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(η^5-Pentamethylcyclopentadienyl)trimethyltitanium as a Precursor for the Syndiospecific Polymerization of Styrene

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An equimolar mixture of Cp*Ti(CH_3)$_3$ (2) and $Ph_3C^+[B(C_6F_5)_4]^-$ (1) forms a highly active and syndioselective catalyst for the polymerization of styrene, producing 96% syndiotactic polystyrene (PS) at an activity of 0.91×10^7 g PS (mol Ti)$^{-1}$ (mol styrene)$^{-1}$ h^{-1}. Both activity and syndioselectivity can be increased using tri-iso-butylaluminum (TIBA) to scavenge the system. ESR measurements indicate that the polymerization proceeds via titanium(IV) intermediates. Catalysts derived from 2/methylaluminoxane (MAO) as well as Cp*$TiCl_3$/MAO also function as syndioselective styrene polymerization catalysts, but are less active than the 'cationic' system derived from 1 and 2.

Keywords: Polystyrene, syndiotactic, syndioselective, MAO, cationic catalysts, trityl tetrakis(pentafluorophenyl)borate

INTRODUCTION

The syndiospecific polymerization of styrene was first reported by Ishihara and coworkers in 1986.[1,2] Syndiotactic polystyrene (*s*-PS) is a relatively new polymeric material which may have a variety of important applications as a high-performance engineering plastic. The most active catalysts have been derived from tetravalent titanium precursors such as Cp$TiCl_3$, CpTi(OR)$_3$, $TiBz_4$, $TiCl_4$ or Ti(OR)$_4$ together with a large molar excess of methylaluminoxane (MAO) as cocatalyst.[1–6]

We have previously shown that the reaction of *rac*-ethylenebis(indenyl)dimethylzirconium and trityl tetrakis(pentafluorophenyl)borate, $Ph_3C^+[B(C_6F_5)_4]^-$ (1), produced *rac*-ethylenebis(indenyl)methylzirconium 'cation', [*rac*-Et(Ind)$_2$Zr(CH_3)]$^+$, which was exceedingly active and stereoselective for propylene polymerization.[7,8] It was of interest in the present study to determine whether the organotitanium precursor Cp*Ti(CH_3)$_3$ (2)[9] (Cp* = η^5-pentamethylcyclopentadienyl) when activated with **1** could likewise be highly active for the syndiospecific polymerization of styrene. For comparison, we have also investigated the catalytic activities of Cp*Ti(CH_3)$_3$/MAO and Cp*$TiCl_3$/MAO systems.

EXPERIMENTAL

All operations were performed under an argon atmosphere using Schlenk or glove-box techniques. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and phosphorus(V) oxide (P_2O_5). Toluene was refluxed for 48 h over sodium under argon and distilled just before use. Styrene was distilled from calcium hydride and stored at −25 °C under argon in darkness. Methylaluminoxane (MAO) was purchased from Akzo. Cp*Ti(CH_3)$_3$,[9] Cp*$TiCl_3$,[10] and Ph_3C^+ $[B(C_6F_5)_4]^-$ [7] were synthesized according to published procedures.

Polymerizations were carried out in 250 cm^3, crown-capped glass pressure reactors equipped with magnetic stirring and thermostated to the desired temperature. For MAO-catalyzed polymerizations, toluene was added first, followed by styrene (5.0 cm^3), MAO and finally the appropriate titanium precursor. For 'free' cationic polymerizations, the organometallic compound and the cocatalyst were dissolved in toluene in the amounts specified, and then the monomer was introduced. For TIBA (tri-iso-butylaluminum)-scavenged polymerizations, the order of addition to toluene was styrene, TIBA, organometallic

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Table 1 Styrene polymerization catalyzed by $Cp^*TiMe_3/Ph_3C^+B^-(C_6F_5)_4$[a]

Run	$[Cp^*TiMe_3]$ (mM)	Cocatalyst (concn. [mM])	Time (min)	Yield PS (g)	A[b]	SY[c]
1	1.85	$Ph_3C^+B^-(C_6F_5)_4$ (1.85)	5	1.65	0.91×10^7	96
2	1.85	$Ph_3C^+B^-(C_6F_5)_4$ (1.85) + TIBA[d] (37)	5	2.14	1.18×10^7	99
3	—	$Ph_3C^+B^-(C_6F_5)_4$ (1.85)	30	4.30	0.39×10^7[e]	0
4	1.85	—	240	0	—	—
5	7.14	$Li^+B^-(C_6F_5)_4$ (7.14)	240	0	—	—
6	7.14	$Li^+B^-(C_6F_5)_4$ (1.43)	240	0	—	—
7	1.85	$B(C_6F_5)_3$ (1.85)	10	1.40	3.85×10^6	97

