

Titanium and Vanadium Ethylene Polymerization Catalysts Containing Tris(Pyrazolyl)Borate Ligand: Effects of Polymerization Parameters on Activity and Polymer Properties

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O comportamento nas reações de polimerização de etileno envolvendo uma série de complexos de titânio(IV) e vanádio(V), $[\text{Tp MXCl}_2]$ (**1**, M= Ti, $\text{Tp}' = \text{Tp}^{\text{Ms}*}$, X = Cl; **2**, M = Ti, $\text{Tp}' = \text{Tp}^{\text{Ms}}$, X = Cl; **3**, M = V, $\text{Tp}' = \text{Tp}^{\text{Ms}*}$, X = N^tBu; **4**, M = V, $\text{Tp}' = \text{Tp}^{\text{Ms}*}$, X = NAr) ($\text{Tp}^{\text{Ms}*} = \text{HB}(3\text{-mesitila-pirazolil})_2(5\text{-mesitila-pirazolil})^-$, $\text{Tp}^{\text{Ms}} = \text{HB}(3\text{-mesitila-pirazolil})_3^-$, Ar = 2,6-^tPr₂-C₆H₃) foi investigado em tolueno ou hexano na presença de MAO ou TiBA/MAO (1:1) como cocatalisadores e variando a temperatura de polimerização. Os resultados de polimerização mostraram que independentemente do tipo de precursor catalítico, altas atividades foram obtidas usando o sistema TiBA/MAO/hexano. Para as espécies de titânio, máxima atividade catalítica foi alcançada à 60 °C enquanto que para as espécies de vanádio as mais altas atividades foram obtidas à 30 °C. Estudos relacionados à influência da razão molar $[\text{Al}]/[\text{M}]$ (M = Ti, V) mostraram que estes precursores catalíticos apresentaram altas atividades catalíticas utilizando concentrações de Al tão baixas quanto 50:1. As curvas de DSC mostraram a produção de polietilenos lineares com temperaturas de fusão entre 123 e 140 °C. Os pesos moleculares viscosimétricos dos polietilenos estão no intervalo de 7×10^3 - $16,4 \times 10^6 \text{ g mol}^{-1}$.

The ethylene polymerization behavior of a series of titanium(IV) and vanadium(V) complexes, $[\text{Tp MXCl}_2]$ (**1**, M= Ti, $\text{Tp}' = \text{Tp}^{\text{Ms}*}$, X = Cl; **2**, M = Ti, $\text{Tp}' = \text{Tp}^{\text{Ms}}$, X = Cl; **3**, M = V, $\text{Tp}' = \text{Tp}^{\text{Ms}*}$, X = N^tBu; **4**, M = V, $\text{Tp}' = \text{Tp}^{\text{Ms}*}$, X = NAr) ($\text{Tp}^{\text{Ms}*} = \text{HB}(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^-$, $\text{Tp}^{\text{Ms}} = \text{HB}(3\text{-mesityl-pyrazolyl})_3^-$, Ar = 2,6-^tPr₂-C₆H₃) was investigated in toluene or hexane using MAO or TiBA/MAO (1:1) as activators, and varying the polymerization temperature. The polymerization results showed that independently of the catalysts precursors used in the polymerization run, higher activities were found using TiBA/MAO/hexane system. For titanium species, the maximum catalytic activities were reached at 60 °C while for vanadium ones the highest activities were attained at 30 °C. Studies related to the influence of the $[\text{Al}]/[\text{M}]$ molar ratio (M = Ti, V) have shown that these catalyst precursors presented highest activities using Al concentrations as low as 50:1. DSC curves showed the production of linear polyethylene with melting temperature in the range of 123-140 °C. The viscosity average molecular weights of the polyethylenes are in the range of 7×10^3 - $16.4 \times 10^6 \text{ g mol}^{-1}$.

