ELSEVIER

Effect of the alkoxyl ligands on ethylene polymerization by TpTiCl₂(OR) complexes

Arquimedes Karam [a],*, Emilio Casas [a], Edgar Catarí [a], Sara Pekerar [b],
Alberto Albornoz [b], Bernando Méndez [c]

[a] *Laboratorio de Polímeros, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC),
Apartado 21827, Caracas 1020-A, Venezuela*
[b] *Centro de Química, IVIC, Venezuela*
[c] *Facultad de Ciencias, Escuela de Química, Universidad Central de Venezuela, Venezuela*

Abstract

The TpTiCl₂(OR) (where Tp = hydrotris(pyrazolyl)borate; R = Me, Et, *i*-Pr, *n*-Bu) and TpTiCl₃ complexes activated with very low concentration of MAO ($\geq$200 Al/Ti) showed very high activity in the ethylene polymerization. The substitution of one chlorine ligand in the TpTiCl₃ for one alkoxyl ligand increases the catalytic activity up to 76 times and 3.4 times respect to Cp₂ZrCl₂ at the same reaction conditions. The TpTiCl₂(OR) precatalysts activity decreases in the following order: TpTiCl₂(OEt) > TpTiCl₂(O*n*-Bu) $\approx$ TpTiCl₂(O*i*-Pr) $\gg$ TpTiCl₂(OMe) > TpTiCl₃.

The alkyl chain size of the alkoxyl ligands strongly affects the catalytic activity and the molecular weights of the polymers, prevailing the steric effect over the electronic effect. The resulting polymers can be classified as ultra-high molecular weight polyethylenes with basically linear structure.

1. Introduction

Since the discovery of the poly(pyrazolyl)borate ligands by Trofimenko in 1967 [1], the main application of these kind of ligands has been in transition metal coordination chemistry studies [2–4]. Other significant areas of application, which have received attention, are homogeneous catalytic transformation of organic molecules [5–13] and olefin polymerization [14–25].

The hydrotris(pyrazolyl)borate (Tp) and the hydrotris(3,5-dimethyl pyrazolyl)borate (Tp*) are the most commonly used of the tris(pyrazolyl)borate ligands, since they are the simplest and the easiest to synthesize. In general, tris(pyrazolyl)borate ligands are very useful due to their

10 possible substituting positions for electron donating or withdrawing groups and for sterically hindered groups which offer wider possibilities for studying their effects on reactivities, catalytic activities and stability of metal centers.

Although it is well known that the tris(pyrazolyl)borate ligands with transition metals (Tp^{R}VCl₂(NAr) (R = H, Me; Ar = 2,6-*i*-Pr-C₆H₃) [14]; Tp^{R}YR₁(THF)$_x$ (R = H, Me, Ph; R₁ = C₆H₅, CH₂SiMe₃); Tp^{R}Ln(alkyl)$_n$(THF)$_x$ (Ln = La³⁺, Nd³⁺, Sm²⁺; R = H, Me) [15]; Tp^{R}Rh(cod) (R = Me, Ph, *i*-Pr) [16]; TpRuCl(=C=CHPh)(PPh₃) [17]) are able to polymerize olefins, little information is available concerning the structural performance of tris(pyrazolyl)borate nor the role of the secondary ligands which complete the metal coordination sphere on the catalytic responses of a particular metal.

In this context, Nakazawa et al. found in ethylene polymerization by Tp^{R}MCl$_n$(OR₁)$_{3-n}$ (n = 1, 2, 3; M = Ti,

* Corresponding author. Tel.: +58 212 5041638; fax: +58 212 5041350.
E-mail address: akaram@ivic.ve (A. Karam).

Zr; R = H, Me; R_1 = Me, *t*-Bu, Ph, C_6H_4Me-4) [18] that when the Tp ligand of $Tp^R MCl_3$ complexes are substituted by Tp*, the activity for Tp*ZrCl$_3$ is enhanced, but not so for Tp*TiCl$_3$.

However, when all secondary ligands (chlorines) of TpZrCl$_3$ were substituted by *t*-butyloxy (O*t*-Bu) or *p*-methylphenoxy (OC$_6$H$_4$Me-4) groups, the activity decreased considerably. The substitution of one chlorine ligand of Tp*TiCl$_3$ by one *t*-butyloxy or *p*-methylphenoxy does not provide an important beneficial effect on the activity.

A valuable contribution for understanding the structural effect of tris(pyrazolyl)borate ligands on the ethylene polymerization was done by Jordan and co-workers [19]. They synthesized a set of $Tp^R TiCl_n(OR_1)_{3-n}$ (*n* = 1, 2, 3; R = H, Me, 2,4,6-trimethylphenyl (Ms); R$_1$ = *t*-Bu, C$_6$H$_4$-*t*-Bu-2) precatalysts with bulky substituents in the pyrazolyl rings (3 and/or 5 positions) which were activated with MAO. At the reaction conditions used in this work, the following catalytic activity tendencies were obtained.

First, the steric substituents enhance the activity over the less hindered substituents in the order Tp^{Ms*} > Tp^{Ms} > Tp* > Tp (where Tp^{Ms*} = HB(3-mesitylpyrazolyl)$_2$(5-mesityl-pyrazolyl); Tp^{Ms} = HB(3-mesitylpyrazolyl)$_3$).

