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Syndiotactic Polymerization of Styrene and Copolymerization with Ethylene Catalyzed by Chiral Half-sandwich Rare-earth Metal Dialkyl Complexes

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E Electronic Supplementary Information

Abstract The syndiotactic polymerization of styrene (St) and the copolymerization of St with ethylene (E) were carried out by using a series of chiral half-sandwich rare-earth metal dialkyl complexes (Cp^{x*}) as the catalysts. The complexes are $\mathrm{Ln(CH_2SiMe_3)_2(THF)}$ (**1**–**4**: Ln = Sc (**1**), Ln = Lu (**2**), Ln = Y (**3**), Ln = Dy (**4**)) bearing chiral cyclopentadienyl ligand containing bulky cylcohexane derivatives in the presence of activator and $\mathrm{Al}^{i}\mathrm{Bu}_3$. For the St polymerization, a high activity up to 3.1×10^6 g of polymer $\mathrm{mol_{Ln}^{-1}\cdot h^{-1}}$ and a high syndiotactic selectivity more than 99% were achieved. The resulting syndiotactic polystyrenes (*s*PSs) have the molecular weights (M_n) ranging from 3700 $\mathrm{g\cdot mol^{-1}}$ to 6400 $\mathrm{g\cdot mol^{-1}}$ and the molecular weight distributions ($M_\mathrm{w}/M_\mathrm{n}$) from 1.40 to 5.03. As for the copolymerization of St and E, the activity was up to 2.4×10^6 g of copolymer $\mathrm{mol_{Sc}^{-1}\cdot h^{-1}\cdot MPa^{-1}}$, giving random St-E copolymers containing syndiotactic polystyrene sequences with different St content in the range of 15 mol%–58 mol%. These results demonstrate that the bulky cyclopentadienyl ligands of the chiral half-sandwich rare-earth metal complexes effectively inhibit the continued insertion of St monomers into the (co)polymer chain to some extent in comparison with the known half-sandwich rare-earth metal complexes.

Keywords Half-sandwich; Rare-earth metal complex; Syndiotacti cpolymerization; Copolymerization; Styrene; Ethylene

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INTRODUCTION

The exploitation of highly efficient and regio-/stereoselective homogeneous organometallic catalysts is a perennial subject of interest in the coordinative-insertive polymerization of olefins, which helps to realize effective preparation of high-performance polymers with controlled structures and desired properties[1]. Nowadays, syndiotactic polystyrene (*s*PS) has drawn considerable attention not only in basic scientific research but also in industrial applications due to its intrinsic properties, such as high melting temperature (*ca.* 270 °C), high modulus of elasticity, fast crystallization rate, good resistance to heat and chemicals, and low dielectric constant[2–4]. Since Ishihara and co-workers firstly reported the preparation of *s*PS *via* the polymerization of styrene (St) by using the half-sandwich titanium complex ($\mathrm{Cp^{*}TiCl_3}$) in combination with MAO to achieve high activity up to 3.6×10^6 g of polymer $\mathrm{mol_{Ti}^{-1}\cdot h^{-1}}$[5, 6], a lot of titanium complexes have been intensively investigated to afford *s*PSs with high content of racemic pentads[7–22]. Recently, the rare-earth metal complexes have entered people's vision, which usually exhibit extremely high activity and high syndiotactic selectivity in the polymerization of St similar to the known titanium complexes[23, 24]. In 2004, the Carpentier's group and Hou's group independently reported the highly syndiospecific polymerization of St catalyzed by the metallocenelanthanideallyl complexes $\mathrm{(Cp\text{-}CMe_2\text{-}Flu)Ln(C_3H_5)(THF)}$ (Ln = Y, La, Nd and Sm) alone[25] or the half-sandwich scandium dialkyl complex $\mathrm{(C_5Me_4SiMe_3)\text{-}Sc(CH_2SiMe_3)_2(THF)}$ in the presence of activator $\mathrm{[Ph_3C][B(C_6F_5)_4]}$[26]. Especially, the latter cationic catalytic system exhibited extremely high activity up to 1.4×10^7 g of polymer $\mathrm{mol_{Sc}^{-1}\cdot h^{-1}}$ at room temperature, affording the *s*PSs with high molecular weights and narrow molecular weight distributions ($M_\mathrm{n} = 9 \times 10^4$ $\mathrm{g\cdot mol^{-1}}$ to 3.8×10^5 g/mol, $M_\mathrm{w}/M_\mathrm{n}$ = 1.29–1.55). Inspired by these fantastic works, numerous attempts have been made to develop new rare-earth metal complexes for highly syndiospecific polymerization of St. For example, Okuda and co-workers found that the half-sandwich scandium dialkyl complex $\mathrm{[C_5Me_4SiMe_2(C_6F_5)]\text{-}Sc(CH_2SiMe_3)_2(THF)}$ was active for the syndiospecific polymerization of St under the activation of $\mathrm{[Ph_3C][B(C_6F_5)_4]}$