Keywords: titanium (IV), vanadium (V), tris(pyrazolyl)borate, ethylene polymerization, HDPE, UHMWPE

Introduction

The chemistry of the non-metallocene catalysts has grown considerably over the past decade, largely due to the remarkable variety of non-cyclopentadienyl ligands available and their high-performance in olefin polymerization.¹⁻³ Among the several classes of the alternative ligands, special attention has been devoted to tris(pyrazolyl)borate.⁴⁻¹³ Tris(pyrazolyl)borate ligands (Tp) have been widely used in coordination and organometallic chemistry as stabilizing groups in high-oxidation state

transition metal complexes considering their strong electron donor ability. Furthermore, the steric and electronic properties of the pyrazolyl donors can be modified by varying substituents 3 and 5 determining attractive properties for the Tp-metal complex.¹⁴ In recent years, we have been interested in exploring the chemistry of Group 4 and 5 complexes that contain sterically hindered tris(pyrazolyl)borate ligands with the aim of developing novel olefin polymerization catalysts.¹⁵⁻²⁴ To date, studies involving a set of $[\text{Tp}'\text{MCl}_3]$ complexes containing Tp' ligands with diverse steric properties (M = Ti, Zr; $\text{Tp}' = \text{HB}(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^-$ ($\text{Tp}^{\text{Ms}*}$), $\text{HB}(3\text{-mesityl-pyrazolyl})_3^-$ (Tp^{Ms}), $\text{HB}(3\text{-neopentyl-}$

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modified Ubelohde viscometer at 135 °C. Based on the experimental intrinsic viscosity values $[\eta]$ it was possible to calculate the viscometric molar mass according to the formula $[\eta] = k(\overline{M}_v)^\alpha$ for $k = 6.7 \times 10^{-4} \text{ dL g}^{-1}$ and the $\alpha = 0.67$.²⁶

Results and Discussion

Polymerization studies involving tris(pyrazolyl)borate titanium catalysts

Ethylene polymerization studies involving $[\text{Tp}^{\text{M}^{\text{s}^*}}\text{TiCl}_3]$ (**1**, $\text{Tp}^{\text{r}} = \text{Tp}^{\text{M}^{\text{s}^*}}$; **2**, $\text{Tp}^{\text{r}} = \text{Tp}^{\text{M}^{\text{s}}}$) were carried out in toluene or hexane at 60, 75 and 90 °C using methylaluminoxane (MAO) or a mixture of triisobutylaluminum (TiBA) and MAO (1:1) as activator system. The polymerization results are summarized in Table 1. As expected, the more sterically open catalyst **1** showed higher activities relative to the catalyst precursor **2** independently of the polymerization conditions used in this study. It is interesting to point out that for the polymerization reactions performed in hexane the activities displayed by **1** and **2** are closer than those ones obtained in toluene. For instance, in toluene at 60 °C the catalyst precursor **1** was ca. 2.2 times more active than **2** (Table 1, entry 1 vs 10) while the use of hexane instead of toluene determined a difference of only 1.4 times (Table 1, entry 4 vs 13).

The influence of the activator is better visualized in Figures 1 and 2. In general, higher activities were found in hexane using TiBA/MAO (1:1) as activator system, mainly in the case of catalyst precursor **2**. It seems that under these

polymerization conditions, the combination of MAO in suitable Al content, combined with the scavenger properties of TiBA affords better conditions to stabilize the active species. Besides, TMA, which is present in commercial MAO, can act as a poison in the polymerization reaction. In recent studies involving **1**, Jordan et al. have suggested that the TMA present in MAO coordinates to active species disfavoring the monomer coordination.^{15,27-29} Therefore, the higher activity observed in the case of TiBA/MAO (1:1) could also be due to the lower nominal amount of MAO which was employed in the polymerization reaction.

The influence of polymerization temperature on activity has been evaluated in the range of 60-90 °C, at $[\text{Al}]/[\text{Ti}] = 1000$. For the polymerization reactions carried

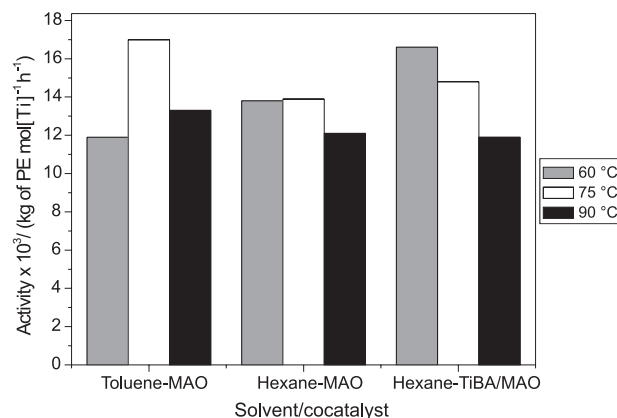


Figure 1. Influence of polymerization temperature and solvent/activator system on activity of **1**.