Second, the substitution of one chlorine ligand of Tp*TiCl$_3$ by one bulky alkoxy group as O*t*-Bu or OC$_6$H$_4$-*t*-Bu-2 slightly increases the activity. In addition, the work confirms that in general the systems $Tp^R MCl_n(OR_1)_{3-n}$/MAO are very sensitive to the steric properties of the tris(pyrazolyl)borate ligands.

Recently, the use $Tp^R TiCl_n(OR_1)_{3-n}$ (*n* = 1, 2, 3; R = H, Me; R$_1$ = Me) complexes for homopolymerization of ethylene was reported. In this work, they studied the effect of the alkoxyl ligand number present at the complex, the steric effect of the tris(pyrazolyl)borate ligands (Tp versus Tp*) and cocatalysts type (MAO versus MMAO). Under the reaction condition used, the following trends were found: First, an increase of cone angle from 199° for Tp to 236° for Tp* conduces to a significant decrease of the catalytic activity.

Second, the addition of one methoxy group to TpTiCl$_3$ slightly increases the activity and a second methoxy has the opposite effect. For Tp*TiCl$_3$ the substitution of one chlorine by one methoxy group causes an activity reduction, and with a second methoxy the reduction became significant. Thus, MAO is a more effective cocatalyst for TpTiCl$_2$(OCH$_3$) than MMAO [20].

Continuing with our studies in order to understand the relation between structural modification of the tris(pyrazolyl)borate complexes and their catalytic responses. Herein, we report the steric and electronic effects of the alkoxyl ligands (OR = OMe, OEt, O*i*-Pr, O*n*-Bu) on the TpTiCl$_2$(OR) catalytic behavior on the ethylene polymerization as well as the effect over the physical properties of the polyethylenes obtained.

2. Experimental

2.1. General

All manipulations of air and/or moisture-sensitive compounds were carried out under nitrogen using standard Schlenk line techniques or a glove box. Toluene was dried over sodium/benzophenone and distilled under nitrogen prior to use. MAO was purchased from Akzo Corp. Ethylene was purchased from BOC Gas and used after passing through columns packed with BASF oxygen scavenger and 4 Å molecular sieve. The compounds TpTiCl$_3$ [26] and TpTiCl$_2$(OR) (R = Me, Et, *i*-Pr, *n*-Bu) [27] were synthesized as previously described.

### 2.2. X-ray photoelectron spectroscopy characterization

The complexes TpTiCl$_3$ and TpTiCl$_2$(OR) (OR = OMe, OEt, O*i*-Pr, O*n*-Bu) were evaluated by X-ray photoelectron spectroscopy (XPS) with a XL 220I VG Scientific spectrometer with monochromated Al Kα X-ray radiation (1486.6 eV). Acquisition was carried out at room temperature under high-resolution mode for the B 1s, N 1s, Cl 2p and Ti 2p regions. The samples were prepared in a glove box and mounted on an aluminum support. After, the samples were introduced into a transfer chamber and later evacuated at 10^{-6} Torr using a turbomolecular pump. During data collection, an ion-getter pump kept the pressure in the analysis chamber under 10^{-9} Torr. Accurate binding energies were referenced to an energy scale with binding energies for C 1s at 285.0 eV. The resultant material from the reaction of the complexes (TpTiCl$_3$ and TpTiCl$_2$(OR)) with MAO were analyzed by XPS. These materials were prepared in toluene, under nitrogen atmosphere using Al/Ti ratio of 200 and were subsequently washed several times with toluene and vacuum dried.

2.3. Polymerization procedure

The polymerization runs were carried out in a thermostated reactor (Buchi-Glauster) fitted with a 500 mL glass vessel, using toluene as solvent. The polymerization conditions were adjusted (25 °C; 1–3 bar; stirring 400–600 rpm) as required. The reactor was charged with an aluminoxane (Al/Ti: 1500–100) toluene solution (80 mL) and after 10 min, a toluene solution (20 mL) of the catalyst (1–3 mg) was added. The polymerization was started by injection of ethylene to the reactor and was stirred for the time required (10 min, 1 h). The ethylene pressure was kept constant during polymerization by a continuous supply of ethylene. The reaction was quenched by addition of 1% HCl solution in methanol. The polymer was stirred in distilled water overnight and filtered. Afterward, the polymer was vacuum dried to constant weight.

