

Ethylene polymerization by $\text{Tp}^{\text{R}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ complexes

Arquimedes Karam^{a,*}, María Jimeno^a, Jesús Lezama^b, Edgar Catarí^a,
Alfredo Figueroa^b, Blanca Rojas de Gascue^b

^a Polymer Laboratory, Chemistry Center, Venezuelan Institute for Scientific Research (IVIC),
Apartado 21827, Caracas 1020-A, Venezuela

^b Polymer Laboratory, Department of Material Science, Research Institute in Biomedicine and
Applied Sciences (IIBCA-UDO), Oriente University, Apartado 245, Cumaná, Venezuela

Received 9 January 2001; received in revised form 22 May 2001; accepted 22 May 2001

Abstract

$\text{Tp}^{\text{R}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ (where Tp = hydrotris(pyrazolyl)borate, $\text{R} = \text{H}$, Tp^* = hydrotris(3,5-dimethylpyrazolyl)borate, $\text{R} = 3,5\text{-CH}_3$; $n = 1, 2, 3$) complexes have been tested for ethylene polymerization. $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2$) activated with MAO or MMAO showed higher catalytic activity than dimethyl substituted analogues $\text{Tp}^*\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2$). Steric effects play a major role on the activity of ethylene polymerization. Successive self-nucleation/annealing (SSA) analysis showed that the polymers produced with use of $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2$) have a higher content of chain branching groups than the polymers deriving from $\text{Tp}^{\text{H}}\text{TiCl}_3$. The resulting polymers have melting temperatures characteristic of HDPE. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotris(pyrazolyl)borate; Alkoxide; Titanium; Ethylene; Polymerization

1. Introduction

Metallocene compounds of Group IV have been used as homogeneous catalysts for olefin polymerization. The most successful catalysts are the formally 14-electron, cationic species $[\text{Cp}'_2\text{MR}]^+$ ($\text{Cp}' =$ cyclopentadienyl; $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{R} =$ alkyl, H) [1–3], which contain a vacant coordination site and an alkyl or hydride ligand which can therefore readily take part in coordination polymerization (Ziegler–Natta) processes with a variety of olefins.

Another family of compounds which satisfies the apparent requirements for Ziegler–Natta catalysts

are 10-electron, monocyclopentadienyl species of the type $[\text{Cp}'\text{MR}_2]^+$. Such electronically less saturated and sterically less hindered species might exhibit even higher activities than their metallocene counterparts. Half-metallocenes have been used with success in the polymerization of hindered olefins such as isobutylene [4–6], 1-hexene [7], norbornene [8], vinyl ethers [9], as well as in the polymerization of less hindered olefins such as ethylene [10–12]. Following the global interest in developing new catalyst families [13] different from metallocenic complexes, we considered iso-electronic analogues of cyclopentadienyl such as hydrotris(pyrazolyl)borate and its 3,5-dimethyl derivatives. They are stronger electron donors and more sterically hindered than the cyclopentadienyl ligand [14,15]. The tris(pyrazolyl)borate ligands having 10

* Corresponding author. Tel.: +58-2-5041-265;

fax: +58-2-5041-350.

E-mail address: akaram@quimica.ivic.ve (A. Karam).

