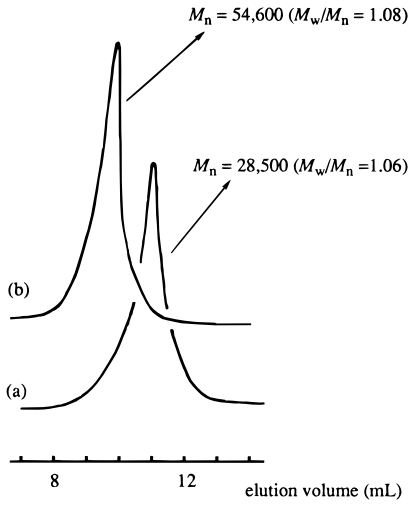
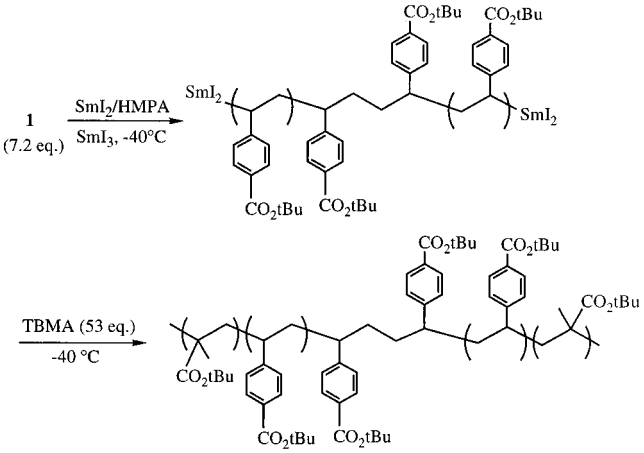


Figure 3. Monomer-addition experiments in the polymerization of **1**: (a) just after the first stage polymerization ($[\mathbf{1}]_0/[SmI_2] = 8.1$); (b) after the consumption of the second charge of **1** (7.0 equiv to SmI_2).

Scheme 2



proceeds in living fashion without termination or chain transfer reaction. These results may suggest that the addition of SmI_3 reduces the reactivity of the propagation centers, depressing the nucleophilic attack of the growing center on the carbonyl carbon. The reduced reactivity of the growing center also enabled the production of the polymer at high temperature; the polymerization of **1** without SmI_3 did not proceed at all at room temperature, whereas a high conversion of **1** (80%) was attainable in the presence of SmI_3.[10]

The ability of this system to induce living polymerization of **1** also provided the block copolymer with alkyl methacrylates (Scheme 2). For instance, after the addition of *tert*-butyl methacrylate (TBMA) into the solution of poly(**1**), the increase in the molecular weight of the prepolymer was recognized, as shown in Figure 4. A quantitative conversion of TBMA was obtained, and the produced polymer showed a quite narrow molecular weight distribution. The ^{1}H NMR spectrum of the resulting polymer clearly revealed the signals attributed to both poly(**1**) and poly(TBMA) segments. These results are indicative of the successful formation of the ABA-type triblock copolymer without the production of respective homopolymers.[7]

In summary, we have demonstrated the first example for the lanthanide-catalyzed living polymerization of a styrene derivative. The combination of SmI_2 with SmI_3

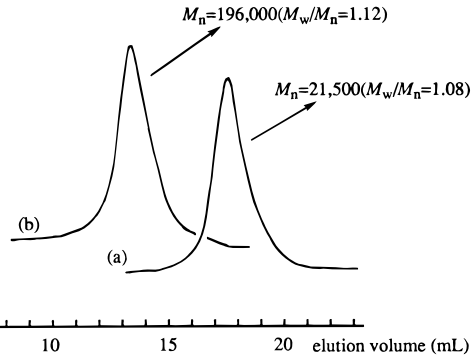


Figure 4. GPC chromatograms of (a) poly(**1**) ($[\mathbf{1}]_0/[SmI_2] = 7.2$) and (b) the block copolymer of **1** with TBMA (52.8 equiv to SmI_2).

has proven to be quite effective in inducing the living polymerization of *tert*-butyl 4-vinylbenzoate. Detailed investigation on the polymerization behavior as well as the availability of other styrene counterparts is now in progress.

References and Notes

(1) (a) Yasuda, H. *Catalysis in Precision Polymerization*; Kobayashi, S., Ed.; John Wiley & Sons: Chichester, England, 1997; Vol. 6, Chapter 4, p 189. (b) Yasuda, H.; Ihara, E. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1745−1767.