2.4. Polyethylenes characterization

Viscosity-average molecular weights were established by one-point determination of intrinsic viscosity measured from
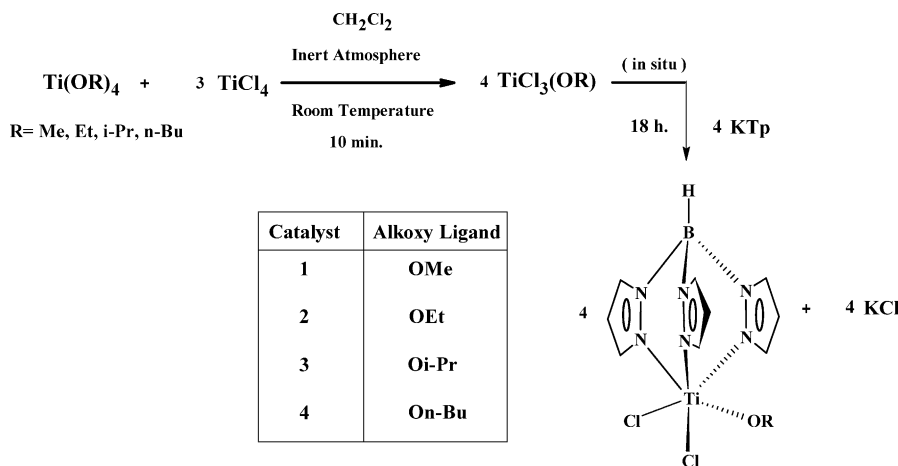
Scheme 1. Synthesis of precatalysts TpTiCl$_2$(OR).

an Ubbehlode dilution viscosimeter in decalin stabilized with 0.2% (v/v) of SANTONOX® at 135 °C. The results were analyzed using the Schulz–Blaschke correlation [28].

The melt flow index (MFI) of the polymers was determined using the standard test method ASTM D1238-79 at 190 °C with 2.16 kg standard charge.

The thermal properties of the polymers were studied in a METTLER TOLEDO, DSC822^e calorimeter, calibrated with Indium. Samples of polyethylene (5–10 mg) were sealed in an aluminum pan and were subjected to the following procedures: heating at 10 °C/min starting at 25–170 °C, and after 5 min at 170 °C isothermally, cooling at 5 °C/min from this temperature to 25 °C, and finally heating at 5 °C/min from 25 to 170 °C to obtain the melting peak temperature (T_m). Melting enthalpies were converted to levels of crystallinity (X_c) from the ratio ($\Delta H_{sample}/\Delta H_{theoric}) \times 100$, with ΔH_{sample} and $\Delta H_{theoric}$ being the apparent and the complete crystalline heats of fusion, respectively. The value of 293 J/g was taken as the enthalpy of a polyethylene crystal $\Delta H_{theoric}$.

Films for Fourier transform infrared (FTIR) analysis were compression-molded at 190 °C for 5 min. FTIR spectra were obtained on a NICOLET Magna-IR 560 E.S.P. spectrometer at a resolution of about 2 cm^{-1} after 16 scans.

The polymers were characterized by ^{13}C NMR using a JEOL 270 Spectrometer operating at the following parameters: 67.93 MHz, 100 °C, 6.88 s of acquisition time, 1 s of delay. The polymer samples were prepared in tetrachloroethane in a 5 mm NMR tube.

3. Results and discussion

Scheme 1 shows the synthesis of TpTiCl$_2$(OR) (R = Me, Et, i-Pr, n-Bu) precatalysts which were tested for ethylene polymerization using MAO as co-catalyst.

3.1. Optimization of polymerization conditions

The Al/Ti ration was optimized under the following polymerization conditions: TpTiCl$_2$(OR) = 3 mg; solvent = toluene (100 ml); co-catalyst = MAO; Al/Ti = 1500–100; P = 3 bar; T = 25 °C; t = 60 min; RPM = 400. The results are summarized in Table 1 and represent averages of two or in some cases three polymerization runs, which showed good reproducibility between them.

The TpTiCl$_2$(OMe) precatalyt was activated with MAO using Al/Ti molar rations from 100 to 1500 (entries 1–5). In general, the catalytic activity of TpTiCl$_2$(OMe) increases when the Al/Ti ratio decreases and the best activity was obtained with a 100/1 ratio (entry 5). In this case, mass transfer problem and occlusion of precatalyst in the middle of the reaction were present, forcing us to stop the polymerization at 15 min. These results are in concordance with previous reports which found that at low Al/Ti ration (200) the Tp^{R}TiCl$_n$(OR$_1$)$_{3-n}$ (n = 1, 2, 3; R = H, Me, 2,4,6-trimethylphenyl (Ms); R$_1$ = t-Bu, C$_6$H$_4$-t-Bu-2) precatalysts show higher activities than Cp$_2$ZrCl$_2$ [19].

Table 1
Optimization of Al/Ti ratio using TpTiCl$_2$(OMe)/MAO

Entry	Precatalyts (mg)	Al/Ti	Temperature (°C)	Pressure (bar)	Time (min)	Yield polymer (g)	Activity × 10^{-6} (g PE/(mol Ti h atm))
1	3	1500	25	3	60	1.25	0.051
2	3	1000	25	3	60	0.59	0.024
3	3	500	25	3	60	1.38	0.056
4	3	200	25	3	15	1.68	0.275
5	3	100	25	3	15	2.74	0.448

Polymerization conditions: solvent = toluene (100 mL); RPM = 400.