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with moderate activities[27, 28]. In 2007, several kinds of half-sandwich rare earth metal bis(aminobenzyl) complexes bearing η^5-phospholyl-, η^5-pyrrolyl-, or η^5-1,2-azaborolyl-ligand(Cp*)Sc(CH_2C_5-H_4NMe_2-*o*)$_2$ were reported by Hou and co-workers. These complexes showed high activity up to 3.1 × 10^6 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ and high syndiospecific selectivity up to 100% for the polymerization of St in the presence of $[Ph_3C][B(C_6F_5)_4]$[29–31]. In 2009, Chen's group described that the high syndiospecific polymerization of St was catalyzed by using a half-sandwich scandium complex bearing indenyl ligand $(Ind)Sc(CH_2SiMe_3)_2(THF)$ activated by $[Ph_3C][B(C_6F_5)_4]$ with an extremely high activity of *ca.* 1.21 × 10^7 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$[32]. At the same time, Visseaux and co-workers demonstrated that half-sandwich scandium borohydrido complex $(Cp^*)Sc(BH_4)_2(THF)$ promoted the high syndiospecific polymerization of St with moderate activity (2.0 × 10^5 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$) and high syndioselectivity (> 99.9%) in combination with $[Ph_3C][B(C_6F_5)_4]$ and Al^iBu_3[33]. In 2011, Luo and coworkers represented that a series of half-sandwich rare-earth metal bis(amide) complexes $(Cp^*)Sc(N(SiMe_3)_2)_2(THF)$ showed high activity up to 3.12 × 10^6 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ and high syndiotacticity (*rrrr* > 99%) in the polymerization of St[34, 35]. In 2012, a series of CGC rare-earth metal complexes $(Flu$-CH_2-$Py)Sc(CH_2SiMe_3)_2(THF)$ were reported by Cui and coworkers, which could serve as the high efficient and syndiotactic catalyst precursors for the polymerization of St with an extremely high activity up to 1.6 × 10^7 g of polymer $mol_{Ln}^{-1}\cdot h^{-1}$ and high syndiotactic selectivity (*rrrr* > 99%)[36, 37]. In 2013, we also discovered the syndiotactic polymerization of St catalyzed by a series of fluorenyl-ligated scandium dialkyl complexes $(Flu)Sc(CH_2SiMe_3)_2(THF)$ in combination with borate and AlR_3 (activity up to 3.4 × 10^7 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$, syndiotactic selectivity (*rrrr*) > 99%)[38].

In comparison with the known titanium complexes, the advantage of these half-sandwich rare-earth metal complexes is that they can promote the copolymerization of St with ethylene (E), affording the random St-E copolymers containing syndiotactic polystyrene sequences[24, 39]. Such St-E copolymer can overcome *s*PS's drawbacks such as brittleness and poor processing performance due to its high melting temperature, and broaden its industrial applications[40]. Despite these rare-earth metal complexes are available for the syndiotactic polymerization of St, only a few rare-earth metal complexes are active for the copolymerization of St with E until now[41, 42]. In 2004, Hou firstly reported the random copolymerization of St and E by using the half-sandwich rare-earth metal complex $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(THF)$ under the activation of $[Ph_3C][B(C_6F_5)_4]$, affording the St-E copolymers containing syndiotactic polystyrene sequences with St content in the range of 13 mol%–87 mol%[26]. In 2013, we also described the random copolymerization of St and E by using the fluorenyl-ligated half-sandwich scandium complexes to give the St-E copolymers containing syndiotactic polystyrene sequences with the St content ranging from 17 mol% to 80 mol%[38]. Nevertheless, almost all of these known half-sandwich rare-earth metal complexes contain an achiral cyclopentadienyl derivative. Up to date, the synthesis of rare-earth metal complexes bearing chiral cyclopentadienyl ligands and the application of them in coordinative-insertive polymerization of olefins have rarely been described[43]. In this work, we report the syndiotactic polymerization of St and the copolymerization of St with E by using a series of chiral half-sandwich rare-earth metal complexes bearing a chiral cyclopentadienyl ligand under the activation of borate and Al^iBu_3. The obtained *s*PSs show low molecular weight, and the random St-E copolymers have the St content ranging from 15 mol% to 58 mol%.

EXPERIMENTAL

Materials

All manipulations of air and moisture-sensitive compounds were performed under a dry nitrogen atmosphere by using Schlenk techniques or in an Mbraun glove box filled with nitrogen. Nitrogen and ethylene (purchased from Beijing AP Beifen Gases Industrial Co., Ltd.) were purified by passing through a dry clean column (4Å molecular sieves, Dalian Replete Science And Technology Co., Ltd.) and a gas clean column (Dalian Replete Science And Technology Co., Ltd.). The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glove box atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure that both of them were always below 0.0001‰. The Cp^{x*}-H ligand and the chiral half-sandwich rare-earth metal complexes **1–4** were prepared according to the procedures reported in the literatures[43–48]. Anhydrous THF, hexane and toluene were purified by a solvent purification system (SPS-800, Mbraun), and dried over fresh Na chips in the glove box. St was purchased from Sigma-Aldrich, dried over CaH_2 and degassed by two freeze-pump-thaw cycles. $[Ph_3C][B(C_6F_5)_4]$, $[PhMe_2NH][B(C_6F_5)_4]$, and $B(C_6F_5)_3$ were purchased from Tosoh Fine chem Corporation and used without purification. $LnCl_3$ (Ln = Sc, Lu, Y, Dy) was purchased from Strem. $LiCH_2SiMe_3$ (1.0 $mol\cdot L^{-1}$ solution in hexane) and Al^iBu_3 (1.1 $mol\cdot L^{-1}$ solution in hexane) were purchased from Aldrich and used as received. $Ln(CH_2SiMe_3)_3(THF)_2$ was synthesized according to the procedures reported in literature[49]. The deuterated solvents benzene-d_6 (D-enrichment ≥ 99.6%), chloroform-d_1 (D-enrichment ≥ 99.8%) and 1,1,2,2,-tetrachloro-ethane-d_2 (D-enrichment ≥ 99.6%) were obtained from Cambridge Isotope.