possible substituting positions for electron donating or withdrawing groups and for sterically more or less hindered groups, offer wider possibilities to study their effects on olefin polymerization activity more easily than with cyclopentadienyl ligands. Although the chemistry of poly(pyrazolyl)borate metal complexes is well known [14,15], only a few examples of this kind of complexes have been reported as olefins polymerization catalysts [16–19], and some of them are protected by patents [20–24]. Vanadium compounds possessing imido and hydrotris(pyrazolyl)borato ligands ($\text{Tp}^{\text{H}}\text{V}(\text{NAr})\text{Cl}_2$, $\text{Tp}^*\text{V}(\text{NAr})\text{Cl}_2$; Ar = 2,6-*i*-Pr₂-C₆H₃) activated with MAO were tested for ethylene and propylene polymerization at atmospheric pressure. The active species was not determined and polymers obtained showed low molecular weights [16]. Complexes of yttrium of the general formula $[\text{Tp}^{\text{R}_1}\text{YR}_2(\text{THF})_x]$; R₁ = H, Me, Ph; R₂ = C₆H₅, CH₂SiMe₃ and their lanthanide analogues $\text{Tp}^{\text{R}_1}\text{Ln}(\text{alkyl})_n(\text{THF})_x$ (Ln = La³⁺, Nd³⁺, Sm²⁺) were found to be active catalysts for ethylene polymerization achieving linear and very high molecular weight polymers [17]. Ring-opening metathesis polymerization (ROMP) of norbornene was performed with vinylideneruthenium complexes of the type $\text{Tp}^{\text{H}}\text{RuCl}(\text{C}=\text{C}=\text{CHPh})(\text{PPh}_3)$ and $\text{Cp}^*\text{RuCl}(\text{C}=\text{C}=\text{CHPh})(\text{PPh}_3)$ that were activated with Lewis acids as co-catalysts. The Tp^{H} complexes were found to be more active than the Cp analogue [18]. Recently, Nakazawa et al. [19] reported the use of hydrotris(pyrazolyl)borate (Tp^{H}) or hydrotris(3,5-dimethylpyrazolyl)borate (Tp^*) titanium and zirconium complexes for homo- and co-polymerization of ethylene and propylene in combination with different organoaluminum compounds. The results suggest that Tp^{H} ligand is preferable to a Cp ligand for an active species and that the dimethyl substitution increases the activity of ethylene polymerization when zirconium complexes are used. However, $\text{Tp}^*\text{Zr}(\text{OR})_3$ with very a bulky alkoxide groups showed very low activity towards ethylene polymerization.

Here, we report our results on ethylene polymerization using sterically less hindered monodimethoxy hydrotris(pyrazolyl)borate or hydrotris(3,5-dimethylpyrazolyl)borate titanium complexes using MAO or MMAO as co-catalyst. Also, the characterization of polyethylenes obtained will be discussed.

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 and MMAO were 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 $\text{Tp}^{\text{H}}\text{TiCl}_3$ [25], Tp^*TiCl_3 [26], $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ and $\text{Tp}^*\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2$) [27] were synthesized as described previously.

2.2. Polymerizations

Polymerization runs were carried out in a thermostated reactor (Buchi, Uster) fitted with a 250 ml glass vessel, using toluene as the solvent, polymerization conditions were adjusted (25–60°C; 1–6 bar; stirring 250 rpm) as required. The ethylene pressure was kept constant during polymerization by a continuous supply of ethylene. The reactor was charged with an aluminoxane toluene solution (80 ml). After saturation of the solvent with ethylene for 10 min, the polymerization was started by injection of a toluene solution (20 ml) of the catalyst (10 mg) and the mixture was stirred for 1 h. After that time, the reaction was quenched by addition of 1% HCl solution in methanol. The polymer was filtered and washed with distilled water. After stirring in distilled water overnight the polymer was filtered and dried in vacuum to constant weight.

2.3. Characterization of polyethylenes

Intrinsic viscosities of the polymer were measured in decalin at 135°C using Ubbelohde viscosimeters.

The thermal properties of the samples were studied in a Perkin-Elmer, DSC-7 calorimeter, calibrated with indium. Samples of polyethylene (10–12 mg) were sealed in an aluminum pan and were subjected to the following steps: heating at 10°C/min from room temperature to 170°C and, after 3 min at 170°C, cooling at 10°C/min from this temperature to 25°C and, finally,

heating at 10°C/min from 25 to 170°C to obtain the melting peak temperature (T_m). Melting enthalpies were converted to levels of crystallinity $(1 - \lambda)\Delta H_u$ from the ratio $\Delta H_a/\Delta H_u$, with ΔH_a and ΔH_u being the apparent and the completely crystalline heats of fusion, respectively. The value of 289 J/g [28] was taken as the enthalpy of a polyethylene crystal, ΔH_u .