Table 2
Optimization of polymerization conditions using TpTiCl$_2$(Oi-Pr)/MAO

Entry	Precatalyts (mg)	Stirring (rpm)	Pressure (bar)	Time (min)	Yield polymer (g)	Activity $\times 10^{-6}$ (g PE/(mol Ti h atm))
6	3	400	3	15	2.69	0.474
7[a]	3	400	3	15	3.09	0.545
8[a]	3	600	3	15	15.83	2.79
9	1.5	600	3	15	14.37	5.06
10	1	600	3	10	11.79	9.33
11	1	600	1	10	6.61	15.31
12	0.5	600	1	10	5.33	25.34

Polymerization conditions: solvent = toluene (100 mL); Al/Ti = 200; T = 25 °C.

[a] Toluene (200 mL).

At Al/Ti ratio of 1500 the activity is 0.051×10^6 g PE/(mol Ti h atm) while at 100 is 0.448×10^6 g PE/(mol Ti h atm), this increasing tendency implies that the chain transfer reactions to MAO or Al(CH$_3$)$_3$ of the co-catalyst predominant in the termination step.

In order to reach better activities, and to avoid the problems mentioned above, the other polymerization conditions were optimized using TpTiCl$_2$(Oi-Pr) as precatalyst. The results are shown in Table 2. When the solvent volume was increased from 100 to 200 mL (entry 6 versus 7) a small improvement of the activity was observed. However, a very significant improvement was achieved when the stirring was raised at 600 rpm (entry 7 versus 8). At this point, polymer precipitation and exothermic reaction became important which compelled us to change the precatalyst mass and reaction time (entry 8 versus 9 and 10). At these conditions the TpTiCl$_2$(Oi-Pr) exhibits an activity of 9.3×10^6 g PE/(mol Ti h atm). Finally, the ethylene pressure was reduced from 3 to 1 bar (entry 10 versus 11) producing an important increase of the activity up to 15.3×10^6 g PE/(mol Ti h atm). At these gentle reaction conditions 1 μmol of TpTiCl$_2$(Oi-Pr) affords an activity of 25.3×10^6 g PE/(mol Ti h atm) (entry 12). At the conditions used in reaction 11, mass transfer problem and occlusion of precatalyst were not present.

3.2. Ethylene polymerization by TpTiCl$_2$(OR)

From the optimization study the following conditions were chosen to evaluate the behavior of TpTiCl$_2$(OR) (R = Me, Et, i-Pr, n-Bu) series: TpTiCl$_2$(OR) = 1 mg; solvent = toluene (100 mL); co-catalyst = MAO, Al/Ti = 200; P = 1 bar; T = 25 °C; t = 10 min; RPM = 600. Table 3 summa-

rizes the influence of alkoxyl ligands on ethylene polymerization. It is worthy to mention that the values reported are averages of two or in some cases three polymerization runs, which showed good reproducibility between them.

As can be seen in the Table 3, the TpTiCl$_2$(OR) (R = Me, Et, i-Pr, n-Bu) precatalysts showed higher catalytic activities than none substituted TpTiCl$_3$ complex (entry 13 versus 14–17). This general trend has been reported in the syndiospecific polymerization of styrene by the catalytic systems IndTiCl$_2$(OR$_1$)/MAO (R$_1$ = Me, Et, i-Pr, cyclohexyl) [29,30] and CpTiCl$_2$(OR$_1$)/MAO (R$_1$ = Me, Et, i-Pr) [31–33]. In both cases the higher activity was attributed to the weakening of the Ti–Cl bond, which makes the methylation and ligand abstraction easier, causing an increase of the active species ([LTiMe]$^+$; L = Cp, Ind) formation rate. Considering that the indenyl (Ind) and cyclopentadienyl ligands are isolectronic to tris(pyrazolyl)borates ligands [34] we can assume a similar explanation for the activity behavior of TpTiCl$_2$(OR) precatalysts.

Additionally, these results show that the electronic and steric effects of the alkoxyl ligands play an important role in the catalytic behavior of the TpTiCl$_2$(OR) precatalysts. When a chlorine ligand is substituted by a OMe group the activity of TpTiCl$_2$(OMe) is 4 times higher than TpTiCl$_3$ (entry 14 versus 13) while for the OEt group the activity increases 76 times (entry 15 versus 13). However, when the alkyl chain size is increased to i-Pr or n-Bu, the activity decreases almost in half as respect to TpTiCl$_2$(OEt) (entry 15 versus 16 and 17), but in comparison with TpTiCl$_3$ the activity rises 40 times for Oi-Pr ligand (entry 16 versus 13) and 42 for On-Bu substituent (entry 17 versus 13). At the conditions used in this work the TpTiCl$_2$(OEt) exhibits an activity

Table 3
Ethylene polymerization by TpTiCl$_2$(OR)/MAO

Entry	Precatalyts	Yield polymer (g)	Activity $\times 10^{-6}$ (g PE/(mol Ti h atm))	$M_v \times 10^{-6}$ (g/mol)
13[a]	TpTiCl$_3$	0.52	0.38	0.29
14	TpTiCl$_2$(OMe)	0.71	1.57	1.94
15	TpTiCl$_2$(OEt)	12.75	29.12	2.33
16	TpTiCl$_2$(Oi-Pr)	6.61	15.31	3.48
17	TpTiCl$_2$(On-Bu)	6.80	16.73	2.56
18	Cp$_2$ZrCl$_2$	4.84	8.60	0.59

Polymerization conditions: TpTiCl$_2$(OR) = 1 mg; solvent = toluene (100 mL); Al/Ti = 200; P = 1 bar; T = 25 °C; t = 10 min; RPM = 600.