Measurements

Samples of half-sandwich metal complexes for nuclear magnetic resonance (NMR) spectroscopic measurements were prepared in the glove box using J. Young valve NMR tubes. The ^1H- and ^{13}C-NMR spectra of catalyst precursors were recorded on an AVANCE 400 spectrometer at room temperature with C_6D_6 as the solvent. The ^1H- and ^{13}C-NMR spectra of polystyrene and copolymer samples were recorded on an AVANCE 400 spectrometer in 1,1,2,2-$C_2D_2Cl_4$ at 120 °C. Elemental analyses were performed on an Elementary Vario MICRO CUBE (Germany). The molecular

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weights and the molecular weight distributions of polystyrenes were determined at 140 °C by gel permeation chromatography (GPC) on a HLC-8320 apparatus. 1,2,4-Trichloro-benzene was used as an eluent at a flow rate of 0.35 $mL\cdot min^{-1}$. The molecular weights and the molecular weight distributions of copolymers were determined at 145 °C by GPC on a PL-GPC 220/HT apparatus (Tosoh Corp.), and *o*-dichlorobenzene was used as an eluent at a flow rate of 1.0 $mL\cdot min^{-1}$. All of the calibrations were made by polystyrene standard EasiCal PS-1 (PL Ltd). Any thermal history difference in the polymers was eliminated by first heating the specimen to 350 °C, cooling to −50 °C at a rate of 10 $K\cdot min^{-1}$, and then recording the second differential scanning calorimetry (DSC) scan.

A Typical Procedure for Synthesis of Chiral Half-sandwich Rare-earth Metal Complexes

$Cp^{x*}Sc(CH_2SiMe_3)_2(THF)$ (1)

To a solution of Cp^{x*}-H ligand (100 mg, 0.45 mmol) in toluene was added $Sc(CH_2SiMe_3)_3(THF)_2$ (205 mg, 0.45 mmol). Then the solution was stirred for 12 h at room temperature. The resulting solution was evaporated in vacuo to give a residue. The residue was recrystallized from a mixed solvent of toluene and hexane at −30 °C to give cubic crystal (179 mg, yield: 78%). ^1H-NMR (C_6D_6, 400 MHz, δ, ppm): −0.35 (s, 1H, $C\underline{H}_2Si(CH_3)_3$), −0.14 (s, 3H, $C\underline{H}_2Si(CH_3)_3$), 0.28 (s, 18H, $CH_2Si(C\underline{H}_3)_3$), 1.11 (br, 4H, THF-$\beta$-$C\underline{H}_2$), 1.38 (m, 3H, $C\underline{H}_3$), 1.48 (m, 6H, $C\underline{H}_3$), 1.53 (s, 3H, $C\underline{H}_3$), 3.38 (m, 1H, $C\underline{H}(CH_3)$), 3.51 (t, J = 6.8 Hz, 4H, THF-α-$C\underline{H}_2$) 3.65 (m, 1H, $C\underline{H}(CH_3)$), 4.15 (m, 1H, $C\underline{H}O$—), 4.66 (m, 1H, $C\underline{H}O$—), 5.82 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$), 6.04 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$), 6.18 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$); ^{13}C-NMR (C_6D_6, 100 MHz, δ, ppm): 4.05, 16.28, 17.13, 24.83, 27.45, 27.47, 32.78, 33.21, 72.21, 75.13, 75.45, 108.57, 110.03, 110.33, 112.66, 129.16, 130.58. Elemental Anal. Calcd. for $C_{26}H_{48}O_3ScSi_2$: C, 61.26; H, 9.49. Found: C, 61.20; H, 9.46.

$Cp^{x*}Lu(CH_2SiMe_3)_2(THF)$ (2)

Cp^{x*}-H ligand (100 mg, 0.45 mmol) and $Lu(CH_2SiMe_3)_3(THF)_2$ (261 mg, 0.45 mmol) were used in the preparation of **2** (190 mg, yield: 66%). ^1H-NMR (C_6D_6, 400 MHz, δ, ppm): −0.82 (d, J = 11.6 Hz, 2H, $C\underline{H}_2Si(CH_3)_3$), −0.70 (d, J = 11.6 Hz, 2H, $C\underline{H}_2Si(CH_3)_3$), 0.30 (s, 18H, $CH_2Si(C\underline{H}_3)_3$), 1.08 (t, J = 6.0 Hz, 4H, THF-β-$C\underline{H}_2$), 1.39 (d, J = 6.8 Hz, 3H, $C\underline{H}_3$), 1.45 (d, J = 7.2 Hz, 3H, $C\underline{H}_3$), 1.48 (s, 3H, $C\underline{H}_3$), 1.54 (s, 3H, $C\underline{H}_3$), 3.40 (br, 4H, THF-α-$C\underline{H}_2$), 3.41 (m, 1H, $C\underline{H}(CH_3)$), 3.63 (m, 1H, $C\underline{H}(CH_3)$), 4.16 (dd, J = 6.4, 10.4 Hz, 1H, $C\underline{H}O$—), 4.65 (dd, J = 6.4, 10.4 Hz, $C\underline{H}O$—), 5.82 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$), 6.05 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$), 6.09 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$); ^{13}C-NMR (C_6D_6, 100 MHz, δ, ppm): 4.51, 16.75, 17.38, 24.86, 27.43, 27.49, 32.50, 33.10, 39.76, 71.42, 75.26, 75.38, 107.52, 108.26, 109.96, 111.98, 128.50, 128.58. Elemental Anal. Calcd. for $C_{26}H_{48}LuO_3Si_2$: C, 48.81; H, 7.56. Found: C, 48.92; H, 7.52.