During thermal properties analysis, some polymers were characterized by the successive self-nucleation/annealing (SSA) technique, which was previously reported [29–31]. The sample was melted at 172°C for 5 min. Then, it was cooled at 10°C/min to 25°C in order to create an initial “standard” thermal history. Subsequently, a heating scan at 10°C/min was performed up to a selected self-seeding and annealing temperature denoted T_s , where the sample was isothermally kept for 5 min before cooling again at 10°C/min down to 25°C. The first applied T_s is chosen so that the polymer will only self-nucleate. So, at the end of the first cooling from T_s , the polymer had been self-nucleated as was defined by Fillon et al. [32]. Then the sample was heated in the DSC once again at 10°C/min but this time up to a T_s , which is 5°C lower than the previous T_s . This procedure is repeated with T_s being lowered at 5°C intervals with respect to the previous step. The chosen T_s range was 134–57°C. Finally, the melting behavior was recorded at 10°C/min when the thermal conditioning was over.

Films for Fourier transform-infrared (FT-IR) analysis were compression-molded at 170°C for 3 min. FT-IR spectra were obtained on a Perkin-Elmer 16PC spectrometer at a resolution of about 2 cm⁻¹ after 32 scans. The FT-IR for the obtained PE showed bands at 2950, 1500–1400 and 720 cm⁻¹ which are characteristic of linear PE.

3. Results and discussion

Fig. 1 displays the structures of the pre-catalysts $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ and $\text{Tp}^*\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$, which were tested for ethylene polymerization.

3.1. Ethylene polymerization with $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2, 3$)

Treatment of $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$ and $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$ with an excess amount of MAO or MMAO results in

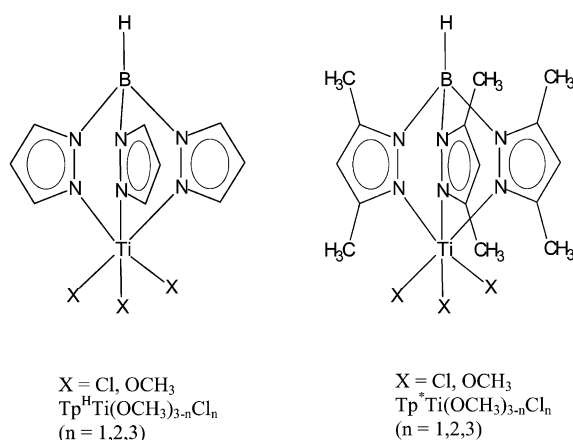


Fig. 1. Structures of $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ and $\text{Tp}^*\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2, 3$).

ethylene polymerization. The reaction conditions and results are summarized in Table 1. The results showed are averages of two or in some cases of three polymerization running, which showed good reproducibility between them. The catalytic activity of ethylene polymerization was optimized as a function of the (Al/Ti) molar ratio and of the aluminoxane used (MAO or MMAO). For $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$ (entries 1–2), the best activity was found with a molar ratio of 1000/1 using MAO as co-catalyst, which is more effective than MMAO (entries 1–6). When $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$ was used (entries 7–8), the results showed that the best activity was obtained when the molar ratio was 1000/1 with MMAO as co-catalyst. In this case, MMAO is more effective than MAO (entries 7–12) for ethylene polymerization. Entries 1 and 13 show that the addition of one methoxy to $\text{Tp}^{\text{H}}\text{TiCl}_3$ slightly increases the polymerization activity. A second methoxy (entry 7) has the opposite effect: the catalytic activity decreases to less than half. Thus, the catalytic activity for ethylene polymerization decreases in the order $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2 > \text{Tp}^{\text{H}}\text{TiCl}_3 > \text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$.

The above order suggests that when a chlorine atom of $\text{Tp}^{\text{H}}\text{TiCl}_3$ is substituted by a methoxy group, the active species $[\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Me}]^+$ might be better stabilized by π donation from the oxygen atom to the titanium center (methoxy group electronic effect) and the activity increases slightly. A second methoxy group rather than further promote the formation of the

Table 1
Ethylene polymerization with $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ and MAO or MMAO^a

Entries	Catalysts	Co-catalyst Al/[Ti] MAO, MMAO	<i>T</i> (°C) MAO, MMAO	<i>P</i> (bar) MAO, MMAO	Activity (gPE/mmol Ti bar h) MAO, MMAO
1	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	25	3	118
		500	25	3	96
2	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$	1000	25	3	131
		1000	25	3	34
3	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	25	1	81
		500	25	1	9
4	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	25	6	58
		500	25	6	31
5	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	40	3	40
		500	40	3	22
6	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	60	3	23
		500	60	3	14
7	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	25	3	39
		500	25	3	62
8	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$	1000	25	3	28
		1000	25	3	107
9	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	25	1	19
		500	25	1	21
10	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	25	6	44
		500	25	6	80
11	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	40	6	46
		500	40	6	20
12	$\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	60	6	22
		500	60	6	41
13	$\text{Tp}^{\text{H}}\text{TiCl}_3$	500	25	3	113
		500	25	3	84