[a] 3 mg.

Table 4
Electron binding energies of the titanium core of complexes without MAO treatment

Precatalyts	BE[a] (eV)	
	Ti (2p$^{1/2}$)	Ti (2p$^{3/2}$)
TpTiCl$_3$	465.1	459.4
TpTiCl$_2$(OMe)	465.9	460.2
TpTiCl$_2$(OEt)	464.9	459.2
TpTiCl$_2$(Oi-Pr)	464.9	459.1
TpTiCl$_2$(On-Bu)	464.8	459.1

[a] *Reference:* C(1S).

of 29.12×10^6 g PE/(mol Ti h atm) which is 3.4 times higher than Cp$_2$ZrCl$_2$ (8.60×10^6 g PE/(mol Ti h atm)) at the same reaction conditions (entry 15 versus 18) and with the exception of TpTiCl$_2$(OMe) all the TpTiCl$_2$(OR) (R = Et, *i*-Pr, *n*-Bu) showed higher activity than Cp$_2$ZrCl$_2$ (entries 15–17 versus 18). In comparison with metallocene-MAO polymerization systems, which require large excess of MAO to show high activity, the TpTiCl$_2$(OR) (R = Et, *i*-Pr, *n*-Bu)/MAO systems can afford very high activities at very low concentration of MAO (Al/Ti: 200, 100).

Thus, the catalytic activity of the TpTiCl$_2$(OR) precatalysts on ethylene polymerization decreases in the order: TpTiCl$_2$(OEt) > TpTiCl$_2$(On-Bu) ≈ TpTiCl$_2$(Oi-Pr) ≫ TpTiCl$_2$(OMe) > TpTiCl$_3$.

The above tendency suggests that when a chlorine ligand of TpTiCl$_3$ is substituted by an alkoxyl ligand, the formation of the active species is promoted and might be better stabilized by π donation from the oxygen atom to the titanium center (electronic effect). This π donation to the titanium center causes the bond distance of Ti–Cl to become longer than in none substituted TpTiCl$_3$, making the methylation and ligands abstraction steps easier. This weakening of the Ti–Cl bond had been reported in

IndTiCl$_2$(OC$_6$H$_{10}$) (Ti(1)–Cl(1) 2.2526(10)Å; Ti(1)–Cl(2) 2.2719(10)Å) and IndTiCl$_2$(OMe) (Ti(1)–Cl(1) 2.274(1)Å; Ti(1)–Cl(2) 2.479(2)Å) [30,35]. In the case of IndTiCl$_3$ the Ti–Cl bonds (Ti(1)–Cl(1) 2.2248(8)Å; Ti(1)–Cl(2) 2.2319(8)Å; Ti(1)–Cl(3) 2.2355(8)Å) are stronger than alkoxide derivatives [29]. Also, this tendency was observed in the case of Tp*TiCl$_2$(O*t*-Bu) (Ti(1)-Cl(1) 2.333(9)Å; Ti(1)–Cl(2) 2.31(1)Å) [19] in comparison to Tp*TiCl$_3$ (Ti(1)–Cl(1) 2.271(1)Å; Ti(1)–Cl(2) 2.258(1)Å) [36]. Over TpTiCl$_2$(OEt) the steric effect of the alkyl chain size became important. Thus, TpTiCl$_2$(O*n*-Bu) and TpTiCl$_2$(O*i*-Pr) decrease their activities, since the coordination and insertion of the olefin to the metal center might be more sterically impeded than in TpTiCl$_2$(OEt) (steric effect).

The analysis of X-ray photoelectron spectroscopy of TpTiCl$_2$(OR) (R = Me, Et, *i*-Pr, *n*-Bu) and TpTiCl$_3$ complexes (Table 4) indicates that the TpTiCl$_2$(OR) complexes almost have the same electronic environment around the titanium center (Ti 2p$^{3/2}$), which suggests that the steric effect of the alkyl chain size might be controlling the catalytic responses.

In general, this study proves that TpTiCl$_2$(OR) derivatives with more electron donating and less steric alkoxyl ligand are more effective to enhance the catalytic response of TpTiCl$_3$.

To date information about the active species involves in these kinds of systems is still limited. However, Jordan and co-workers reported that the tris(pyrazolyl)borate ligands remain coordinated to the metallic center and a low-coordinate [Tp^r]Ti(alkyl) species is responsible for the high activity exhibit by Tp^{R}TiCl$_n$(OR$_1$)$_{3-n}$ (n = 1, 2, 3; R = H, Me, 2,4,6-trimethylphenyl (Ms); R$_1$ = *t*-Bu, C$_6$H$_4$-*t*-Bu-2). Depending on AlMe$_3$ and MAO concentration, the active species undergoes or not efficient chain transfer to AlMe$_3$, which explains the broad polydispersities observed [19].

