Supporting Information

Syndiospecific, Living Copolymerization of Styrene with ε-Caprolactone by Scandium Catalysts

Li Pan, Kunyu Zhang, Masayoshi Nishiura and Zhaomin Hou*

General Procedures and Materials. All manipulations of air and moisture-sensitive compounds were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques or an Mbraun glovebox. Nitrogen (Takachiho Chemical Industrial Co., Ltd.) was purified by being passed through a Dryclean column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in a glovebox.

Styrene and ε-caprolactone (Junsei Chemical Co., Ltd.) were dried by stirring with CaH₂ for 48 hours, and distilled under reduced pressure prior to polymerization experiments. [Ph₃C][B(C₆F₅)₄] was purchased from Tosoh Finechem Corporation and used without purification. (C₅Me₄SiMe₃)Sc(CH₂SiMe₃)₂(THF) (1)¹² and (C₅Me₄(C₆H₄OMe-o))Sc(CH₂SiMe₃)₂ (2)² were synthesized according literatures. The deuterated solvent 1,1,2,2-tetrachloroethane-d₂ (99.6 atom% D) was obtained from Cambridge Isotope.

The ¹H and ¹³C NMR data of the polymers were obtained in 1,1,2,2-C₂D₂Cl₄ on a JNM-EX 300 (FT, 300 MHz for ¹H; 75 MHz for ¹³C) spectrometer at 25 °C and 100 °C, respectively. The DSC measurements were performed on a Perkin-Elmer Pyris Diamond Differential Scanning Calorimeter at a heating or cooling rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C, cooling at 20 °C/min to 0 °C, and then recording the second DSC scan. The molecular weight and molecular weight distribution (Mₘ/Mₙ) of the polymers were determined by gel permeation chromatography (GPC) with a refractive index (RI) detector against polystyrene standards, on TOSOH HLC-8220 GPC (Column: Super HZM-H×3) at 40 °C using THF as an eluent at a flow rate of 0.35 mL/min, or on TOSOH HLC-8221 GPC (column: TSK gel GHM-H × 2.30 x 7.8 mm φ ID) at 145 °C using o-dichlorobenzene (o-DCB) as a solvent at a flow rate of 1.0 mL/min.

A Typical Procedure for the Syndiospecific Polymerization of Styrene (run 3, Table 1). In a glove box, a toluene solution (4 mL) of [Ph₃C][B(C₆F₅)₄] (19 mg, 21 μmol) was added to a toluene solution (2 mL) of (C₅Me₄(C₆H₄OMe-o))Sc(CH₂SiMe₃)₂ (2) (9.4 mg, 21 μmol) in a 50-mL flask. After the mixture was stirred at room temperature for a few minutes, 0.21 g (2.1 mmol) of styrene was added under vigorous stirring. After ca. 1 min, methanol (2 mL) was added to terminate the polymerization. The mixture was poured into methanol (400 mL) to precipitate the polymer product. The white polymer powder was collected by filtration, and dried under vacuum at 60 °C to a constant weight (0.21 g, 100%).

A Typical Procedure for the Polymerization of ε-Caprolactone (run 8, Table 1). In a glove box, a toluene solution (4 mL) of [Ph₃C][B(C₆F₅)₄] (19 mg, 21 μmol) was added to a toluene solution (2 mL) of (C₅Me₄(C₆H₄OMe-o))Sc(CH₂SiMe₃)₂ (2) (9.4 mg, 21 μmol) in a 50-mL flask. After the mixture was stirred at
room temperature for a few minutes, 0.24 g (2.1 mmol) of ε-caprolactone was added under vigorous stirring. After ca. 5 min, methanol (2 mL) was added to terminate the polymerization. The mixture was poured into methanol (400 mL) to precipitate the polymer product. The white polymer powder was collected by filtration, and dried under vacuum at 60 °C to a constant weight (0.24 g, 100%).