Table 1. Ethylene polymerization results using $[\text{Tp}^{\text{M}^{\text{s}^*}}\text{TiCl}_3]$ (**1**) and $[\text{Tp}^{\text{M}^{\text{s}}}\text{TiCl}_3]$ (**2**)^a

Entry	cat.	[Ti] (μmol)	cocat.	solvent	T_p (°C)	Activity ^b (10^{-3})	T_m (°C)	χ (%)	η^c (dL g^{-1})	(\overline{M}_v) ($\times 10^{-3}$)
1	1	14.41	MAO	toluene	60	11.9	137	81	1.50	100
2	1	14.27	MAO	toluene	75	17.0	131	98	1.10	78
3	1	13.85	MAO	toluene	90	13.3	129	92	0.25	7
4	1	15.79	MAO	hexane	60	13.8	139	68	1.80	130
5	1	13.99	MAO	hexane	75	13.9	134	76	1.75	126
6	1	15.24	MAO	hexane	90	12.1	132	81	0.38	13
7 ^d	1	13.85	TiBA/MAO ^d	hexane	60	16.6	134	84	2.18	180
8	1	14.27	TiBA/MAO	hexane	75	14.8	132	86	1.52	102
9	1	14.27	TiBA/MAO	hexane	90	11.9	128	88	0.22	6
10	2	13.44	MAO	toluene	60	5.3	137	79	3.55	360
11	2	13.44	MAO	toluene	75	9.9	133	91	0.71	33
12	2	13.58	MAO	toluene	90	8.8	130	86	-	-
13	2	14.27	MAO	hexane	60	10.1	136	59	5.60	710
14	2	13.85	MAO	hexane	75	10.7	138	79	2.81	255
15	2	14.96	MAO	hexane	90	9.0	133	99	0.61	26
16	2	13.44	TiBA/MAO	hexane	60	16.1	136	65	6.18	830
17	2	14.13	TiBA/MAO	hexane	75	12.3	137	89	4.78	564
18	2	13.71	TiBA/MAO	hexane	90	8.7	134	73	3.47	350

Polymerization conditions: ^a Reactor Büchi (2L); $\text{PC}_2\text{H}_4 = 5.2 \text{ atm}$, $[\text{Al}]/[\text{Ti}] = 1000$, Polymerization time = 5 min, volume of solvent = 1L; ^b kg of PE $\text{mol}[\text{Ti}]^{-1} \text{ h}^{-1}$; ^c Calculated from the experimental intrinsic viscosities ($[\eta]$, decaline at 135°C) according to the $[\eta] = k(\overline{M}_v)^\alpha$ with $k = 6.7 \times 10^{-4} \text{ dL g}^{-1}$ and $\alpha = 0.67$; ^d Polymerization time = 3 min; molar ratio TiBA/MAO = 1:1.

out in the presence of MAO, higher activities were obtained at 75 °C, with a slight decrease at 90 °C suggesting that higher temperatures can result in higher rates of catalyst deactivation as can be seen in Figures 1 and 2. On the other hand, for the polymerization reactions performed using a combination of activators (TiBA/MAO), higher activities were found at 60 °C, which decrease at higher polymerization temperatures (75 and 90 °C). Based on these results above mentioned we can speculate that the catalytic species generated under TiBA/MAO activation are more thermal sensitive than those produced in the presence of MAO. Nevertheless, we cannot neglect the higher solubility of TMA in hexane at higher temperature, which would be responsible to initiate a deactivation process of the catalytic species.

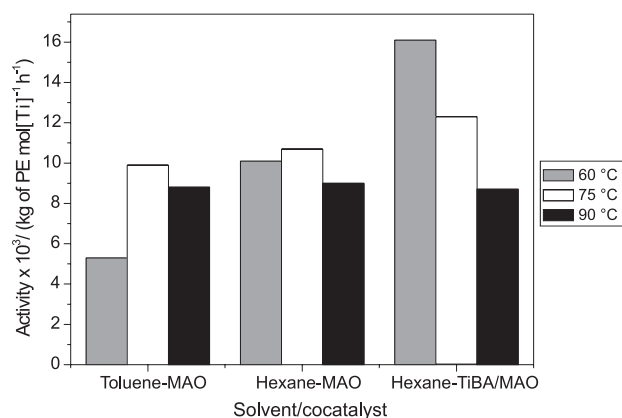


Figure 2. Influence of polymerization temperature and solvent/activator system on activity of **2**.