Table 5
Electron binding energies of the titanium core of complexes after MAO treatment

Precatalyst	Ti^{n+} species	BE[a] (eV)		BE[a] (eV) deconvoluted		Total area	Percentage (%)	Ti^{3+} vs. Ti^{4+} (%)
		Ti (2p$^{1/2}$)	Ti (2p$^{3/2}$)	Ti (2p$^{1/2}$)	Ti (2p$^{3/2}$)			
TpTiCl$_3$	Ti^{3+}	466.1	460.9	464.1	459.0	20545.0	41.34	41.3
	Ti^{4+}	467.1	461.9	465.9	461.1	14472.3	29.12	56.7
	Ti^{4+}			468.3	462.7	14672.6	29.54	
TpTiCl2(OMe)	Ti^{3+}	466.3	460.8	464.6	458.9	16956.8	49.24	49.2
	Ti^{4+}	467.1	461.7	466.2	460.8	8495.9	24.67	50.8
	Ti^{4+}			468.1	462.7	8987.4	26.09	
TpTiCl2(OEt)	Ti^{3+}	464.9	459.3	462.7	457.1	16978.7	45.57	45.6
	Ti^{4+}	465.9	460.5	465.2	459.7	12249.6	32.87	54.4
	Ti^{4+}			466.7	461.2	8035.5	21.56	
TpTiCl2(O*i*-Pr)	Ti^{3+}	465.3	459.6	463.6	457.9	6918.0	28.44	28.4
	Ti^{4+}	466.2	460.4	465.2	459.2	6680.1	27.46	71.6
	Ti^{4+}			467.2	461.6	10730.3	44.10	
TpTiCl2(O*n*-Bu)	Ti^{3+}	467.7	462.2	464.9	459.2	3526.7	11.63	11.6
	Ti^{4+}	469.1	463.7	467.9	462.3	12543.4	41.37	88.4
	Ti^{4+}			470.4	465.2	14248.3	46.99	

[a] *Reference:* C(1S).

Table 6
Physical properties of synthesized polyethylenes by $TpTiCl_2(OR)/MAO$

Entry	Precatalyts	$M_v \times 10^{-6}$ (g/mol)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	(X_c) (%)
13	$TpTiCl_3$	0.29	117,1	134.5	93.9	32
14	$TpTiCl_2(OMe)$	1.94	119,7	135.3	127.7	44
15	$TpTiCl_2(OEt)$	2.33	117,6	134.7	120.0	41
16	$TpTiCl_2(Oi\text{-}Pr)$	3.48	117,8	136.1	136.5	47
17	$TpTiCl_2(On\text{-}Bu)$	2.56	117,6	137.0	135.4	46

On the other hand, Nakazawa et al. proposed the formation of more than one active species as $[TpZrMe_2]^+$ for unsubstituted $TpZrCl_3$ derivative. While for $Tp*TiCl_2(OR_1)$ ($R_1 = Ph$, $C_6H_4CN\text{-}4$, $C_6H_4Me\text{-}4$) was assumed to be $[Tp*TiR(OR_1)]^+$ which may be stabilized by π donation from the alkoxy group to the titanium center [18].

In the styrene polymerization by $IndTiCl_2(OR_1)/MAO$ ($R_1 = Me$, Et, i-Pr, cyclohexyl) and $CpTiCl_2(OR_1)/MAO$ ($R_1 = Me$, Et, i-Pr) systems, It was assumed that a really active species can be represented as $[LTiMe]^+.[MAOX]^- \cdot nMAO$ ($L = Cp$, Ind; $X = Cl$, OR_1) which activates the polymerization as a whole [29–33].

In order to have an idea about the active species number present in the ethylene polymerization process, the $TpTiCl_2(OR)$ ($R = Me$, Et, i-Pr, n-Bu) and $TpTiCl_3$ complexes were treated with MAO (Al/Ti = 200) in a nitrogen atmosphere and evaluated by XPS. The area under the curve for peaks Ti $2p^{1/2}$ and Ti $2p^{3/2}$ were deconvoluted (Table 5). Theses results show that at least two actives species can be formed which involve Ti^{3+} and Ti^{4+}. For the all precatalyst, the predominant active species is Ti^{4+}.

