Supporting Information for the Manuscript Entitled

Isotactic-b-Syndiotactic Stereoblock Poly(methyl methacrylate) by Chiral Metallocene/Lewis Acid Hybrid Catalysts
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Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high vacuum line (10⁻⁶ to 10⁻⁷ Torr), or in an Argon-filled glove box (< 1.0 ppm O₂ and moisture). NMR-scale reactions were conducted in Teflon-valve-sealed sample J-Young tubes. Organic solvents were first saturated with nitrogen and then dried by passage through activated alumina and Q-5™ catalyst (Englehardt Chemicals Inc.) stainless steel columns prior to use. Benzene-d₆, toluene-d₈, and THF-d₈ were dried over sodium/potassium alloy and vacuum-distilled and/or filtered prior to use. CDCl₃ was dried over activated Davison 4 Å molecular sieves. Methyl methacrylate (MMA) monomer was degassed and dried over CaH₂ overnight, and then freshly vacuum-distilled before use. NMR spectra were recorded on either Varian Inova 300 (FT 300 MHz, ¹H; 75 MHz, ¹³C; 282 MHz, ¹⁹F) or Varian Inova 400 spectrometer. Chemical shifts for ¹H and ¹³C spectra were referenced to internal solvent resonances and reported as parts per million relative to tetramethylsilane. ¹⁹F NMR spectra were referenced to external CFCl₃.

Tris(pentafluorophenyl)borane B(C₆F₅)₃ was obtained as a research gift from Boulder Scientific Company and used without further purification for preparative reactions, or purified by recrystallization from hexanes at −35 °C for NMR-scale and polymerization reactions. Tris(pentafluorophenyl)alane (Al(C₆F₅)₃, as a toluene adduct) was prepared by exchange reaction between tris(pentafluorophenyl)borane and trimethylaluminum as disclosed by Biagini, et al. (Biagini, P.; Lugli, G.; Abis, L.; Andreussi, P. U.S. Pat. 5,602269, 1997). Extra caution should be exercised when handling this material due to its thermal and shock sensitivity).
Trimethylaluminum (neat), Cp₂ZrCl₂, and rac-Et(Ind)₂ZrCl₂ were purchased from Strem Chemical. Indene, MMA, n-BuLi in hexanes (1.6 M), MeMgBr (3.0 M) in diethyl ether, methyl isobutyrate, diisopropylamine, Me₅SiCl₂, and ZrCl₄, isobutyryl chloride were purchased from Aldrich Chemical Co.

rac-(SBI)ZrCl₂ and rac-(SBI)ZrMe₂ were prepared according to literature procedures (Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. Organometallics 1996, 15, 4038-4044; Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. Organometallics 1994, 13, 2235-2243). rac-(EBI)ZrMe₂ was prepared from reaction of the dichloride with two equiv of MeMgBr in diethyl ether at room temperature and purified by recrystallization from a mixture of toluene and hexanes at −35 °C. Preparation and characterization of rac-(SBI)ZrMe⁺MeM(C₆F₅)₃⁻ (M = B, Al) have been previously described in detail (Chen, E. Y.-X.; Kruper, W. J.; Roof, G.; Wilson, D. R. J. Am. Chem. Soc. 2001, 123, 745-746) and the analogous rac-(EBI)ZrMe⁺MeM(C₆F₅)₃⁻ was prepared in a similar manner.

Cp₂Zr(Me)Cl was prepared using a reported procedure (Wailes, P. C.; Weigold, H.; Bell, A. P. J. Organomet. Chem. 1971, 33, 181-189). Modified literature methods (Kim, Y.-J.; Bernstein, M. P.; Galiano Roth, A. S.; Romesberg, F. E.; Williard, P. G.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. J. Org. Chem. 1991, 56, 4435-4439) were used to prepare tert-butyl isobutyrate and the lithium enolate of this ester (tert-butyl lithioisobutyrate). Other alkyl isobutyrate esters and the corresponding lithium enolates were synthesized in a similar manner. A general procedure of Collins (Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. Macromolecules 1997, 30, 1875-1883) was followed to prepare methyl zirconocene alkylisobutyrate esters Cp₂Zr(Me)O(OR)C=CMe₂ (R = Me, Et, ’Pr, tert-Bu).

Cp₂Zr(Me)O(O’Pr)C=CMe₂. ¹H NMR (THF-d₈, 23 °C): δ 6.11 (s, 10H, Cp), 3.96 (sept, J = 6.3 Hz, 1H, -CH₂Me), 1.53 (s, 3H, =CMe₂), 1.45 (s, 3H, =CMe₂), 1.09 (d, J = 5.7 Hz, 6H, -CHMe₂), 0.16 (s, 3H, Zr-CH₃). ¹³C NMR (THF-d₈, 23 °C): δ 155.93 (O(O’Pr)C=), 112.41
(Cp), 83.53 (=CMe₂), 68.43 (-OCHMe₂), 23.18 (Zr-Me), 22.49 (OCHMe₂), 17.77 (=CMe₂), 17.37 (=CMe₂).