^a Polymerization conditions: $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n = 10$ mg; solvent: toluene (100 ml).

active species, increases the bulk around the titanium center (methoxy group steric effect), thus decreasing the activity. Following this assumption, we expect almost no activity for $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_3$ due to reinforcement of the steric effect on the metal center, which prevents that the alkylating reagent access the Ti–OCH₃ bond, therefore eliminating any possibility of the formation of the active species.

Although the catalytic activity was optimized for a co-catalyst to catalyst ratio of 1000/1, temperature and pressure effects were determined using a 500/1 ratio in order to minimize the aluminoxane amounts used. Entries 1, 5–6, 10–12 show the temperature dependence of the complexes $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$ and $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$, respectively. In both cases, the activity decreases when the temperature increases from 25 to 60°C. The highest activities are obtained at 25°C (entries 1 and 10). At this temperature there may be less decomposition of the active species. An early report [19] has shown that large values of M_w/M_n even

at 40°C are found with this type of catalyst system, which are characteristic of different active species in the reaction medium. During the initial stage of the polymerizations the reaction temperature increases a few degrees over the selected polymerization temperature. In some cases it was almost impossible to control the temperature effectively at the beginning of the reactions.

The values of ethylene polymerization activity rise with increasing monomer pressures (from 1 to 6 bar). For $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$ a maximum activity (entries 1–4) is reached at 3 bar whereas with $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$ the rate goes up continuously (entries 7 and 9–10).

3.2. Ethylene polymerization by $\text{Tp}^*\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2, 3$)

Activation of $\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$ and $\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$ with aluminoxanes cause ethylene polymerization.

Table 2
Ethylene polymerization with $\text{Tp}^*\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ and MAO or MMAO^a

Entries	Catalysts	Co-catalyst Al/[Ti]		<i>T</i> (°C)	<i>P</i> (bar)		Activity (gPE/mmol Ti bar h)
		MAO, MMAO	MAO, MMAO		MAO, MMAO	MAO, MMAO	
14	$\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	25	25	3	30	
		500	25		3	7	
15	$\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$	1000	25	25	3	12	
		1000	25		3	5	
16	$\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	25	25	1	5	
		500	40		1	2	
17	$\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	25	25	6	11	
		500	40		6	5	
18	$\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	40	40	3	10	
		500	40		3	10	
19	$\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$	500	60	60	3	9	
		500	60		3	5	
20	$\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	25	25	3	9	
		500	25		3	14	
21	$\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$	1000	25	25	3	6	
		1000	25		3	9	
22	$\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	25	25	1	9	
		500	25		1	19	
23	$\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	25	25	6	8	
		500	25		6	9	
24	$\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	40	40	6	9	
		500	40		6	15	
25	$\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$	500	60	60	6	9	
		500	60		6	17	
26	Tp^*TiCl_3	500	25	25	3	37	
		500	25		3	14	

^a Polymerization conditions: $\text{Tp}^*\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n = 10$ mg; solvent: toluene (100 ml).

The reaction conditions and results are summarized in Table 2. Good reproducibility was observed for the different polymerizations running at the same reaction conditions. Entries 14–15 and 20–21 show that the best activities were obtained when Al/Ti ratios are 500/1 in both cases. As it is observed in the cases of $\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$ and $\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$, MAO and MMAO are more effective combined with $\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$ and $\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$, respectively. It is not clear why MMAO is more effective as co-catalyst than MAO for dimethoxy complexes.

Entries 14, 18–19 and 16–17 show the influence of temperature and pressure on the polymerization when $\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$ is employed as catalyst. As can be seen, the catalytic activity decreases with increasing temperature and overall the maximum rates were observed at pressures of 3 bar. Similar behavior was

observed with $\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$. On the other hand, for $\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$ (entries 21–25) the temperature and pressure do not have any significant effect on polymerization activity. In a few polymerizations was observed slight increasing of temperature over the selected reaction temperature during the initial stage.

