

# Scandium Half-Metallocene-Catalyzed Syndiospecific Styrene Polymerization and Styrene–Ethylene Copolymerization: Unprecedented Incorporation of Syndiotactic Styrene–Styrene Sequences in Styrene–Ethylene Copolymers

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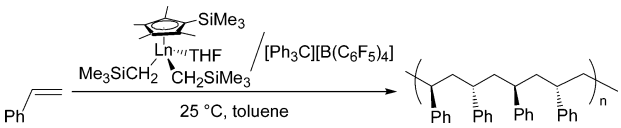
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The development of homogeneous single-site polymerization catalysts has opened a new avenue in the synthesis of polymer materials having controlled microstructures and desired properties. Syndiotactic polystyrene (sPS), discovered by Ishihara and co-workers at Idemitsu in 1986 by use of homogeneous titanium catalysts,<sup>1</sup> is a very promising new polymer material for a large number of applications in industry, because of its high melting point (ca. 270 °C), high crystallinity, high modulus of elasticity, low dielectric constant, and excellent resistance to heat and chemicals.<sup>2</sup> A drawback that may limit the application scope of sPS, however, is its brittleness. For improvement of the toughness of sPS, the incorporation of a comonomer such as ethylene is expected to be a useful method, and toward this end, extensive studies on the copolymerization of styrene with ethylene have been carried out by both academic and industrial researchers.<sup>2–4</sup> Despite these efforts, however, the synthesis of a styrene–ethylene copolymer having syndiotactic styrene–styrene sequences has not been achieved to date, and in many cases mixtures of homopolyethylene, homopolystyrene, and varying amounts of styrene–ethylene copolymers with no regio- or stereoregular styrene–styrene sequences were obtained.<sup>3</sup> Attempts to solve this problem were hampered by the fact that the catalysts that were effective for syndiospecific styrene polymerization such as Cp'TiX<sub>3</sub>/MAO or Cp'TiR<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (Cp' = substituted or unsubstituted cyclopentadienyl or indenyl; X = halide, alkoxy; R = alkyl; MAO = methylaluminoxane) usually contained a family of different active species, in which the species to produce sPS (probably a Ti(III) species) and that to give polyethylene (probably a Ti(IV) species) were different from that to afford styrene–ethylene copolymers (unknown species).<sup>3,5</sup> Therefore, the synthesis of a sPS-containing styrene–ethylene copolymer via copolymerization of the two monomers remained a challenge.

During our studies on rare earth metal complexes bearing mono(cyclopentadienyl) ligands,<sup>4a,b,6,7</sup> we envisioned that cationic rare earth metal alkyl species bearing mono(cyclopentadienyl) ligands might mediate unusual styrene–ethylene copolymerization patterns.<sup>8,9</sup> We report here that the scandium half-metallocene complex (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF), in combination with 1 equiv of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], not only exhibits excellent activity and selectivity for syndiospecific styrene polymerization and styrene–ethylene copolymerization but also affords syndiotactic styrene–styrene sequences with broad-range controllable styrene contents in the styrene–ethylene copolymers.

The results of styrene homopolymerization by several rare earth half-metallocene catalysts are summarized in Table 1.<sup>10</sup> The neutral complexes (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) (Ln = Sc, Y, Gd, Lu) alone did not show an activity for styrene polymerization at room temperature in toluene.<sup>11</sup> When treated with 1 equiv of [Ph<sub>3</sub>C]-[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], however, all of these complexes became active for the syndiospecific polymerization of styrene.<sup>12</sup> Among these complexes,

**Table 1.** Syndiospecific Polymerization of Styrene by Rare Earth Half-Metallocene Catalysts<sup>a</sup>



run	Ln	[M]/[Ln]	t (min)	yield <sup>b</sup> (%)	activity <sup>c</sup>	sPS <sup>d</sup> (%)	M <sub>w</sub> <sup>e</sup> (×10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>e</sup>	T <sub>m</sub> <sup>f</sup> (°C)	efficiency <sup>g</sup> (%)
1	Sc	500	1	100	≥3125	100	8.85	1.38	271	58
2	Sc	700	1	100	≥4376	100	11.96	1.29	271	61
3	Sc	1000	1	100	≥6034	100	13.55	1.45	272	77
4	Sc	1500	1	100	≥9362	100	18.96	1.55	271	82
5	Sc	2000	1	100	≥12 498	100	26.94	1.36	272	77
6	Sc	2500	1	87	13 618	100	37.86	1.37	273	60
7	Y	100	30	60	13	100	1.07	1.39	269	
8	Gd	100	30	69	15	100	0.92	1.35	269	
9	Lu	100	30	25	6	100	0.49	1.38	268	

<sup>a</sup> Conditions: Ln, 21 μmol; [Ln]/[B] = 1/1 (mol/mol); solvent/monomer = 5:1 (v/v). <sup>b</sup> Weight of polymer obtained/weight of monomer used. <sup>c</sup> Given in kg of sPS/(mol Ln·h). <sup>d</sup> Percentage of polymers insoluble in refluxing 2-butanone; *rrrr* > 99%. <sup>e</sup> Determined by GPC in 1,2-dichlorobenzene at 145 °C against polystyrene standard. <sup>f</sup> Determined by DSC. <sup>g</sup> Catalyst efficiency = M<sub>n</sub>(calculated)/M<sub>n</sub>(measured).