$Cp^{x*}Y(CH_2SiMe_3)_2(THF)$ (3)

Cp^{x*}-H ligand (100 mg, 0.45 mmol) and $Y(CH_2SiMe_3)_3(THF)_2$ (223 mg, 0.45 mmol) were used in the preparation of **3** (187 mg, yield: 75%). ^1H-NMR (C_6D_6, 400 MHz, δ, ppm): −0.64 (dd, J = 2.8, 11.2 Hz, 2H, $C\underline{H}_2Si(CH_3)_3$), −0.51 (dd, J = 2.8, 11.2 Hz, 2H, $C\underline{H}_2Si(CH_3)_3$), 0.29 (s, 18H, $CH_2Si(C\underline{H}_3)_3$), 1.23 (br, 4H, THF-$\beta$-$C\underline{H}_2$), 1.37 (d, J = 7.2 Hz, 3H, $C\underline{H}_3$), 1.44 (d, J = 7.2 Hz, 3H, $C\underline{H}_3$), 1.47 (s, 3H, $C\underline{H}_3$), 1.53 (s, 3H, $C\underline{H}_3$), 3.38 (m, 1H, $C\underline{H}(CH_3)$), 3.43 (br, 4H, THF-α-$C\underline{H}_2$), 3.61 (m, 1H, $C\underline{H}(CH_3)$), 4.16 (dd, J = 6.4, 10.0 Hz, 1H, $C\underline{H}O$—), 4.62 (dd, J = 6.4, 10.0 Hz, 1H, $C\underline{H}O$—), 5.89 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$), 6.09 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$), 6.13 (t, J = 2.8 Hz, 1H, $Cp\underline{H}$); ^{13}C-NMR (C_6D_6, 100 MHz, δ, ppm): 4.7, 5.3, 17.3, 25.4, 27.7, 27.8, 27.9, 33.0, 33.3, 75.8, 75.9, 107.2, 108.5, 109.6, 110.3, 113.0, 130.8. Elemental Anal. Calcd. for $C_{26}H_{48}YO_3Si_2$: C, 56.40; H, 8.74. Found: C, 56.62; H, 8.77.

$Cp^{x*}Dy(CH_2SiMe_3)_2(THF)$ (4)

Cp^{x*}-H ligand (100 mg, 0.45 mmol) and $Dy(CH_2SiMe_3)_3(THF)_2$ (255 mg, 0.45 mmol) were used in the preparation of **4** (198 mg, yield: 70%). No NMR spectrum was recorded because of the paramagnetism of dysprosium. Elemental Anal. Calcd. for $C_{26}H_{48}DyO_3Si_2$: C, 49.78; H, 7.71. Found: C, 49.76; H, 7.69.

A Typical Procedure for St Polymerization by Using Chiral Half-sandwich Rare-earth Metal Complexes/ Activator/Al^iBu_3 Systems (Table 2, Entry 9)

In the glove box, into a round-bottom flask containing toluene (10 mL) was added Al^iBu_3 (95 μL, 1.1 $mol\cdot L^{-1}$ in toluene) with well-stirring, then St (0.6 mL, 5.2 mmol), the chiral half-sandwich rare-earth metal complex $Cp^{x*}Sc(CH_2SiMe_3)_2(THF)$ (5.4 mg, 10.5 μmol), and $[Ph_3C][B(C_6F_5)_4]$ (9.7 mg, 10.5 μmol) were added subsequently at room temperature. A large amount of polystyrene solid was precipitated out after 10 min. The reaction mixture was stirred for 30 min. Then the flask was taken out of the glove box, quenched with methanol (150 mL containing 5% butylhydroxytoluene (BHT)), and filtered. The precipitate was dried under vacuum at 30 °C overnight to a constant weight (410 mg, yield: 75%). The resulting polymer is soluble in 1,1,2,2-tetrachloroethane at 120 °C.

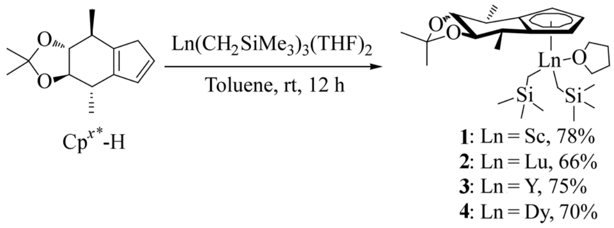
A Typical Procedure for the Copolymerization of Styrene with Ethylene by Using Chiral Half-sandwich Scandium Complex 1/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 System (Table 3, Entry 2)

In the glove box, into a two-necked flask containing toluene (10 mL) was added Al^iBu_3 (48 μL, 1.1 $mol\cdot L^{-1}$ in toluene), then St (0.6 mL, 5.2 mmol) was added with well stirring. The flask was taken out of the glove box, put into a water bath (25 °C), and connected to a well-purged Schlenk E line and a mercury-sealed stopper by a three-way cock. Ethylene (0.1 MPa) was introduced into the mixed solvents and was saturated in the solution by stirring for 5 min. Then a toluene solution (5 mL) of chiral half-sandwich scandium complex $Cp^{x*}Sc(CH_2SiMe_3)_2(THF)$ (5.4 mg, 10.5 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (9.7 mg, 10.5 μmol) was added through a syringe under vigorous stirring. The polymerization was quenched after 15 min by the addition of methanol (200 mL, containing 5% BHT). The resulting mixture was collected by filtration. The precipitates were washed with methanol, and then dried in vacuum at 40 °C to a constant weight (184 mg, 7.0×10^5 g of copolymer $mol_{Sc}^{-1}\cdot h^{-1}\cdot MPa^{-1}$). The resulting copolymer is soluble in 1,1,2,2-tetrachloroethane at 120 °C.