In contrast to Tp^*ZrCl_3 catalyst systems [19], entries 13 and 26 show that substitution of Tp^* by Tp^* in Tp^*TiCl_3 system has an important effect on the activity. The steric effect of Tp^* exceeds its beneficial electronic effect, therefore decreasing catalytic activity for ethylene polymerization. This is in accordance with an increase of the cone angle from 199° for Tp^* to 236° for Tp^* [15]. The substitution of one chlorine ligand of Tp^*TiCl_3 by one methoxy (entries 14 and 26) causes a reduction of the activity and with a second methoxy (entries 14, 20 and 26)

the reduction became significant (steric effect versus electronic effect). In all these cases, the steric effect around the titanium center is increased each time and therefore it prevails over any favorable electronic effect. Thus, ethylene polymerization activity for the $\text{Tp}^*\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2, 3$) catalysts decreases in the order $\text{Tp}^*\text{TiCl}_3 > \text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2 > \text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$.

In a previous report, no substantial activity for ethylene and propylene homo- and co-polymerization was found when three chlorine atoms of Tp^*ZrCl_3 were replaced by *t*-butoxy or *p*-methylphenoxy groups [19]. Therefore, we expect very low activity or no activity at all for $\text{Tp}^*\text{Ti}(\text{OCH}_3)_3$ due to the fact that the Ti–OCH₃ bond might be inert towards the alkylating reagent. Furthermore, strong steric effects around the titanium atom might prevent alkylation of the metal center.

The results imply that the activity for $\text{Tp}^R\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ decreases in the order $\text{Tp}^H\text{Ti}(\text{OCH}_3)\text{Cl}_2 > \text{Tp}^H\text{TiCl}_3 > \text{Tp}^H\text{Ti}(\text{OCH}_3)_2\text{Cl} > \text{Tp}^*\text{TiCl}_3 > \text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2 > \text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$.

3.3. Polyethylene characterization

Crystallization (T_c) temperatures, melting enthalpies (ΔH_m), crystallinity ($1 - \lambda$) and the viscosimetric molecular weights of representative polymers obtained from $\text{Tp}^R\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ are shown in Table 3. The PE's samples showed melting temperatures in the interval from 130 to 135°C, which is characteristic for high density polyethylene (HDPE). However, some of their crystallinities are lower than expected for commercial HDPE [29,33], which suggest chain branching has occurred during the polymerization processes.

In order to find a relation between catalyst structures and obtained polymers, the $\text{Tp}^H\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ ($n = 1, 2, 3$) resins (entries 1, 7 and 13) were evaluated by SSA technique to determine qualitatively the short chain branching content present in the polymers. This technique is based upon accumulating several self-nucleation and annealing steps at increasingly lower temperatures every 5°C until finally a heating scan reveals the distribution of melting points of the thermally segregated fractions [29–31].

Fig. 2 shows the results of performing SSA on the HDPEs. It can be seen that the polymers have a different endotherm which suggest different content of short chain branching groups. The melting endotherm (B) reveals that the polymer obtained from $\text{Tp}^H\text{Ti}(\text{OCH}_3)\text{Cl}_2$ has several minor melting maximum in the range of lower temperature (100–128°C). The melting endotherm (A) shows that the polymer synthesized from Tp^HTiCl_3 does not present minor melting maximums in the same temperature range. These results suggest that $\text{Tp}^H\text{Ti}(\text{OCH}_3)\text{Cl}_2$ induces higher formation of branched chains in the resulting polymer than the one produced by Tp^HTiCl_3 . In the case of $\text{Tp}^H\text{Ti}(\text{OCH}_3)_2\text{Cl}$ (melting endotherm (C)), a second methoxy induces almost the same short chain branching content as $\text{Tp}^H\text{Ti}(\text{OCH}_3)\text{Cl}_2$. The melting endotherms ((A)–(C)) show in the high temperature range (128–140°C) that the polymer obtained from Tp^HTiCl_3 displays less crystallizable fractions than the polymers obtained from $\text{Tp}^H\text{Ti}(\text{OCH}_3)\text{Cl}_2$ and even less than $\text{Tp}^H\text{Ti}(\text{OCH}_3)_2\text{Cl}$, which suggest that the main chains of the polymers from $\text{Tp}^H\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ have been branched more frequently. Therefore, the addition of methoxy groups to Tp^HTiCl_3 induces branching of the main chain.