The polymer properties have been evaluated by means of differential scanning calorimetry (DSC), and intrinsic viscosity measurements. Characteristics of the resulting polymers are shown in Table 1.

According to Table 1, most of the melting temperatures (T_m) of the polyethylenes are higher than 130 °C, indicating the formation of high-density polyethylene (HDPE). In addition, most of the resulting polymers present high crystallinities. According to viscosity measurements, molecular weight remained comprised between 6 and $830 \times 10^3 \text{ g mol}^{-1}$. Higher viscosity average molecular weights (\overline{M}_v) were found using the most sterically crowded titanium catalyst **2** in hexane and using TiBA/MAO as activator system as consequence of lower degree of chain transfer process to Al as demonstrated previously.¹⁵ Figure 3 represents the correlation between solvent system and (\overline{M}_v) varying the polymerization temperature using catalyst precursor **2**.

Polymerization runs in which the temperature was varied reveal that an increase in temperature results in large decreases in molecular weight. For instance, the viscosity

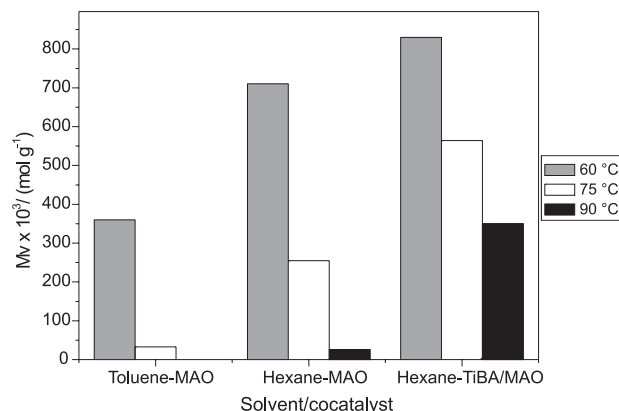


Figure 3. Influence of polymerization temperature and solvent/activator system on the viscosity average molecular weight using **2**.

average molecular weight (\overline{M}_v) is considerably reduced [from 100 000 at 60 °C to 7 000 at 90 °C (**1**, toluene/MAO catalyst system, entries 1-3); from 710 000 at 60 °C to 26 000 at 90 °C (**2**, hexane/MAO catalyst system, entries 13-15)]. For these cases, the lower molecular weight products obtained at elevated temperatures can be reasonably ascribed to the higher chain-transfer rates.

To investigate the effects of the [Al]/[Ti] molar ratio on activity, polymerizations of ethylene were performed with catalyst precursor **1** at 60 °C, varying the [Al]/[Ti] ratio from 100 to 2000. Representative data for ethylene polymerizations are summarized in Table 2.

Table 2. Effect of the [Al]/[Ti] molar ratio on activity using [Tp^{Ms}*TiCl₃] (**1**)^a

Entry	[Ti] (μmol)	[Al]/[Ti]	activity ^b (10^{-3})	T _m (°C)	χ (%)
19	14.27	100	13.6	134	83
20	13.99	500	14.1	132	85
21	13.85	1000	16.6	134	84
22	14.55	2000	21.4	134/129	63

Polymerization conditions: ^a Büchi reactor (2L); PC₂H₄ = 5.2 atm; hexane (1 L); temperature of polymerization = 60 °C; polymerization time = 3 min; molar ratio TiBA/MAO = 1:1; ^b kg of PE mol [Ti]⁻¹ h⁻¹.

The polymerization results show that the use of a ratio of at least 100:1 is necessary to produce a highly active catalyst system. Nevertheless, it is worth to point out that the use of higher [Al]/[Ti] molar ratios (500 and 1000) did not cause an accentuated increase in activity (Table 2, entry 19 vs 20-21). The maximum activity was achieved at 2000:1 (Table 2, entry 22, $21.4 \times 10^3 \text{ kg of PE mol [Ti]}^{-1} \text{ h}^{-1}$). The DSC results have shown that the [Al]/[Ti] molar ratio does not seem to have a relevant effect on T_m of the polyethylenes ($T_m = 132\text{-}134 \text{ °C}$). However, it should be pointed out that the appearance of two peaks in the

polyethylene produced using high concentration of Al (Table 2, entry 22) suggests the formation of at least two different catalytic species.