RESULTS AND DISCUSSION

Synthesis and Characterization of Chiral Half-sandwich Rare-earth Metal Dialkyl Complexes 1–4

More recently, we reported the synthesis and structural characterization of a series of chiral half-sandwich rare-earth metal dialkyl complexes, including $(Cp^{x*})Ln(CH_2SiMe_3)_2(THF)$ (**1**–**4**: Ln = Sc (**1**), Ln = Lu (**2**), Ln = Y (**3**), Ln = Dy (**4**)) bearing chiral cyclopentadienyl ligand containing bulky cylcohexane derivatives (Cp^{x*}-H = (3aR, 8aR)-2,2,4,4,8,8-hexamethyl-4,5,8,8a-tetrahydro-3aH-indeno-[5,6-d]-[1,3]dioxole)[43]. Such chiral complexes in combination with activator and $Al^{i}Bu_3$ could serve as the first highly regio-/stereoselective catalysts for the polymerization of ocimene. The obtained polyocimenes had different microstructures such as syndiotactic *cis*-1,4-polyocimene (for Sc complex **1**, *cis*-1,4-selectivity up to 100%, *rrrr* = 100%) and isotactic *trans*-1,2-polyocimenes (for Lu-Dy complexes **2**–**4**, *trans*-1,2-selectivity up to 100%, *mm* = 100%) depending on the central metal of these complexes. The excellent catalytic performances in the polymerization of ocimene inspired us to explore their application in the coordinative-insertive polymerization of other olefins. The chiral cyclopentadienyl ligand Cp^{x*}-H was synthesized according to the procedures described in the literatures[43–48]. The acid-base reactions between the rare-earth metal trialkyl complexes $Ln(CH_2SiMe_3)_3(THF)_2$ and 1 equiv. of Cp^{x*}-H directly afforded the corresponding chiral mono (cyclopentadienyl) rare-earth metal dialkyl complexes $Cp^{x*}Ln(CH_2SiMe_3)_2(THF)$ (**1**–**4**: Ln = Sc (**1**), 78%; Ln = Lu (**2**), 66%; Ln = Y (**3**), 75%; Ln = Dy (**4**), 70%) (Scheme 1).



Scheme 1 Synthesis of chiral half-sandwich rare-earth metal dialkyl complexes

Complexes **1**–**4** have good solubility in common solvents such as hexane, benzene, toluene, and tetrahydrofuran (THF), and give well resolved NMR spectra in standard solvents without the ligand redistribution (see electronic supplementary information, ESI). The single crystal of Lu complex **2** was obtained from hexane/toluene mixed solution at −30 °C. The ORTEP drawing of complex **2** is shown in Fig. 1. Its selected bond lengths and angles are summarized in Table 1. Similar to the Sc and Y complexes **1** and **3** reported by our group before, the Lu complex **2** also contained one cyclopentadienyl ligand, two trimethylsilylmethyl ligands, and one THF molecule. Among the bond distances of five carbon atoms C(1)–C(5) to the metal center, the bond distance of Lu—C(3) is apparently shorter than the bond distances of Lu—C(1) and Lu—C(5), and the bond distances of Lu—C(2) and Lu—C(4) are in the middle of them. In contrast, the bond distances of Ln—Cp_{cent} decrease in the order of Lu—Cp_{cent} (2.353 Å) > Y—Cp_{cent} (1.995 Å) > Sc—Cp_{cent} (1.851 Å). The bond distances of Ln—C(15), Ln—C(19) and Ln—O(3) bonds decrease in the order of Y—C(15) (2.372(4) Å) > Lu—C(15) (2.362(10) Å) > Sc—C(15) (2.253(3) Å), Y—C(19) (2.390(4) Å) > Lu—C(19) (2.337(10) Å) > Sc—C(19) (2.225(3) Å), and Y—O(3) (2.305(3) Å) > Lu—O(3) (2.253(8) Å) > Sc—O(3) (2.177(2) Å), respectively.

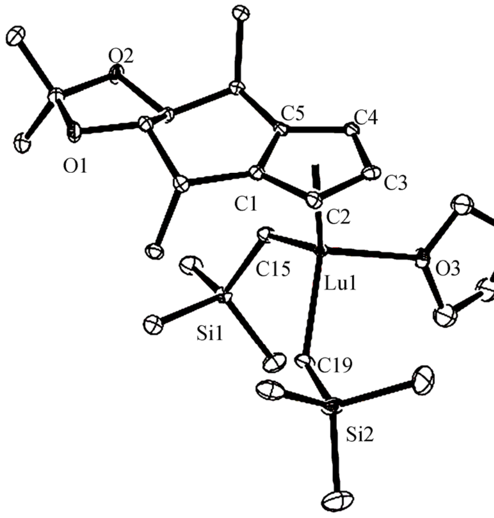


Fig. 1 ORTEP drawing of complex **2** with 30% thermal ellipsoids (The hydrogen atoms are omitted for clarity.)

Table 1 Selected bond distances (Å) and angles (°) of complex **2**

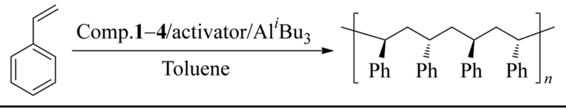
Lu—Cp_{cent}	2.353
Lu—C(1)	2.671(10)
Lu—C(2)	2.630(12)
Lu—C(3)	2.606(12)
Lu—C(4)	2.620(10)
Lu—C(5)	2.677(10)
Lu—C(15)	2.362(10)
Lu—C(19)	2.337(10)
Lu—O(3)	2.253(8)
O(3)—Lu—C(15)	96.3(4)
O(3)—Lu—C(19)	98.7(4)
C(15)—Lu—C(19)	106.0(3)

Homopolymerization of St

The chiral half-sandwich rare earth metal complexes **1**–**4** alone were inert for the St polymerization. In the presence of activator ($[Ph_3C][B(C_6F_5)_4]$ (**A**), $[PhMe_2NH][B(C_6F_5)_4]$ (**B**), and $B(C_6F_5)_3$ (**C**)) and $Al^{i}Bu_3$, these complexes could serve as high efficient and high syndiotactic selective catalysts for the polymerization of St under mild conditions, indicating that the cationic active species were essential for the St polymerization. Some representative results are summarized in Table 2.