Table 3
Physical properties of synthesized polyethylenes with MAO

Entries	Catalysts	T_c (°C)	ΔH_m (J/g)	(1 - λ) (%)	M_v (10^4)
1	$\text{Tp}^H\text{Ti}(\text{OCH}_3)\text{Cl}_2$	114	164	57	18.5
7	$\text{Tp}^H\text{Ti}(\text{OCH}_3)_2\text{Cl}$	114	126	44	34.6
13	Tp^HTiCl_3	115	153	53	38.7
14	$\text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2$	115	76	26	4.2
20	$\text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$	115	160	56	47.1
26	Tp^*TiCl_3	114	192	67	3.7

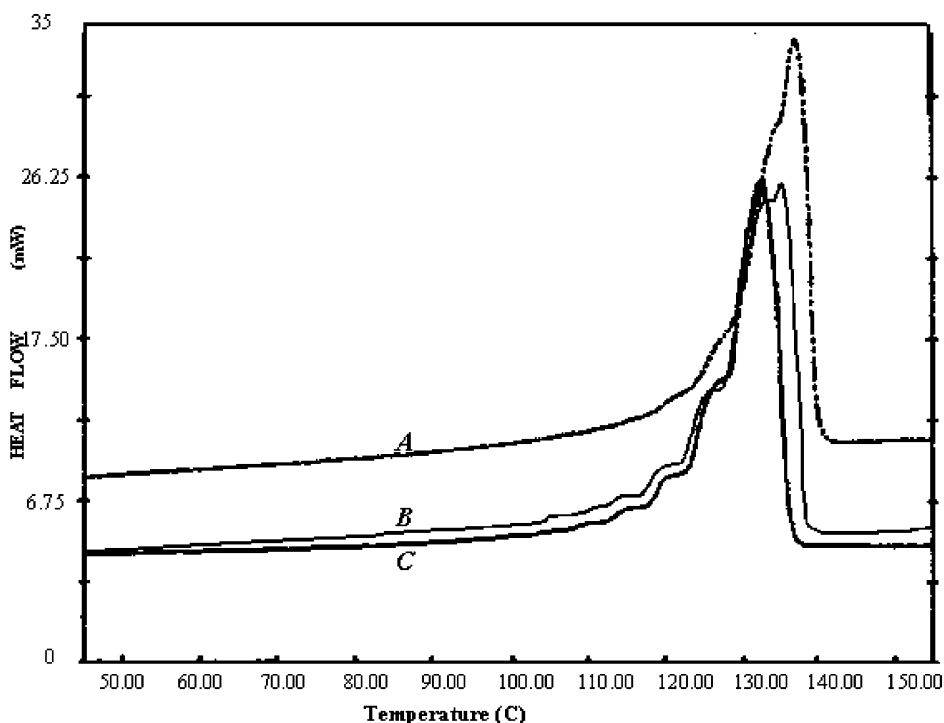


Fig. 2. Final DSC heating scans at 10°C/min after applying successive self-nucleation/annealing (SSA) to HDPEs obtained from $\text{Tp}^{\text{H}}\text{TiCl}_3$ (A), $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2$ (B) and $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$ (C).

4. Conclusions

The addition of one methoxy group to $\text{Tp}^{\text{H}}\text{TiCl}_3$ slightly increases the polymerization activity and a second one decreases the activity. The catalytic activity for ethylene polymerization decreases in the order $\text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)\text{Cl}_2 > \text{Tp}^{\text{H}}\text{TiCl}_3 > \text{Tp}^{\text{H}}\text{Ti}(\text{OCH}_3)_2\text{Cl}$. The substitution of Tp^{H} by Tp^* in $\text{Tp}^{\text{R}}\text{Ti}(\text{OCH}_3)_{3-n}\text{Cl}_n$ systems strongly decreases the polymerization activity. The catalytic activity decreases in the order $\text{Tp}^*\text{TiCl}_3 > \text{Tp}^*\text{Ti}(\text{OCH}_3)\text{Cl}_2 > \text{Tp}^*\text{Ti}(\text{OCH}_3)_2\text{Cl}$. The addition of just one methoxy group to $\text{Tp}^{\text{H}}\text{TiCl}_3$ induces chain branching within linear HDPE.