Polymerization studies involving tris(pyrazolyl)borate vanadium catalysts

To get a survey of the polymerization activity of tris(pyrazolyl)borate vanadium catalysts, $[\text{Tp}^{\text{Ms}^*}\text{VCl}_2(\text{NR})]$ (**3**, R = ^tBu; **4**, R = 2,6-ⁱPr₂-C₆H₃) the ethylene polymerizations have been investigated at a temperature range from 0 to 60 °C and using different activator systems (MAO or TiBA/MAO). The results are summarized in Table 3. Figures 4 and 5 show the influence of the temperature, solvent, and activator system on the performance of **3** and **4**.

Higher activities were obtained using hexane as solvent (Table 3, entries 23-25 vs 26-28 or 32-34 vs 35-37). The

available data for these catalytic systems are very limited at present, however, based on the studies performed by McConville *et al.* related to non-metallocene titanium compounds,^{30,31} we speculate that the lower activity of these catalytic species in toluene could be associated to the coordination capacity of toluene to vanadium, which might engender a competition between the coordinating olefin and the solvent itself as presented in Scheme 1.

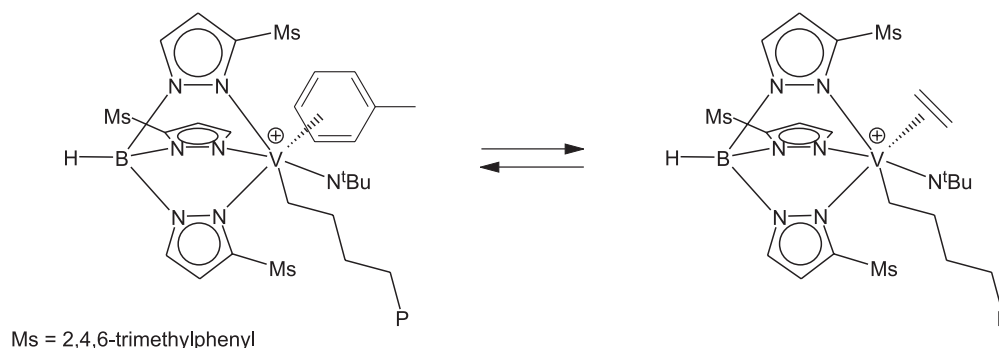
The vanadium complex **3** was somewhat more active than **4**, and very high activities ($> 10.1 \times 10^3$ kg of PE mol[V]⁻¹ h⁻¹) can be achieved utilizing TiBA/MAO as activator system (Table 3, entries 29-31). As observed for titanium catalyst precursors **1-2**, the optimized catalytic activity for **3-4** has been found using hexane as solvent in the presence of TiBA and MAO as activator system.

In general, the influence of the polymerization temperature on the activity of **3** and **4** demonstrates a

Table 3 - Results of ethylene polymerization using $[\text{Tp}^{\text{Ms}^*}\text{VCl}_2(\text{N}^t\text{Bu})]$ (**3**) and $[\text{Tp}^{\text{Ms}^*}\text{VCl}_2(\text{NAr})]$ (**4**)^a

Entry	cat.	[V] (μmol)	Cocat.	Solvent	T _p (°C)	activity ^b (10 ⁻³)	T _m (°C)	η ^c (dL g ⁻¹)	\overline{M}_v (× 10 ⁻⁶)
23	3	7.24	MAO	toluene	0	3.7	132	-	-
24	3	7.11	MAO	toluene	30	10.6	137	38.4	12.5
25	3	6.85	MAO	toluene	60	3.8	134	-	-
26	3	6.71	MAO	hexane	0	4.6	136	-	-
27	3	7.24	MAO	hexane	30	11.6	138	-	-
28	3	7.14	MAO	hexane	60	10.9	127	28.2	7.9
29	3	7.30	TiBA/MAO ^d	hexane	0	10.3	139	-	-
30	3	7.11	TiBA/MAO	hexane	30	14.5	137	46.1	16.4
31	3	7.50	TiBA/MAO	hexane	60	10.1	139	-	-
32	4	7.53	MAO	toluene	0	1.8	140	-	-
33	4	7.53	MAO	toluene	30	3.3	123	9.0	1.4
34	4	7.18	MAO	toluene	60	1.8	109/132	-	-
35	4	7.76	MAO	hexane	0	3.0	139	-	-
35	4	7.87	MAO	hexane	30	3.6	140	23.9	6.2
37	4	7.29	MAO	hexane	60	2.3	137	-	-
38	4	6.71	TiBA/MAO	hexane	0	2.1	139	-	-
39	4	6.83	TiBA/MAO	hexane	30	4.0	139	19.7	4.6
40	4	7.06	TiBA/MAO	hexane	60	1.2	137	-	-