[a] Conditions: 5.0 cm^{-3} styrene; $T_p = 50\,°C$; for runs 1–4 and 7, 22 cm^3 toluene; for runs 5 and 6, 30 cm^3 toluene. [b] A = g PS (mol Ti)$^{-1}$ (mol styrene^{-1}) h^{-1}. [c] SY = wt % of *s*-PS insoluble in refluxing 2-butanone. [d] TIBA = tri(isobutyl)aluminum. [e] Activity is based on $Ph_3C^+B^-(C_6F_5)_4$.

compound, and finally $Ph_3C^+[B(C_6F_5)_4]^-$. All polymerizations were terminated by addition of acidified methanol. The polymer was washed with methanol and dried *in vacuo* to constant weight. The polymer obtained was extracted with refluxing 2-butanone for 12 h and the insoluble fractions again dried *in vacuo* to constant weight. The reproducibility of the amount of the total polymer and syndiotactic polymer obtained is estimated at ±5% and ±2%, respectively.

ESR spectra were recorded on an IBM ESP 300 spectrometer.

RESULTS AND DISCUSSION

Table 1 summarizes the results for the 'cationic' polymerization of styrene. The reaction between **1** and **2** most probably forms an organometallic cationic species, as shown in Eqn [1] [this catalyst system has previously been prepared from a reaction between **2** and triethylammonium tetrakis(pentafluorophenyl)borate, and was demonstrated to produce highly syndiotactic polystyrene].[11]

$$\underset{\mathbf{2}}{Cp^*Ti(CH_3)_3} + \underset{\mathbf{1}}{Ph_3C^+[B(C_6F_5)_4]^-} \rightarrow Cp^*Ti(CH_3)_2^+[B(C_6F_5)_4]^- + Ph_3CCH_3 \qquad [1]$$

In a typical polymerization at 50 °C involving 5.0 cm^3 of styrene in 22 cm^3 of toluene, **1** and **2**, each at 1.85 mM, were employed to produce 96% *s*-PS at an activity of 0.91×10^7 g PS (mol Ti)$^{-1}$ (mol styrene)$^{-1}$ h^{-1} (run 1). This activity is approximately twice as high as that reported for **2** when activated with $B(C_6F_5)_3$ in a 1 : 1 molar ratio (5.0×10^6 g PS (mol Ti)$^{-1}$ (mol styrene)$^{-1}$ h^{-1}).[12] In order to ensure a meaningful comparison of these two organoboron cocatalysts, we have repeated styrene polymerizations using the **2**/$B(C_6F_5)_3$ catalyst system under our conditions and obtained $A = 3.85 \times 10^6$ g PS (mol Ti)$^{-1}$ (mol styrene)$^{-1}$ h^{-1} and a syndiotactic yield (*SY*) of 97% (run 7), in excellent agreement with the earlier findings.[12] We have previously compared **1** and $B(C_6F_5)_3$ as cocatalysts for propylene polymerization and found the former to be superior by virtue of their difference in ion-pair interactions.[13]

An alternative, highly efficient route to metallocenium catalysts for propylene polymerization involves reacting *rac*-$Et(Ind)_2ZrCl_2$ with **1** in the presence of a judicious amount of triethylaluminum (TEA) or tri-iso-butylaluminum (TIBA), just sufficient to scavenge any monomer or solvent impurities and to alkylate the *rac*-$Et(Ind)_2ZrCl_2$.[8, 13] In the present study involving styrene, 37 mM TIBA was added to the catalyst system in run 1. The activity was raised to 1.18×10^7 g PS (mol Ti)$^{-1}$ (mol styrene)$^{-1}$ h^{-1} and the product was 99% *s*-PS (run 2).

Compound **1** in the absence of **2** is also a highly active cationic catalyst, but polymerizes styrene to atactic polymer (run 3). In contrast, **2** alone is not an active styrene polymerization catalyst (run 4), and combinations of **2** and $Li^+[B(C_6F_5)_4]^-$ in two different ratios (1 : 1 and 5 : 1) also gave no observable activity in polymerizations of up to 4 h (runs 5, 6). These findings demonstrate that the $[B(C_6F_5)_4]^-$ anion itself in the presence of the catalyst precursor **2** does not initiate any polymerization.

