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SHORT PAPER

Low-temperature isospecific polymerization of propylene catalyzed by alkylzirconocene-type 'cations'

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The *rac*-ethylenebis(indenyl)methylzirconium 'cation' (1), generated from *rac*-$Et(Ind)_2ZrMe_2$ and $Ph_3CB(C_6F_5)_4$, has recently been shown to be exceedingly active and stereoselective in propylene polymerization. The ethyl analog (2) can be produced by an alternate, efficient route involving a reaction between *rac*-$Et(Ind)_2ZrCl_2$ and $AlEt_3$ (TEA), followed by addition of $Ph_3CB(C_6F_5)_4$. The use of excess $AlEt_3$ serves both to alkylate the zirconium complex as well as to scavenge the system. The propylene polymerization activity of the 'cation' 2 is about 7000 times greater than the activity of *rac*-$Et(Ind)_2ZrCl_2$/methylaluminoxane (MAO) at $T_p = -20$ °C. The related catalyst system *rac*-$Me_2Si(Ind)_2ZrCl_2$/TEA/$Ph_3CB(C_6F_5)_4$ (3) was found to produce 98.3% i-PP with T_m 156.3 °C and an activity of 1.8×10^9 g PP $\{(\text{mol Zr})\ [C_3H_6]\ h\}^{-1}$.

Keywords: Polypropylene, polymerization, isospecificity, alkylzirconocene-type cations, stereoselectivity, MAO, cationic catalysts, trityl tetrakis(pentafluorophenyl)borate.

INTRODUCTION

The bis-(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2; $Cp = \eta^5$-cyclopentadienyl)/alkylaluminum chlorides system was the first homogeneous ethylene polymerization catalyst.[1] The catalyst exhibited low polymerization activity ($A = 5 \times 10^4$ g PE (mol Ti atm h)$^{-1}$ at 15 °C) for ethylene[2] and none for propylene. Recently, many 'cationic' metallocene alkyls, usually with BPh_4 as the counterion, have been reported.[3-8] They were found to exhibit modest ethylene polymerization activity.[3-7,9,10] They showed either no activity for propylene polymerization or they gave low yields of atactic products.[9-11] This is probably due to a freely rotating Cp ligand and lack of an asymmetric center. When the metallocene complex was activated with methylaluminoxane[12-17] (MAO), very high ethylene polymerization activity of 10^8 g PE (mol Zr atm h)$^{-1}$ was achieved. Still, the catalytic site does not impose stereochemical control on the polymerization of prochiral monomers.

Stereoselective polymerizations of α-olefins were possible with chiral metallocene complexes. For instance, the *rac*-$Et(Ind)_2ZrCl_2$/MAO or analogous tetrahydroindenyl catalyst systems can produce isotactic polypropylene of varying degrees of stereoregularity, depending upon the temperature of polymerization.[16,17] The stereoregularity was improved markedly by lowering the temperature of polymerization (T_p). However since the activation energy for the log (polymerization activity) vs T^{-1} is 12.4 kcal mol^{-1} (52.08 kJ mol^{-1}) the zirconocene/MAO is virtually without catalytic activity for $T_p \leq -20$ °C.[17] This may be explained by the complexation of the catalytic sites with MAO, resulting in appreciably reduced catalytic activity.

The low polymerization activities found previously for zirconocene cationic species[3-7,9-11] may be explained by complexation with strongly coordinating solvent molecules and also the electrophilic attack on the anion by the alkylzirconocenium species. These considerations have caused investigators to gravitate from BF_4^-, PF_6^-, and $B(C_6H_5)_4^-$ anions to $B(C_6F_5)_4^-$ and carborane counterions. We have reported previously[18] that the *rac*-ethylenebis(indenyl)methylzirconium cation (1), which was produced from the reaction of *rac*-ethylenebis(indenyl)dimethylzirconium (4) and triphenylcarbenium (trityl) tetrakis(pentafluorophenyl)borate (5), is exceedingly active and stereoselective in propylene polymerization, and that its catalytic activity and stereospecificity increase with a decrease of T_p. Ewen *et al.*[19] have

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Table 1 Propylene polymerization at $T_p = 20$ °C