Polymerization conditions: ^a Büchi reactor (2L); PC₂H₄ = 5.2 atm; [Al]/[V] = 878; polymerization time = 5 min; volume of solvent = 1L; ^b kg of PE mol[V]⁻¹ h⁻¹; ^c Calculated from the experimental intrinsic viscosities ([η], decaline at 135 °C) according to the $[\eta] = k(\overline{M}_v)^\alpha$ with $k = 6.7 \times 10^{-4}$ dL·g⁻¹ and $\alpha = 0.67$; ^d molar ratio TiBA/MAO = 1:1.



Scheme 1. Plausible competition between toluene and ethylene monomer towards coordination to the vanadium atom using the catalyst system $[\text{Tp}^{\text{Ms}^*}\text{VCl}_2(\text{N}^t\text{Bu})]$ /activator.

significant increase of the polymerization conversion by an enhancement of the temperature from 0 to 30 °C as a consequence of higher solubility of the activator at this temperature (30 °C) (Figures 4 and 5). A further increase to 60 °C leads to a decrease of the polymerization conversion, indicating reduced complex stability, resulting in a lower activity of the vanadium catalyst systems in the presence of TiBA and MAO at higher temperatures, mainly for catalyst precursor **4**.

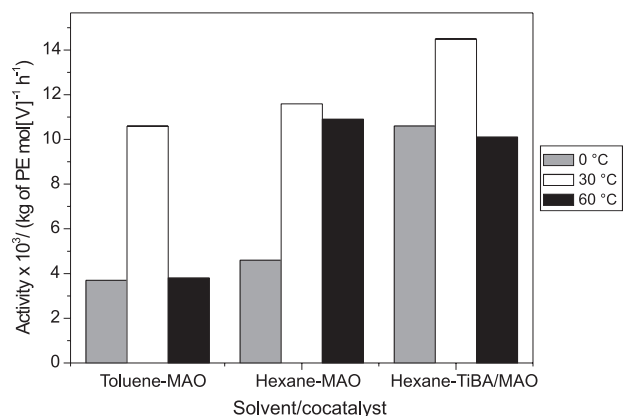


Figure 4. Influence of polymerization temperature and solvent/activator system on activity of catalyst precursor **3**.

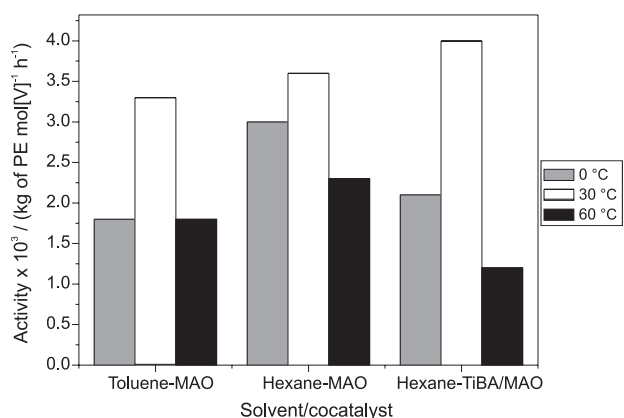


Figure 5. Influence of polymerization temperature and solvent/activator system on activity of catalyst precursor **4**.

Polyethylenes produced by **3** and **4** were firstly characterized by differential scanning calorimetry (DSC). DSC curves of the PE showed T_m in the range from 123 to 140 °C. Exceptionally, the DSC curve of the PE produced by **4** with MAO in toluene at 60 °C (Table 3, entry 34) shows clearly the appearance of two peaks in distinct temperature regions suggesting formation of two different catalyst species in the polymerization medium (Figure 6).