The metal center of these complexes significantly affected the polymerization activity. Similar to the known half-sandwich rare-earth metal complexes, activated by borate **B** and $Al^{i}Bu_3$, Sc complex **1** exhibited the highest activity (*ca.* 6.9 × 10^4 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$) for the

Table 2 Syndiospecific polymerization of styrene by the chiral half-sandwich rare-earth metal complexes **1**–**4**/activator/Al^iBu_3 catalytic systems [a]



Entry	Comp.	A. [b]	[Al]/[Ln]	[St]/[Ln]	t (min)	T (°C)	Yield (%)	Act. [c]	Syndio. Sel. [d] (*rrrr*) (%)	M_n [e] × 10^{-3}	M_w/M_n [e]	T_m [f] (°C)
1	**1**	**B**	10	500	30	25	67	69	> 99	5.3	1.40	266
2	**1**	**B**	10	500	120	25	90	26	> 99	3.7	1.50	270
3	**2**	**B**	10	500	90	25	0.8	0.3	–	–	–	268
4	**3**	**B**	10	500	90	25	2	0.7	–	–	–	266
5	**4**	**B**	5	500	720	25	19	0.8	> 99	–	–	267
6	**1**	**C**	10	500	300	25	trace	–	–	–	–	–
7	**1**	**A**	10	500	2	25	55	857	> 99	5.7	2.51	265
8	**1**	**A**	10	500	4	25	61	477	> 99	5.2	1.83	266
9	**1**	**A**	10	500	30	25	75	78	> 99	5.9	4.88	269
10	**1**	**A**	5	500	3	25	100	1041	> 99	4.8	3.52	266
11	**1**	**A**	2	500	3	25	84	874	> 99	6.1	5.03	267
12	**1**	**A**	–	500	240	25	3	0.4	> 99	–	–	267
13	**1**	**A**	5	500	160	–10	29	5.7	> 99	6.4	1.49	272
14	**1**	**A**	5	500	8	50	13	51	> 99	4.4	1.59	260
15	**1**	**A**	5	1500	3	25	100	3126	> 99	5.6	5.74	259
16	**1**	**A**	5	2000	3	25	50	2038	> 99	–	–	265
17	**1**	**A**	5	3000	3	25	31	323	> 99	5.3	1.78	266

[a] Conditions: 10.5 μmol of Ln, 10.5 μmol of activator, 10 mL of toluene; [b] Activator: **A** = $[Ph_3C][B(C_6F_5)_4]$, **B** = $[PhMe_2NH][B(C_6F_5)_4]$, **C** = $B(C_6F_5)_3$; [c] Activity, kg of polymer $mol_{Ln}^{-1}\cdot h^{-1}$; [d] Determined by ^{13}C-NMR spectra; [e] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C; [f] Measured by DSC

syndiospecific polymerization of St when 500 equivalent of St was used (Table 2, entry 1). However, for the Lu complex **2**, the Y complex **3**, and the Dy complex **4**, they showed much low activities (*ca.* (3.0–8.0) × 10^2 g of polymer $mol_{Ln}^{-1}\cdot h^{-1}$) under the similar conditions (Table 2, entries 3–5). The activator also had an obvious effect on the polymerization of St. Upon activation with activator **A** and Al^iBu_3, the complex **1** exhibited higher activity up to 8.6 × 10^5 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ for the polymerization of St (Table 2, entries 1 and 7). When borane **C** was used as an activator, only trace amount of polystyrene was obtained even during a long polymerization time (5 h) (Table 2, entry 6). When the reaction time was prolonged from 2 min to 30 min, the yield slightly increased from 55% to 75%. However, the catalytic activities dramatically decreased from 8.6 × 10^5 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ to 7.8 × 10^4 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ (Table 2, entries 7–9), affording the polystyrene with high content of racemic pentads (*rrrr* > 99%) and low molecular weights (M_n = 5200–5900 g·mol^{-1}). The amount of Al^iBu_3 also played an important role on the polymerization activity of the complex **1** in the St polymerization (Table 2, entries 9–12). In the absence of Al^iBu_3, the scandium complex **1**/$[Ph_3C][B(C_6F_5)_4]$ binary system showed very low activity with the value of *ca.* 4.0 × 10^2 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ (Table 2, entry 12). When 2 equiv. of Al^iBu_3 was added, the catalytic activity dramatically increased to 8.7 × 10^5 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ for the complex **1**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 catalytic system (Table 2, entry 11). A much higher activity *ca.* 1.0 × 10^6 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ was obtained when 5 equiv. of Al^iBu_3 was used, in which 500 equiv. of St was completely consumed within 3 min to give syndiotactic polystyrene (*s*PS) (Table 2, entry 10). Further increasing the amount of Al^iBu_3, the activity decreased to (4.8–8.6) × 10^5 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$ (Table 2, entries 7 and 8). The influence of polymerization temperature on the polymerization activity was also explored. When the polymerization of St was conducted at −10 °C, the complex **1**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 system showed low activity (5.7 × 10^3 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$), affording the *s*PS with slightly higher molecular weight and narrower molecular weight distribution (M_n = 6400 g·mol^{-1}, M_w/M_n = 1.49) (Table 2, entry 13). When the reaction temperature rose up to 50 °C, the catalytic activity of the complex **1**/Al^iBu_3/$[Ph_3C][B(C_6F_5)_4]$ system dramatically increased to 5.1 × 10^4 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$, and the molecular weight of resulting *s*PS decreased to 4400 g·mol^{-1} (Table 1, entry 14). The highest activity (*ca.* 3.1 × 10^6 g of polymer $mol_{Sc}^{-1}\cdot h^{-1}$) was obtained for the complex **1**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 system when 1500 equiv. of St was used in the polymerization (Table 2, entry 15).