3.3. Polyethylene characterization

Under the conditions of the standard test method ASTM D 1238-79 the polyethylenes obtained from $TpTiCl_2(OR)$ ($R = Me$, Et, i-Pr, n-Bu) did not show melting flow index. Some properties such as crystallization temperatures (T_c), melting enthalpies (ΔH_m), crystallinity (X_c) and the viscosimetric molecular weights are shown in Table 6. The polyethylenes showed melting temperatures in the interval from 135 to 137 °C and crystallinities between 41 and 47%. The viscosimetric molecular weights are in the range of
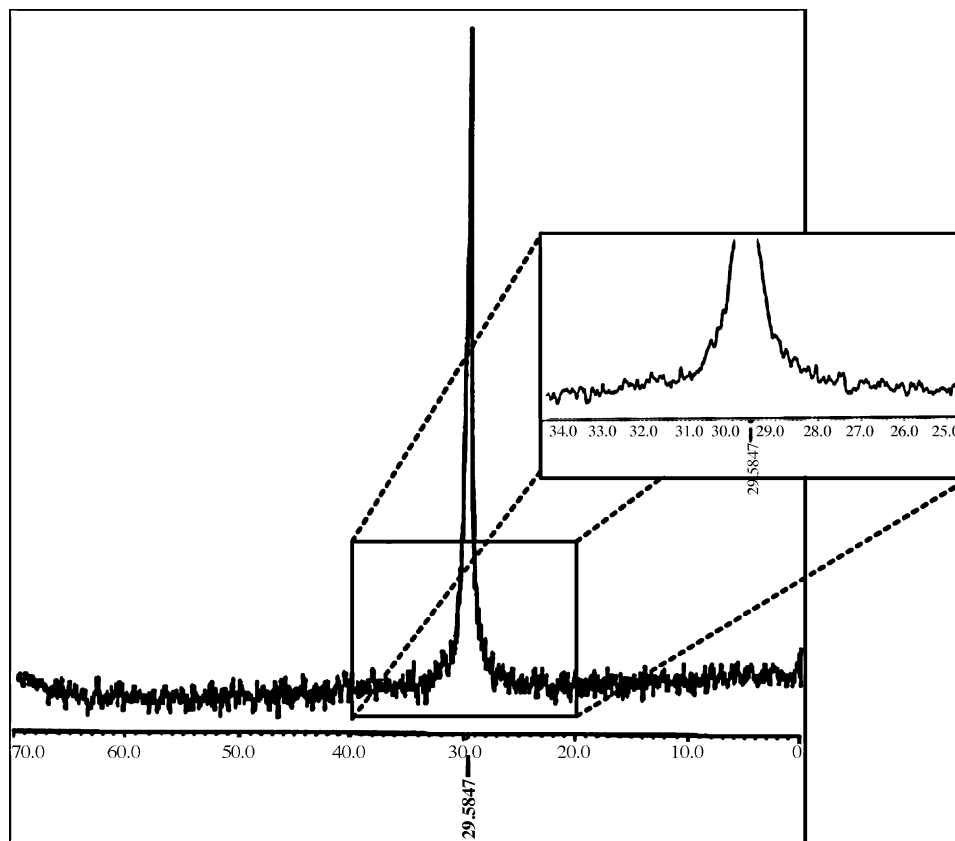

Fig. 1. ^{13}C NMR of polyethylene produce by $TpTiCl_2(On\text{-}Bu)$.

$1.94–3.48 \times 10^6$ g/mol. All these properties correspond to an ultra-high molecular weight polyethylene (UHMWPE).

The FTIR spectrum for the polyethylenes showed bands at 2950–2800, 1500–1350 and 720 cm^{-1}. Absorption bands from 850 to 1000 cm^{-1} were not observed, which indicates absence of vinyl groups (RCH=CHR′, RCH=CH$_2$, RR′C=CH$_2$) [28].

The ^{13}C NMR analysis of the polyethylenes showed only one signal of methylene group (−CH$_2$−) at 29.5 ppm (Fig. 1). Signals corresponding to terminal methyl groups (−CH$_3$) and methynyl groups (−CH−) were not detected due to their relatively low concentration with respect to the methylene groups (−CH$_2$−), which show that all polymers were mainly linear.

It is worthy to mention that the viscosimetric molecular weight is strongly influenced by the alkoxyl ligand. For example, when a chlorine ligand of TpTiCl$_3$ is substituted by methoxyl ligand the M_v increases from 0.28 to 1.94×10^6 g/mol (Table 6, entry 13 versus 14). Also, when the alkyl chain size is increased in the TpTiCl$_2$(OR) (R = Me > Et > i-Pr) the M_v increases from 1.98 to 3.48×10^6 g/mol (Table 6, entry 14 versus 15–16), suggesting that the alkyl chain reduces the chain transfer reactions and increases the propagations reactions.

4. Conclusions

In this work, we proved that the substitution of one chlorine ligand in the TpTiCl$_3$ complex for one alkoxyl ligand (OR = OMe, OEt, Oi-Pr, On-Bu) strongly increases the productivity. The catalytic activity for ethylene polymerization decreases in the order TpTiCl$_2$(OEt) > TpTiCl$_2$(On-Bu) ≈ TpTiCl$_2$(Oi-Pr) ≫ TpTiCl$_2$(OMe) > TpTiCl$_3$. The alkyl chain size of the alkoxyl ligand strongly affects the catalytic activity and the molecular weight of the polymers. Thus, at higher alkyl chain size higher activities and molecular weights. The predominant oxidation state of active species is a Ti^{4+} and Ti^{3+} can be present in minor amount. The activation of the TpTiCl$_2$(OR) (R = Me, Et, i-Pr, n-Bu) requires a very low Al/Ti ratio. The polyethylenes produced with these systems can be classified as ultra-high molecular weight with a basically linear structure.

Acknowledgements

References

[1] S. Trofimenko, J. Am. Chem. Soc. 88 (1966) 1842.

[2] K. Niedenzu, S. Trofimenko, Prog. Inorg. Chem. 34 (1986) 115;
(a) S. Trofimenko, Scorpionates; The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, 1999.

[3] S. Trofimenko, Chem. Rev. 93 (1993) 943;
(a) S. Trofimenko, Acc. Chem. Res. 4 (1971) 17;
(b) S. Trofimenko, Chem. Rev. 72 (1972) 497.