Table 2 summarizes styrene polymerization results for the $Cp^*Ti(CH_3)_3$/MAO catalyst system at 50 °C and at various Al/Ti ratios. At an opti-

Table 2 Styrene polymerization catalyzed by Cp*TiMe$_3$/MAO[a]

Run	Al/Ti	Yield PS (g)	A[b]	SY[c]
1	100:1	—	—	—
2	300:1	0.045	0.21×10^6	93
3	500:1	0.267	1.22×10^6	99
4	1000:1	0.229	1.15×10^6	96
5	2000:1	0.190	0.87×10^6	97
6	4000:1	0.165	0.76×10^6	97

[a] Conditions: [Cp*TiMe$_3$] = 100 μM, $t_p = 60$ min, $T_p = 50$ °C, 50 cm^3 toluene, 5.0 cm^3 styrene. [b] A = g PS (mol Ti)$^{-1}$ (mol styrene)$^{-1}$ h^{-1}. [c] SY = wt% of *s*-PS insoluble in refluxing 2-butanone.

mum Al/Ti ratio of 500, it has the highest activity of 1.22×10^6 g PS (mol Ti)$^{-1}$ (mol styrene)$^{-1}$ h^{-1} (run 3). However, this activity is about ten times smaller than for the optimized conditions for the Cp*Ti(CH$_3$)$_3$/1 system. Nearly pure *s*-PS was produced by both catalysts. In the case of the MAO cocatalyst, the active species is probably formed as shown in Eqn [2].

$$\underset{\mathbf{2}}{\mathrm{Cp^*Ti(CH_3)_3}} + \mathrm{MAO} \rightarrow [\mathrm{Cp^*Ti(CH_3)_2}]^+[\mathrm{CH_3 \cdot MAO}]^- \qquad [2]$$

The lower activity may be due to the lower efficiency of extraction of methide ion (CH$_3$)$^-$ by MAO (Eqn [2]) than by **1** (Eqn [1]). However, such a conclusion is inconsistent with the fact that the activity becomes lower when the Al/Ti ratio exceeds 500. This behavior suggests that the [Cp*Ti(CH$_3$)$_2$]$^+$ cation is coupled with the [CH$_3$ · MAO]$^-$ counter-ion, or is complexed with a neutral MAO molecule. Either species is likely to be much less active for steric reasons in catalyzing polymerizations than the 'bare' [Cp*Ti(CH$_3$)$_2$]$^+$ cation generated by **1**.

Styrene polymerizations were also carried out with another precursor, Cp*TiCl$_3$. Table 3 gives the polymerization results. The maximum activity was achieved at an Al/Ti ratio of 4000 instead of a ratio of 500 in the case of **2**. Such a finding is understandable since MAO is also serving as an alkylating agent in this system. Otherwise, Cp*TiCl$_3$/MAO exhibits essentially the same maximum polymerization activity and syndiospecificity as does Cp*Ti(CH$_3$)$_3$/MAO.

In order to determine whether or not Ti(III) species are involved in these styrene polymerizations, several ESR experiments were performed. Samples were prepared and measured using **2** activated either with **1** or with B(C$_6$F$_5$)$_3$ at polymerization concentrations. Neither of these mixtures was found to be ESR-active. These results demonstrate that Ti(IV) species function as catalytically active intermediates in styrene polymerizations involving **1** and **2**.

Table 3 Styrene polymerization catalyzed by Cp*TiCl$_3$/MAO[a]

Run	Al/Ti	Yield PS (g)	A[b]	SY[c]
1	100:1	—	—	—
2	300:1	—	—	—
3	500:1	0.19	0.44×10^6	95
4	1000:1	0.30	0.68×10^6	95
5	2000:1	0.34	0.78×10^6	97
6	4000:1	0.50	1.15×10^6	98

[a] Conditions: [Cp*TiCl$_3$] = 100 μM, $t_p = 120$ min, $T_p = 50$ °C, 50 cm^3 toluene, 5.0 cm^3 styrene. [b] A = g PS (mol Ti)$^{-1}$ (mol styrene)$^{-1}$ h^{-1}. [c] SY = wt% of *s*-PS insoluble in refluxing 2-butanone.

We have previously shown that CpTiCl$_3$ in the presence of MAO is reduced to paramagnetic Ti(III) intermediates which retain the Cp ligand.[14] In the present study, quantitative ESR measurements were made on the **2**/MAO system at Al/Ti = 500 and on the Cp*TiCl$_3$/MAO system at Al/Ti = 4000, at concentrations employed for styrene polymerizations. Approximately 11% and 28%, respectively, of Ti(III) species were observed. The detection of Ti(III) species is attributable to reduction of the titanium precursors by MAO, and does not exclude the possibility that Ti(III) intermediates may also be active catalysts during the polymerization process.

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