Solvent fractionation experiment demonstrated that either atactic polystyrene or isotactic polystyrene could be produced. The microstructures of resulting polystyrenes were highly syndiotactic with the racemic pentad configuration *rrrr* more than 99%, as evidenced in ^{13}C-NMR spectra with the signals at 145.5 (ipso-C), 44.5 ($S_{\alpha\alpha}$), and 41.2 ppm ($T_{\beta\beta}$) (see ESI). The high melt point values around 270 °C measured by DSC also confirmed the formation of *s*PSs. GPC profiles indicated that the *s*PSs obtained by the chiral half-sandwich rare-earth metal complexes **1**–**4**/activator/Al^iBu_3 ternary catalytic systems possessed low molecular weights (M_n = 3700–6400 g·mol^{-1}), which were much lower than those obtained

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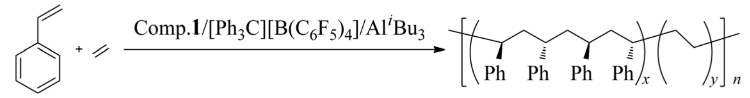
by the known half-sandwich rare-earth metal complexes. The unimodal GPC curves (M_w/M_n = 1.40−5.03) also implied the generation of the single-site cationic active species by these catalytic systems in the St polymerization.

Copolymerization of Styrene with Ethylene

The chiral half-sandwich Sc complex **1**/[Ph_3C][$B(C_6F_5)_4$]/Al^iBu_3 ternary catalytic system was also active for the copolymerization of St with E under 0.1 MPa E pressure in toluene at 25 °C, affording the random St-E copolymers containing syndiotactic polystyrene sequences with different St contents in the range of 15 mol%−58 mol%. Representative results are displayed in Table 3.

Before the copolymerization, the homopolymerization of E was also carried out by using the complex **1**/[Ph_3C][$B(C_6F_5)_4$]/Al^iBu_3 catalytic system under atmospheric E pressure in toluene at 25 °C (Table 3, entry 1). A moderate activity *ca.* 8.5 × 10^5 g of copolymer $mol_{Sc}^{-1}\cdot h^{-1}\cdot MPa^{-1}$ was obtained, and the resulting polyethylene had moderate molecular weight and bimodal molecular weight distribution (M_n = 2.8 × 10^4 g·mol^{-1}, M_w/M_n = 21.22). In the copolymerization of St with E under the same conditions, as the [St]/[complex **1**] molar ratio increased from 500 to 2000, the catalytic activity gradually increased from 7.0 × 10^5 to 2.35 × 10^6 g of copolymer $mol_{Sc}^{-1}\cdot h^{-1}\cdot MPa^{-1}$ (Table 3, entries 2−5). For the resulting St-E copolymers, the molecular weights gradually decreased from 1.2 × 10^4 g·mol^{-1} to 1000 g·mol^{-1}, and the molecular weight distributions decreased from 40.99 to 1.52. However, the St content of

Table 3 Copolymerization of styrene with ethylene by $Cp^{x*}Sc(CH_2SiMe_3)_2(THF)$/[$Ph_3C$][$B(C_6F_5)_4$]/$Al^iBu_3$ catalytic system [a]



Entry	[St]/[Comp.**1**]	Yield (mg)	Act. [b]	PS cont. [c] (mol%)	M_n [d] × 10^{-4}	M_w/M_n [d]	T_m [e] (°C)
1	–	224	85	–	2.8	21.22	135
2	500	184	70	15	1.2	40.99	121
3	1000	229	87	44	0.4	8.31	115
4	1500	480	183	54	0.1	1.40	117/273
5	2000	616	235	58	0.1	1.52	125/256

[a] Conditions: 10.5 μmol of complex **1**, 10.5 μmol of [Ph_3C][$B(C_6F_5)_4$], [Al^iBu_3]/[Ln] = 5, 0.1 MPa of E, 10 mL of toluene, 25 °C, 15 min; [b] Activity, 10^4 g of copolymer $mol_{Sc}^{-1}\cdot h^{-1}\cdot MPa^{-1}$; [c] Determined by ^{1}H-NMR; [d] Determined by GPC in *o*-dichlorobenzene at 145 °C; [e] Measured by DSC