[4] N. Kitajima, W.B. Tolman, Prog. Inorg. Chem. 43 (1995) 419.

[5] C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 15 (1996) 3998.

[6] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, Organometallics 15 (1996) 5275.

[7] C. Slugovc, R. Schmid, K. Kirchner, Coord. Chem. Rev. 185–186 (1999) 109.

[8] S.M. Gorun, Z. Hu, R.T. Stibrany, G. Carpenter, Inorg. Chim. Acta 297 (2000) 383.

[9] C. Slugovc, I. Padilla-Martínez, S. Sirol, E. Carmona, Coord. Chem. Rev. 213 (2001) 129.

[10] M. Onishi, K. Ikemoto, K. Hiraki, Inorg. Chim. Acta 190 (1991) 157.

[11] W. Chan, C. Lau, Y. Chen, Y. Fang, S. Ng, Organometallics 16 (1997) 34.

[12] C. Vicente, G.B. Shul'pin, B. Moreno, S. Sabo-Etienne, B. Chaudret, J. Mol. Catal. A: Chem. 98 (1995) L5–L8.

[13] Y. Alvarado, M. Busolo, F. López-Linares, J. Mol. Catal. A: Chem. 142 (1999) 163.

[14] S. Scheuer, J. Fischer, J. Kress, Organometallics 14 (1995) 2627.

[15] D.P. Long, P.A. Bianconi, J. Am. Chem. Soc. 118 (1996) 12453.

[16] H. Katayama, K. Yamamura, Y. Miyaki, F. Ozawa, Organometallics 16 (1997) 4497.

[17] H. Katayama, T. Yoshida, F. Ozawa, J. Organomet. Chem. 562 (1998) 203.

[18] H. Nakazawa, S. Ikai, K. Imaoka, Y. Kai, T. Yano, J. Mol. Catal. A: Chem. 132 (1998) 33.

[19] S. Murtuza, O.L. Casagrande, R.F. Jordan, Organometallics 21 (2002) 1882;
(a) K. Michiue, R.F. Jordan, Macromolecules 36 (2003) 9707.

[20] A. Karam, M. Jimeno, J. Lezama, E. Catarí, A. Figueroa, B.R. De Gascue, J. Mol. Catal. A: Chem. 176 (2001) 65.

[21] F.A. Kunrath, R.F. de Souza, O.L. Casagrande, Macromol. Rapid Commun. 21 (2000) 277;
(a) M.P. Gil, O.L. Casagrande, J. Organomet. Chem. 689 (2004) 286;
(b) M.P. Gil, J.H.Z. dos Santos, O.L. Casagrande, J. Mol. Catal. A: Chem. 209 (2004) 163.

[22] L.G. Furlan, M.P. Gil, O.L. Casagrande, Macromol. Rapid Commun. 21 (2000) 1054.

[23] M.P. Gil, J.H.Z. dos Santos, O.L. Casagrande, Macromol. Chem. Phys. 202 (2001) 319.

[24] F. López-Linares, A.D. Barrios, H. Ortega, A. Karam, G. Agrifoglio, E. González, J. Mol. Catal. A: Chem. 179 (2002) 87.

[25] R. Santi, A.M. Romano, A. Sommazzi, M. Grande, C. Bianchini, G. Mantovani, J. Mol. Catal. A: Chem. 229 (2005) 191;
(a) L.G. Furlan, F.A. Kunrath, R.S. Mauler, R.F. de Souza, O.L. Casagrande, J. Mol. Catal. A: Chem. 214 (2004) 207;
(b) F.A. Kunrath, R.F. de Souza, O.L. Casagrande, N.R. Brooks, V.G. Young, Organometallics 22 (2003) 4739.

[26] J.K. Kouba, S.S. Wreford, Inorg. Chem. 15 (1976) 2313.

[27] J. Ipaktschi, W. Sulzbach, J. Organomet. Chem. 426 (1992) 59.

[28] J. Brandrup, E.H. Immergut (Eds.), Polymer Handbook, second ed., John Wiley & Sons, New York, 1975, p. V-14.

[29] T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, Macromolecules 26 (1993) 5822.

[30] H. Ma, B. Chen, J. Huang, Y. Qian, J. Mol. Catal. A: Chem. 170 (2001) 67.

[31] J. Liu, J. Huang, Y. Qian, F. Wang, A.S.C. Chan, Polym. Bull. 37 (1996) 719.

[32] J. Liu, J. Huang, Y. Qian, F. Wang, A.S.C. Chan, Polym. J. 29 (1997) 182.

[33] J. Liu, H. Ma, J. Huang, Y. Qian, Eur. Polym. J. 36 (2000) 2055.

[34] J.L. Koch, P. Shapley, Organometallics 16 (1997) 4071.

[35] J. Okuda, P. König, I.L. Rushkin, H. Kang, W. Massa, J. Organomet. Chem. 501 (1995) 37.

[36] A. Antiñolo, F. Carrillo-Hermosilla, A.E. Corrochano, J. Fernández-Baeza, M. Lanfranchi, A. Otero, M.A. Pellinghelli, J. Organomet. Chem. 577 (1999) 174.