the scandium complex showed the highest activity (up to 1.36 × 10<sup>4</sup> kg of sPS/(mol Sc·h)), which can be compared with the most active titanium catalysts reported for syndiospecific styrene polymerization.<sup>13,14</sup> The molecular weight of the resulting polymers increased almost linearly as the monomer-to-catalyst ratio was increased, while the molecular weight distribution remained very narrow (M<sub>w</sub>/M<sub>n</sub> = 1.29–1.55) (Table 1, runs 1–6). In the present polymerizations, neither atactic nor isotactic polystyrene was observed. Therefore, solvent fractionation was not required to obtain pure sPS (*rrrr* > 99% for all polymers obtained).<sup>15</sup>

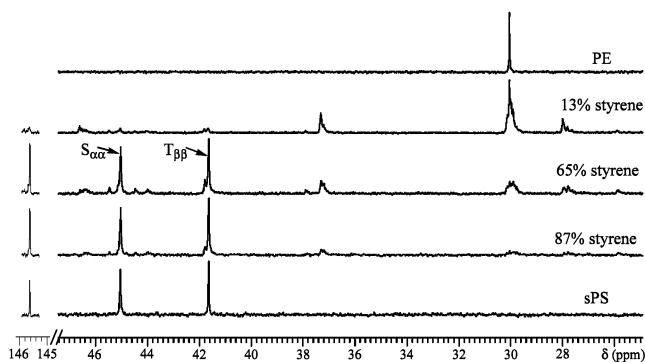
More remarkably, in the presence of ethylene, the copolymerization of styrene with ethylene occurred rapidly and selectively (Table 2). The styrene content in the copolymers could be controlled simply by changing the styrene feed under 1 atm of ethylene and reached 87 mol % when 41 mmol of styrene was used (Table 2, run 6). Solvent fractionation experiments<sup>5e</sup> confirmed that the copolymer products did not contain homopolymers. The GPC curves of the copolymers were all unimodal with very narrow molecular weight distributions (M<sub>w</sub>/M<sub>n</sub> = 1.14–1.26) (Table 2, runs 3–6), indicative of single-catalyst behavior. <sup>13</sup>C NMR analyses revealed that this copolymer consists of syndiotactic styrene–styrene sequences (blocks) connected by repeated ethylene units, as evidenced by the peaks at δ 145.7 (phenyl C-1), 45.0 (S<sub>αα</sub>), and 41.6 (T<sub>ββ</sub>) (Figure 1). Signals for tail-to-tail or head-to-head styrene sequences<sup>3f,i,5e</sup> were not observed. These results are in striking contrast with what was observed for group 4 metal-based catalysts, which afforded no stereo- or regioregular styrene sequences.<sup>3</sup>

**Table 2.** Syndiospecific Copolymerization of Styrene with Ethylene by a Scandium Half-Metallocene Catalyst<sup>a</sup>

run	styrene (mmol)	ethylene (atm)	yield (g)	activity <sup>b</sup>	PS cont <sup>c</sup> (mol %)	M <sub>n</sub> <sup>d</sup> (×10 <sup>-4</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>	T <sub>m</sub> <sup>e</sup> (°C)
1	0	1	0.55	786	0	17.23	1.72	127
2	21	0	0.45	643	100	6.04	1.41	268
3	10	1	0.40	600	13	7.92	1.14	n.o. <sup>f</sup>
4	21	1	0.79	1123	56	11.13	1.19	214
5	31	1	0.92	1314	65	16.26	1.17	233
6	41	1	1.62	2314	87	15.09	1.26	245

<sup>a</sup> Conditions: toluene, 50 mL; Sc, 21 μmol; [Sc]/[B] = 1/1 (mol/mol).

<sup>b</sup> Given in kg of polymer/(mol Sc·atm·h). <sup>c</sup> Determined by <sup>1</sup>H NMR in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 120 °C (PS mol % = 4A<sub>ar</sub>/(5A<sub>al</sub> + A<sub>ar</sub>), where A<sub>ar</sub> = area of aromatic protons and A<sub>al</sub> = area of aliphatic protons). <sup>d</sup> Determined by GPC in 1,2-C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> at 145 °C against polystyrene standard. <sup>e</sup> Determined by DSC. <sup>f</sup> Not observed.



**Figure 1.** Part of <sup>13</sup>C NMR spectra of polyethylene, polystyrene, and styrene–ethylene copolymers from Table 2 in 1,2-dichlorobenzene-*d*<sub>4</sub> at 130 °C (75.5 MHz, HMDS scale).

In summary, we have demonstrated that the combination of a mono(cyclopentadienyl) rare earth metal bis(alkyl) complex such as (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(THF) with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] acts as an excellent catalyst system for syndiospecific styrene polymerization and styrene–ethylene copolymerization. By use of this catalyst system, styrene–ethylene copolymers containing syndiotactic styrene–styrene sequences have been successfully synthesized for the first time. Further evaluation of the properties of these new polymers and application of the present and related catalyst systems to polymerization/copolymerization of other monomers are in progress.

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**Supporting Information Available:** Experimental details, an ORTEP drawing and X-ray structure data of the Sc complex, a GPC curve, <sup>13</sup>C NMR spectra, and DSC charts of representative polymer products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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