Acknowledgements

We acknowledge the Chemistry Center of Venezuelan Institute for Scientific Research (IVIC) for finan-

cial support of this research. Also CONICIT for the Grants S1-2000000519 and S1-98001906.

References

- [1] H.H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143.
- [2] M. Bochmann, *J. Chem. Soc., Dalton Trans.* (1996) 255.
- [3] P.C. Mohring, N.J. Coville, *J. Organomet. Chem.* 479 (1994) 1.
- [4] F. Barsan, M.C. Baird, *J. Chem. Soc., Chem. Commun.* (1995) 1065.
- [5] F. Barsan, A.R. Karam, M.A. Parent, M.C. Baird, *Macromolecules* 31 (1998) 8439.
- [6] M.C. Baird, A.R. Karam, M.A. Parent, US Provisional Patent Application 60/083,276 (1998).
- [7] M.C. Murray, M.C. Baird, *J. Mol. Catal.* 128 (1998) 1.
- [8] J. Dusan, Q. Wang, Q. Rukhsana, M. Baird, *J. Organomet. Chem.* 497 (1995) 143.
- [9] Q. Wang, M.C. Baird, *Macromolecules* 28 (1995) 8021.
- [10] Q. Rukhsana, Q. Wang, M.J. Tudoret, M.C. Baird, D.J. Gillis, *J. Am. Chem. Soc.* 116 (1994) 6435.

- [11] B. Rieger, *J. Organomet. Chem.* 420 (1991) C17.
- [12] C. Pellecchia, P. Longo, A. Proto, A. Zambelli, *Makromol. Chem. Rapid Commun.* 13 (1992) 277.
- [13] G.J. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 428.
- [14] S. Trofimenko, *Chem. Rev.* 93 (1993) 943.
- [15] N. Kitajima, W.B. Tolman, *Prog. Inorg. Chem.* 43 (1995) 419.
- [16] S. Scheuer, J. Fischer, J. Kress, *Organometallics* 14 (1995) 2627.
- [17] D.P. Long, P.A. Bianconi, *J. Am. Chem. Soc.* 118 (1996) 12453.
- [18] H. Katayama, T. Yoshida, F. Ozawa, *J. Organomet. Chem.* 562 (1998) 203.
- [19] H. Nakazawa, S. Ikai, K. Imaoka, Y. Kai, T. Yano, *J. Mol. Catal.* 132 (1998) 33.
- [20] Dow Chemical, US Patent 5,237,069 (1993).
- [21] Industrial Technology Research Institute, US Patent 5,519,099 (1996).
- [22] Asahi Chemicals, Japanese Laid Patent 70224 (1995).
- [23] Tonen Chemicals, Japanese Laid Patent 95110 (1989).
- [24] Dow Chemicals, Japanese Laid Patent, 305585 (1992).
- [25] P. Burchill, M.G.H. Wallbridge, *Inorg. Nucl. Chem. Lett.* 12 (1976) 93.
- [26] J.K. Kouba, S.S. Wreford, *Inorg. Chem.* 15 (1976) 93.
- [27] J. Ipaktschi, W. Sulzbach, *J. Organomet. Chem.* 426 (1992) 59.
- [28] J.G. Fatou, *Morphology and Crystallization in Polyolefins*, in: C. Vasile, R.B. Seymour (Eds.), *Handbook of Polyolefins*, Marcel Dekker, 1993 (Chapter 8).
- [29] A.J. Muller, Z. Hernandez, M. Arnal, J. Sanchez, *Polym. Bull.* 39 (1997) 465.
- [30] L. Marquez, I. Rivero, A.J. Muller, *Macromol. Chem. Phys.* 200 (1999) 330.
- [31] M.L. Arnal, A.J. Muller, *Macromol. Chem. Phys.* 200 (1999) 2559.
- [32] B. Fillon, J.C. Wittman, B. Lotz, A. Thierry, *J. Polym. Sci. Polym. Phys. Ed.* 23 (1989) 265.
- [33] J. Brandrup, E.H. Immergut (Eds.), *Polymer Handbook*, 2nd Edition, Wiley, New York, 1975, p. V-14.