A Typical Procedure for the Copolymerization of Styrene and ε-Caprolactone (run 4, Table 2). In a glove box, a toluene solution (4 mL) of [Ph3C][B(C6F5)4] (19 mg, 21 μmol) was added to a toluene solution (4 mL) of (C5Me4(C6H4OMe-ο))Sc(CH2SiMe3)2 (2) (9.4 mg, 21 μmol) in a 50-mL flask. The mixture was stirred at room temperature for a few minutes, and then 0.21 g (2.1 mmol) styrene was added under vigorous stirring. Five minutes later, 12 mL of toluene was added to the slurry reaction mixture followed by addition of 0.96 g (8.4 mmol) of ε-caprolactone. The mixture was then stirred for 30 minutes. The polymerization was terminated by addition of 10 mL of methanol, and the mixture was poured into methanol (400 mL) to precipitate the polymer product. The white polymer powder was collected by filtration, and dried under vacuum at 60 °C to a constant weight. To remove PCL homopolymer, the polymer powder was poured into 30 ml of acetone and stirred for 30 minutes. The polymer was collected by filtration and washed with acetone several times, and dried under vacuum at 60 °C to a constant weight.

Mechanical Property Study. The films (around 0.3 mm thick) for tensile test were prepared by casting from a o-DCB solution (3 wt%) of a sample. A polymer sample was first dissolved in o-DCB at 120 °C for 2 h and then casted at 70 °C in 24 h. The resulting film was dried under vacuum for one week at 60 °C to completely remove any residual solvent. Uniaxial tensile testing experiments were performed at room temperature on an Instron 3342 Tensile Instrument molded according to ASTM 882-09 at a crosshead speed of 20 mm/min, by using a film of about 0.3 mm thickness. At least three tensile measurements were performed for each sample.

Reference
Figure 1. GPC traces of the sPS synthesized by $\text{2/}[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (run 3 ($M_n = 20.0 \times 10^3$, $M_w/M_n = 1.26$) and 4 ($M_n = 41.3 \times 10^3$, $M_w/M_n = 1.36$) in Table 1) in THF at 40°C.

Figure 2. GPC traces of polycaprolactones synthesized by $\text{1/}[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (runs 6 ($M_n = 17.0 \times 10^3$, $M_w/M_n = 1.14$) and 7 ($M_n = 34.2 \times 10^3$, $M_w/M_n = 1.11$) in Table 1) in THF at 40°C.
**Figure 3.** GPC traces of polycaprolactones synthesized by 2/[Ph₃C][B(C₆F₅)₄] (runs 8 \(M_n = 12.5 \times 10^3, M_w/M_n = 1.21\)) and 9 \(M_n = 24.2 \times 10^3, M_w/M_n = 1.23\) in Table 1) in THF at 40°C.

**Figure 4.** GPC profiles of sequential styrene-CL block copolymerization by 2/[Ph₃C][B(C₆F₅)₄] (first step, sPS, \(M_n = 41.3 \times 10^3, M_w/M_n = 1.36\); second step, sPS-\textit{b}-PCL, \(M_n = 165.2 \times 10^3\); run 7 in Table 2) in THF at 40°C.
**Figure 5.** $^1$H NMR spectrum of PCL synthesized by 1/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (Run 6, Table 1).

**Figure 6.** $^{13}$CNMR spectrum of polystyrene synthesized by 1/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (Run 1, Table 1).
**Figure 7.** $^{13}$C NMR spectrum of polystyrene synthesized by $2/[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]$ (Run 3, Table 1).

**Figure 8.** $^1$H NMR spectrum of sPS-$b$-PCL diblock copolymer containing 22 mol % of sPS (Run 4 in Table 2).
Figure 9. $^1$H NMR spectrum of sPS-$b$-PCL diblock copolymer containing 33 mol % of sPS (Run 6 in Table 2).

Figure 10. $^{13}$C NMR spectrum of sPS-$b$-PCL diblock copolymer containing 48 mol% of sPS (Run 5 in Table 2).
**Figure 11.** DSC curve of sPS-b-PCL diblock copolymer containing 57 mol% of sPS (Run 2 in Table 2).

**Figure 12.** DSC curve of sPS-b-PCL diblock copolymer containing 48 mol% of sPS (Run 5 in Table 2).
**Figure 13.** DSC curve of sPS-\(b\)-PCL diblock copolymer containing 18 mol% of sPS (Run 7 in Table 2).

**Figure 14.** Engineering stress-strain curves of (a) sPS/PCL blend (run 6 in Table 3), (b) PCL (run 2 in Table 3), (c–e) sPS-\(b\)-PCL diblock copolymers (runs 3-5 in Table 3).