Run no.	Catalyst[a] Compd	[Zr] (μM)	Cocatalyst[a] Compd	[Al] (mM)	Compd	[B] (μM)	$A^b \times 10^{-6}$	IY[c] (%)	T_m (°C)	$M_w \times 10^{-3d}$
1	**6**	125	MAO	312	—	—	1.4	59.6	134.8	24
2	**4**	75	—	—	**5**	75	8.5	36.9	128.8	24
3	**6**	10	TEA	0.50	**5**	10	90	36.9	128.3	24
4	**7**	100	MAO	250	—	—	1.4	58.0	145.6	56
5	**7**	10	TEA	0.50	**5**	10	66	52.2	143.5	60

[a] **6**, $Et(Ind)_2ZrCl_2$; **4**, $Et(Ind)_2ZrMe_2$; **7**, $Me_2Si(Ind)_2ZrCl_2$; **5**, $Ph_3CB(C_6F_5)_4$. [b] A measured in g PP {(mol Zr) $[C_3H_6]$ h}$^{-1}$. [c] Weight percentage of PP insoluble in refluxing heptane. [d] $\log M_w = 1.25 \times (\log [\eta] + 4)$ (Ref. 25).

employed *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate to achieve the same objective.

While the catalyst system **4/5** is highly active, it must be employed in relatively high concentrations in propylene polymerizations in order to scavenge impurities. In this contribution, we report an alternate and efficient method to produce alkylzirconocene-type 'cation' polymerization catalysts.

EXPERIMENTAL

All operations were performed using Schlenk tube techniques under an argon atmosphere. *rac*-$Et(Ind)_2ZrCl_2$[20,21] (**6**), *rac*-$Me_2Si(Ind)_2ZrCl_2$[22] (**7**), $Ph_3CB(C_6F_5)_4$[18] (**5**) and MAO[23] were prepared according to published procedures. Toluene was dried over refluxing sodium; the propylene (polymer purity grade) purchased from Matheson was passed through two Matheson Gas Purifiers (Model 6406) and used directly. A detailed comparison was made of propylene polymerization catalyzed by alkylzirconocene-type 'cations' and by the zirconocene/MAO system for T_p ranging from −55 °C to 20 °C. The polymerizations were carried out as follows. A 250 cm^3 crown-capped glass pressure bottle containing a magnetic stir bar was evacuated, back-flushed with argon several times; then 50 cm^3 of toluene was injected. The argon was replaced with 1.6 bar of propylene, and TEA and the zirconocene complex were added. The mixture was stirred for 5 min at room temperature, the system was cooled to the desired polymerization temperature, and after monomer saturation was achieved, the $Ph_3CB(C_6F_5)_4$ (**5**) dissolved in toluene was added via a syringe to start the polymerization. After the polymerization, the unreacted monomer was vented and the mixture was quenched with acidic methanol (1% HCl). The polymer was filtered, washed with methanol and finally dried at 70 °C to constant weight.

Melting and crystallization curves were recorded on a Perkin–Elmer DSC IV system. The molecular weight was determined by intrinsic viscosity measurements. The values of A were calculated using the measured solubility of propylene[16] {in g PP (mol Zr $[C_3H_6]$ h)$^{-1}$} except $T_p = -55$ °C [in g PP (mol Zr h)$^{-1}$].

Table 2 Propylene polymerization at $T_p = 0$ °C

Run no.	Catalyst Compd	[Zr] (μM)	Cocatalyst Compd	[Al] (mM)	Compd	[B] (μM)	$A \times 10^{-6}$	IY (%)	T_m (°C)	$M_w \times 10^{-3}$
1	**6**	125	MAO	312	—	—	0.09	74.4	141.5	59
2	**4**	75	—	—	**5**	75	6.7	88.4	142.4	59
3	**6**	10	TEA	0.75	**5**	10	88	88.4	146.8	60
4	**7**	100	MAO	250	—	—	0.32	81.5	150.0	76
5	**7**	5	TEA	0.75	**5**	5	120	90.1	150.6	87

Table 3 Propylene polymerization at $T_p = -20$ °C

Run no.	Catalyst Compd	[Zr] (μM)	Cocatalyst Compd	[Al] (mM)	Compd	[B] (μM)	$A \times 10^{-6}$	IY (%)	T_m (°C)	$M_w \times 10^{-3}$
1	**6**	125	MAO	312	—	—	0.033	75.0	146.8	70
2	**4**	100	—	—	**5**	100	21	93.6	152.9	110
3	**6**	5	TEA	1.00	**5**	5	230	93.6	156.1	110
4	**7**	100	MAO	250	—	—	0.015	83.8	152.5	110
5	**7**	2.5	TEA	1.00	**5**	2.5	1800	98.3	156.3	170