Resulting polyethylenes were insoluble in decaline using standard viscosimetric analysis procedures (135 °C/concentrations of 0.1 g dL⁻¹). Thus, a modified procedure was adopted wherein the PE sample was dissolved in

decaline at 165 °C using 0.02 g dL⁻¹ and the solution was quickly transferred to a viscosimeter at 135 °C. The viscosity-average molecular weights (\bar{M}_v) of the PE's produced with **3-4** are in the range of 1.4–16.4 x 10⁶ g mol⁻¹ indicating the production of ultra-high molecular weight polymers (UHMWPE). The lower (\bar{M}_v) obtained for the PE's produced with **4** related to those ones obtained using **3** (entry 24 vs 33 and entry 30 vs 39) can be associated to higher activity of this latter catalyst.

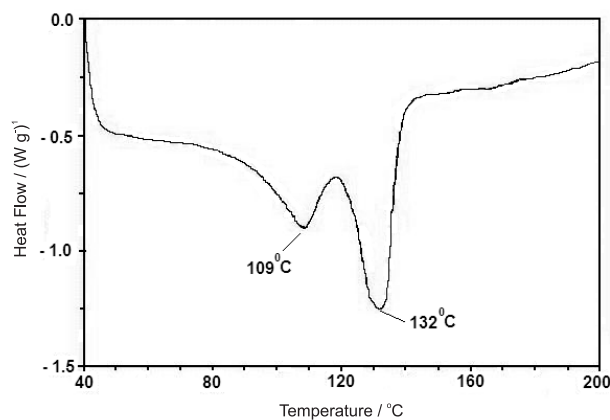


Figure 6. DSC curve corresponding to the PE produced by **4** in the polymerization reaction using toluene/MAO polymerization system at 60 °C.

Considering the higher activity of **3**, an additional study was carried out aiming at evaluating the influence of the [Al]/[V] molar ratio on activity. One set of experiment was performed using hexane as solvent at 30 °C, utilizing TiBA/MAO as the activator system. The results are summarized in Table 4. As observed for titanium compounds, the use of low concentrations of Al determines the formation of highly active catalytic species. Polymerization runs varying the [Al]/[V] molar ratio from 50:1 to 3000:1 revealed that the system is active at [Al]/[V] molar ratio as low as 50:1 (6.6 x 10³ kg of PE mol[V]⁻¹ h⁻¹). Maximum activity was attained using [Al]/[V] molar ratio of 2000:1 (14.6 x 10³ kg of PE mol[M]⁻¹ h⁻¹). Increasing the [Al]/[V] molar ratio to 3000 resulted in lower activity (11.0 x 10³ kg of PE mol[M]⁻¹ h⁻¹). According to these results and taking into account the high cost of the MAO, the optimum Al concentration required to obtain a good performance of the vanadium catalyst has been found using [Al]/[V] molar ratio of 100:1.

The viscosimetric analysis of the PE produced varying the [Al]/[V] molar ratio failed due to the insolubility of these polymer samples in decaline even using high temperature (165 °C). From the DSC analysis, it was observed that the [Al]/[V] molar ratio does not seem to have a relevant effect on melting temperatures of the polyethylenes (T_m = 138–140 °C).

Table 4. Effect of the [Al]/[V] molar ratio on the activity using [Tp^{Me}VCl₂(NtBu)](3)^a

entry	[V] (μmol)	[Al]/[V]	activity ^a (10 ⁻³)	T _m (°C)	χ (%)
41	7.37	50	6.6	138	55
42	6.58	100	10.2	138	58
43	7.24	878	11.6	138	31
44	6.45	2000	14.6	140	55
45	7.37	3000	11.0	138	61

Polymerization conditions: ^a Büchi reactor (2L); PC₂H₄ = 5.2 atm; hexane (1 L); temperature of polymerization = 30°C; polymerization time = 5 min; ^b kg of PE mol[V]⁻¹ h⁻¹; molar ratio TiBA/MAO = 1:1.

Conclusions

Our studies have demonstrated that the performance of the titanium and vanadium catalysts is strongly influenced by the polymerization parameters such as solvent, polymerization temperature, and activator systems. Higher activities have been found in hexane under TiBA/MAO activation conditions. Furthermore, higher activities were obtained using very low concentration of Al. Titanium catalysts showed best polymerization performance at 60 °C while the vanadium catalysts displayed higher activities at 30 °C. These catalyst systems produce polymers with a wide range of molecular weights, depending on the metal center and polymerization conditions; titanium species produced polyethylenes with lower (\overline{M}_v) than those ones produced by vanadium catalysts which have been characterized as ultra-high molecular weight.

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