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\text{[Cp₂Zr(THF)O(O'Pr)C=CMe₂]⁺MeB(C₆F₅)₃⁻.}
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\^H NMR (THF-\textit{d₈}, 23 °C): \(\delta \) 6.72 (s, 10H, Cp), 4.06 (sept, \(J = 6.3 \text{ Hz} \), 1H, -CHMe₂), 1.65 (s, 3H, =CMe₂), 1.63 (s, 3H, =CMe₂), 1.24 (d, \(J = 6.0 \text{ Hz} \), 6H, -CH₂Me₂), 0.51 (s br, 3H, B-CH₃). \(^{19}\text{F} \) NMR (THF-\textit{d₈}, 23°C): \(\delta \) -129.62 (d, \(3J_{\text{F-F}} = 16.2 \text{ Hz} \), 6F, o-F), -163.77 (t, \(3J_{\text{F-F}} = 21.6 \text{ Hz} \), 3F, p-F), -165.88 (m, 6F, m-F).

For spectroscopic data of Al(C₆F₅)₃·THF, see Belgardt, T.; Storre, J.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. Inorg. Chem. 1995, 34, 3821-3822. We independently isolated the adduct Al(C₆F₅)₃·THF and found the chemical shifts are slightly different from the reported values. \(^{1}\text{H} \) NMR (C₆D₆, 23°C): \(\delta \) 3.43 (m, 4H), 1.05 (m, 4H). \(^{19}\text{F} \) NMR (C₆D₆, 23°C): \(\delta \) -123.13 (d, 6F, o-F), -151.23 (t, 3F, p-F), -160.81 (tt, 6F, m-F). \(^{19}\text{F} \) NMR (THF-\textit{d₈}, 23°C): \(\delta \) -119.84 (d, 6F, o-F), -151.14 (t, 3F, p-F), -159.71 (tt, 6F, m-F).

**Polymerization Procedures and Polymer Characterizations.** MMA polymerizations were performed in 50 mL Schlenk tubes with an external temperature-controlled bath on a high vacuum line or a Schlenk line or in an Argon-filled glove box. For MMA homopolymerizations, the procedures have been previously described (Bolig, A. D.; Chen, E. Y.-X. J. Am. Chem. Soc. 2001, 123, 7943-7944). In a typical stereoblock polymerization procedure, \(\text{rac-(SBI)ZrMe}^+\) MeB(C₆F₅)₃⁻ (23.35 \(\mu\text{mol}\)), isolated or generated in situ by mixing 1:1 molar ratio of \(\text{rac-(SBI)ZrMe}_2\) and B(C₆F₅)₃ in toluene for 10 min at room temperature, was loaded into the tube in the glove box and toluene was added (10 mL total volume). The tube was removed out of the box and attached onto the high vacuum line. After the external bath temperature was stabilized to 23 °C, MMA (0.50 mL, 4.67 mmol) was quickly injected through the septum via gas-tight syringe. The solution mixture gradually turned to be more viscous and color changed from orange yellow to orange red. After stirring for 45 min, a solution of \(\text{rac-(SBI)ZrMe}^+\text{MeAl(C₆F₅)}_3^\; (23.35 \(\mu\text{mol}\)),}
isolated or generated in situ by mixing 1:1 molar ratio of rac-(SBI)ZrMe₂ and Al(C₆F₅)₃ in 2 mL toluene in the glove box, was injected via gas-tight syringe. The mixture was stirred at this temperature for additional 10 min during which time the color changed to yellow. This clear yellow solution was then cooled down to –78 °C and the second portion of MMA (0.50 mL, 4.67 mmol) mixed with Al(C₆F₅)₃ (0.093 mmol) was quickly injected via gas-tight syringe. The reaction mixture was stirred for additional 1 h and quenched by adding 2 mL of acidified methanol. The polymer product was precipitated into 50 mL methanol, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight.

Glass transition temperatures of the polymers were measured by differential scanning calorimetry on a DSC 2920, TA Instruments, or a Mettler Toledo Star² System at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) analyses of polymer samples were carried out at 40 °C using THF as eluent on a Waters 150CV instrument or on a Polymer Laboratory-210 instrument at a flow rate of 1.0 mL/min. Number-average molecular weights and polydispersities of PMMA were given relative to monodispersed PMMA or polystyrene standards. ¹H and ¹³C spectra for the analysis of PMMA microstructures were recorded in CDCl₃ and analyzed according to the literature (Bovey, F. A.; Mirau, P. A. NMR of Polymers; Academic Press: San Diego, 1996).