(2) For example, the lanthanide-modified Ziegler−Natta catalysts, i.e., the combination of lanthanide salts and group I−III organometallic compounds with or without a third component, are not capable of producing polystyrene with low polydispersity. See: (a) Kobayashi, E.; Kaita, S.; Aoshima, S.; Fukukawa, J. *J. Polym. Sci., Polym. Chem.* **1994**, *32*, 1195. (b) Yang, M.; Chan, C.; Shen, Z. *Polym. J.* **1990**, *22*, 919. Single component initiators such as $[(Me_3Si)_2N]_2Sm(THF)$, $[(Me_3Si)_2CH]_3Sm$, $La(C_5Me_5)[CH(SiMe_3)_2]_2(THF)$, and $[(t\text{-}BuCp)_2NdCH_3]_2$ also failed to achieve the living polymerization of styrene. See: (c) Hu, J.; Shen, Q. *Cuihua Xuebao* **1993**, *11*, 16. And also ref 1.

(3) The conventional living anionic polymerization of **1** was reported by Nakahama et al. See: (a) Nakahama, S.; Ishizone, T.; Hirao, A. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 223. (b) Ishizone, T.; Watabayashi, S.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2895.

(4) The initiation appears to involve one electron reduction of the monomer, giving an anion radical that probably dimerizes to form a dianion, as outlined in Scheme 1. Although the dimerized product could not be isolated in the present study, the reduction of amide-substituted styrene (*N*,*N*-diethyl-4-vinylbenzamide) with an excess of SmI_2 gave the corresponding dimerized product in 52% isolated yield. See ref 11.

(5) For recent examples for the use of divalent samarium complexes as polymerization catalysts, see: (a) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134. (b) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 4011. (c) Nakayama, Y.; Shibahara, T.; Fukumoti, H.; Nakamura, A.; Mashima, K. *Macromolecules* **1996**, *29*, 8014. (d) Nomura, R.; Narita, M.; Endo, T. *Macromolecules* **1996**, *29*, 3669. (e) Wang, J.; Nomura, R.; Endo, T. *Macromolecules* **1996**, *29*, 2707. (f) Boffa, L. S.; Novak, B. M. *Macromolecules* **1997**, *30*, 3494. (g) Boffa, L. S.; Novak, B. M. *Tetrahedron* **1997**, *53*, 15367.

(6) The procedure is as follows: into a 0.1 M THF solution of SmI_2 (2 mL, 0.2 mmol) and HMPA (0.2 mL, 1.2 mmol) was added **1** (1.49 mmol), and the solution was kept stirring at −40 °C for 24 h. After pouring into methanol, the precipitate was collected and dried in vacuo to give the polymer.

(7) Nomura, R.; Endo, T. *The Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 3, p 2016.

(8) Remarkable improvments of the living nature of (meth)acrylate polymerization by the addition of common cationic ions have been reported. For example: (a) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1990**, *23*, 2618. (b) Wang, J.-S.; Jérôme, R.; Warin,

R.; Teyssié, Ph. *Macromolecules* **1993**, *26*, 5984. (c) Wang, J.-S.; Warin, R.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1993**, *26*, 6776. (d) Varshney, S. K.; Gao, Z.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 1076. (e) Antoun, S.; Wang, J.-S.; Jérôme, R.; Teyssié, Ph. *Polymer* **1996**, *37*, 5755. Although the motivation to add SmI_3 originated from the above-mentioned reports, we are not sure, at present, the exact role of SmI_3 in this polymerization. Further investigation to clarify the mechanism is ongoing.

(9) A typical procedure is as follows: into a 0.1 M THF solution of SmI_2 (1.8 mL, 0.18 mmol), a 0.1 M THF solution of SmI_3 (0.2 mL, 0.02 mmol), and HMPA (0.18 mL, 1.08 mmol) was added **1** (1.31 mmol), and the solution was kept stirring at −40 °C for 24 h. After pouring into methanol, the precipitate was collected and dried in vacuo to give the polymer in 100% yield. ^{1}H NMR analysis indicated that the stereoregularity of the obtained polymer was atactic.

(10) The polymerization at room temperature without SmI_3 gave no polymer, and the monomer was recovered, although smooth oxidation of Sm(II) into Sm(III) was confirmed by the color change of the solution.

(11) Gosho, A.; Nomura, R.; Endo, T. *Jpn. J. Polym. Sci. Technol.* **1997**, *54*, 886.

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