RESULTS AND DISCUSSION

We had previously[18] shown that the reaction of *rac*-$Et(Ind)_2ZrMe_2$ and trityl tetrakis(pentafluorophenyl)borate (**5**) produced *rac*-ethylenebis(indenyl)methylzirconium [*rac*-$Et(Ind)_2ZrMe$] 'cation' (**1**) which is exceedingly active for propylene polymerization.

It has been proposed that reaction of Cp_2ZrCl_2 with TEA (triethylaluminum) produces a series of alkylated zirconocene complexes including Cp_2ZrEt_2.[24] In a similar manner, treatment of *rac*-$Et(Ind)_2ZrCl_2$ and AlR_3 (R = Et, i-Bu) can generate the intermediate $Et(Ind)_2ZrR_2$, which on subsequent reaction with **5** can produce the 'cation' $[Et(Ind)_2ZrR]^+$ (**2**), which exhibits activity much higher than **1** in propylene polymerization with almost identical stereospecificity. Like the catalyst system **1**, *rac*-$Et(Ind)_2ZrCl_2$/TEA/$Ph_3CB(C_6F_5)_4$ (**8**) has an A which is also *greater at lower temperature*. At $T_p \leq -20$ °C the polymerization was agitation-limited after just a few minutes; it is about 7000 times greater than the activity of the **6**/MAO (**9**) system (compare runs 1 and 3, Table 3). This behavior is in contrast to Ziegler–Natta catalysis involving MAO as cocatalyst (Tables 1–4, runs 1 and 4) in which A decreases sharply with a decrease in T_p. The catalyst **8** is also about 10 times more active than **1** (compare runs 2 and 3, Tables 1–4). The stereospecificity as judged by IY (the percentage yield of refluxing n-heptane-insoluble i-PP), T_m (melting temperature) and M_w of the polypropylene produced by the cationic systems (**1** or **8**) is generally higher than for the PP produced at 20 °C (Table 1) and became greater at lower polymerization temperatures. At −55 °C, **8** produced 95.9% i-PP with T_m 159.2 °C, whereas the polypropylene produced by **9** (**6**/MAO) has IY only 86.2% and T_m 152.0 °C.

The *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO (**10**) system was found to produce polypropylene of higher stereoregularity and molecular weight than did **9**. This polymerization behavior was even more significant for the $Me_2Si(Ind)_2ZrCl_2$/TEA/$Ph_3CB(C_6F_5)_4$ (**11**) system. At $T_p = -20$ °C, highly stereospecific (IY = 98·3%, T_m = 156.3 °C) and high-molecular-weight (M_w = 170 000) polypropylene was produced with A 1.8×10^9 g PP (mol Zr $[C_3H_6]$ h$)^{-1}$. This result is about 120 000 times greater than the activity of **10** (compare runs 4 and 5, Table 3).

Table 4 Propylene polymerization at $T_p = -55$ °C

Run no.	Catalyst Compd	[Zr] (μm)	Cocatalyst Compd	[Al] (mM)	Compd	[B] (μM)	$A \times 10^{-6a}$	IY (%)	T_m (°C)	$M_w \times 10^{-3}$
1	**6**	125	MAO	312	—	—	0.002	86.2	152.0	
2	**4**	100	—	—	**5**	100	14	96.3	161.1	160
3	**6**	5	TEA	1.00	**5**	5	160	95.9	159.2	150
4	**7**	100	MAO	250	—	—				
5	**7**	2.5	TEA	1.00	**5**	2.5	270	99.4	159.9	220

[a] A (measured in g PP [(mol Zr) h]$^{-1}$.

CONCLUSION

The reaction of metallocene dichlorides, TEA and $Ph_3CB(C_6F_5)_4$ to produce alkylzirconocene-type 'cations' is facile. These cations are very reactive and unstable in the absence of monomer. In the presence of monomer, however, polymerization occurs at an extremely rapid rate which is faster at lower T_p. The resulting polypropylene produced at low T_p is highly isotactic.

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