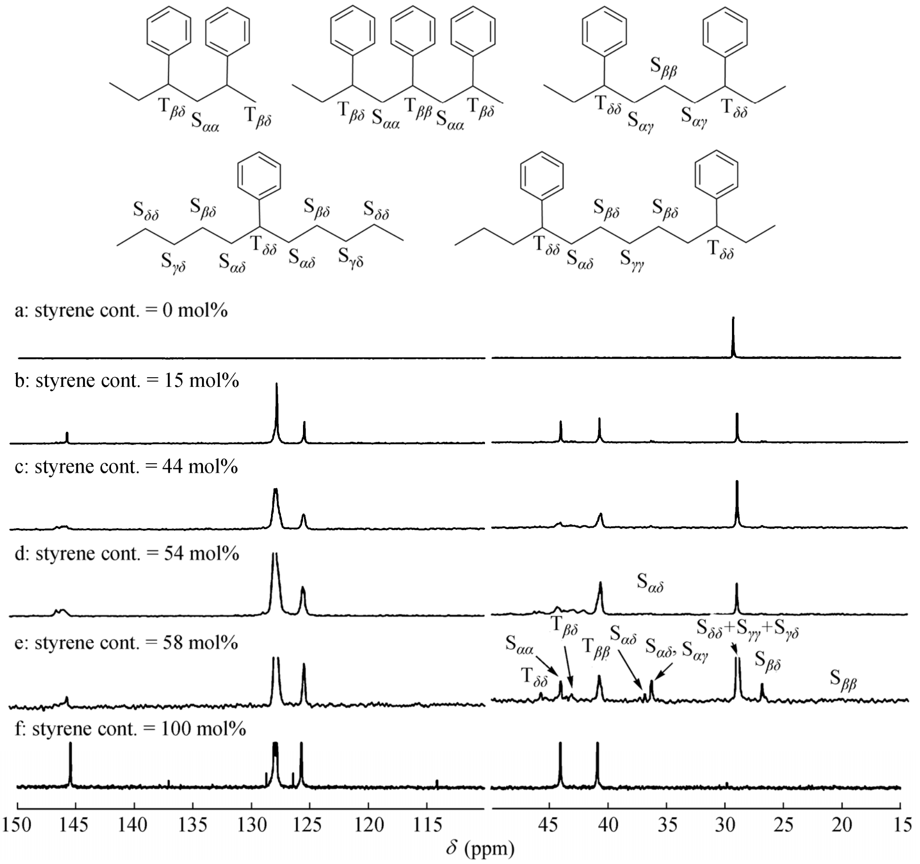


Fig. 2 ^{13}C-NMR spectra of styrene-ethylene copolymers

the random St-E copolymers gradually increased from 15 mol% to 58 mol%. In comparison with the St-E copolymers obtained by the known half-sandwich rare-earth metal complexes, these results demonstrated that the bulky cyclopentadienyl ligand of the chiral half-sandwich rare-earth metal complexes effectively inhibited the continued insertion of St monomers into the copolymer chain to some extent.

The copolymers obtained are white elastomers. All of them have good solubility in 1,1,2,2-$C_2H_2Cl_4$ and *o*-$C_6H_4Cl_2$ at 120 °C. The ^{13}C-NMR spectra of these copolymers produced by the complex **1**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 catalytic systems are shown in Fig. 2. The St-E copolymers possess almost random microstructures consisting of syndiotactic St-E sequences (blocks) connected by repeated E units, as evidenced by the peaks at 27.2−28.0 ppm (StEESt, $S_{\beta\delta}+S_{\beta\gamma}$), 29.7 ppm (StEESt, EEE, EEStEE, $S_{\delta\delta}$, $S_{\gamma\delta}+S_{\gamma\gamma}$), 37.0−38.3 ppm (StStSt, EStStE, $S_{\alpha\delta}$), 41.2 ppm (StStSt, $T_{\beta\beta}$), 43.6−43.9 ppm (EStStE, StStSt, $T_{\beta\delta}+S_{\alpha\alpha}$), 44.5 ppm (StEESt, EEStEE, $T_{\delta\delta}+T_{\gamma\delta}+T_{\gamma\gamma}$), and 145.5 ppm (StStSt, ipso-C) (Fig. 2, c−e). Signals at 34−35 ppm for $S_{\alpha\beta}$ demonstrate no tail-to-tail or head-to-head St sequences in these random St-E copolymers. GPC curves show the bimodal molecular weight distributions (M_w/M_n: 40.99 and 8.31) for the copolymers obtained under the 500 and 1000 of [St]/[complex **1**] molar ratio, which are similar to that of the polyethylene obtained by the same catalytic systems. However, the unimodal molecular weight distributions (M_w/M_n: 1.52 and 1.40) were observed for the copolymers obtained under the 1500 and 2000 of [St]/[complex **1**] molar ratio. These results suggest that the single-site cationic active species play the dominant role in the copolymerization with the increasing St concentration. DSC data demonstrate that these copolymers have melting temperature around 120 °C. In some cases, the high melting temperature at 256 °C for the syndiotactic polystyrene sequences was also observed for the copolymers with high St content.

CONCLUSIONS

The chiral half-sandwich rare-earth metal complexes $(Cp^{x*})Ln(CH_2SiMe_3)_2(THF)$ (**1**−**4**: Ln = Sc (**1**), Ln = Lu (**2**), Ln = Y (**3**), Ln = Dy (**4**)) activated by borate and Al^iBu_3 could serve as the high efficient and high syndiotactic catalysts for the syndiospecific polymerization of St, and the copolymerization of St with E under the mild conditions. Under optimized conditions, these chiral complexes showed high activity up to 3.1×10^6 g of polymer $mol_{Ln}^{-1}\cdot h^{-1}$ for the syndiospecific polymerization of St, affording the syndiotactic polymers of St with low molecular weight and moderate molecular weight distribution (syndiotactic selectivities above 99%, M_n *ca.* 6000 $g\cdot mol^{-1}$, M_w/M_n = 1.40−5.03). This differed from those polymers obtained by the known half-sandwich rare-earth metal complexes. Moreover, the complex **1**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 catalytic system also exhibited high activity up to 2.4×10^6 g of copolymer $mol_{Sc}^{-1}\cdot h^{-1}\cdot MPa^{-1}$ for the copolymerization of St with E at 25 °C under 0.1 MPa E pressure, giving random St-E copolymers containing syndiotactic polystyrene sequences with different St contents in the range of 15 mol%−58 mol%. These results demonstrate that the bulky cyclopentadienyl ligand of these chiral half-sandwich rare-earth metal complexes effectively inhibited the continued insertion of St monomer into the polymer chain to some extent in comparison with the known half-sandwich rare-earth metal complexes.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-018-2060-8.

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