

Ethylene polymerization with hafnocene adamantolate/MAO system

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Summary

A new alcoholate of cyclopentadienyl metallocene with voluminous group as ligand substituting chlorine atoms and formula $Cp_2Hf(OMAd)_2$ (where Cp = cyclopentadienyl and OMAAd = derived of 2-methyl-2-adamantol) was synthesized and employed as catalyst for olefin polymerization. The compound was evaluated in ethylene polymerization activated by methylaluminoxane (MAO) using several experimental conditions. These conditions were determined by a statistic method, and a model for dependent variables like catalyst activity and average molecular weight of polymers were developed. The hafnocene alcoholate produced polyethylenes with molecular weights in the same range of the corresponding metallocene dichloride. The new catalyst system showed high stability under temperature of 100°C. In the presence of H_2 as molecular weight controlling agent, the catalyst showed a maximum of activity in the concentration range used.

Introduction

During the last 15 years the research activities in the field of olefin polymerization focused many aspects of metallocene catalyst systems. This interest can be observed by the scientific and patent literature and the demand for these studies have been increasing throughout the years. The reason is that metallocene/methylaluminoxane systems can be more active than the conventional Ziegler-Natta catalysts, offer the control of microstructure to quiral monomers, are single site catalysts and offer better polymer properties.(1) The literature reports several aspects, mainly about the changes of the catalyst structure.(2) The metallocene compound symmetry is responsible for the polymer microstructure control.(3,4) Some studies involve changes in the substituents on the cyclopentadienyl ligand.(5,6) These modifications can increase the activity and also produce polymers with different characteristics.(7,8) The presence of a bridge between the ligands is another important characteristic which influences the polymer properties. (9,10) Nevertheless, systematic investigation on the influence of σ ligands on catalyst behavior have been less investigated. An early study comparing dichloride and pre-methylated precursors showed that differences on polymerization rate occur. (11) Zirconocene binaphtholate produces a significant fraction of uncyclized monomer when used in cyclopolymerization of 1,5-hexadiene. (12, 13) Recently, alcoholated (14) and fluorinated (15) half-sandwich complexes has been reported to be more active than the chlorinated analogous.

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In the present work, we discuss the ethylene polymerization with a hafnocene alcoholate. We have synthesized the hafnocene with an adamantane framework (Fig.1) in order to investigate the influence of a voluminous σ ligand on the catalyst performance.

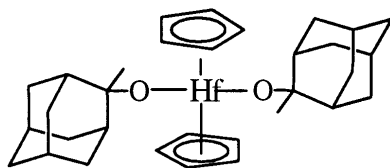


Figure 1: Structure of bis(cyclopentadienyl) hafnium di(2-methyl-2-adamantolate)

Experimental

All reactions were carried out under purified nitrogen atmosphere, using glove bag and schlenk techniques.

Materials

Research grade ethylene was purified by passing through molecular sieve 3Å columns. Nitrogen was used after passing through molecular sieve 3Å and copper catalyst columns. MAO 10wt% toluene solution kindly donated by Witco was used as received. Toluene was used after refluxing over sodium/benzophenone. Bis(cyclopentadienyl) hafnium di(2-methyl-2-adamantolate) was synthesized by a method similar to that described previously by Grafov.(16)

Polymerization procedures

Ethylene polymerization was performed in a 500ml autoclave equipped with mechanical stirrer. 100ml of toluene and a half-prescribed amount of MAO were added to the reactor under nitrogen atmosphere. The monomer was introduced until the pressure reach 2bar. In a schlenk flask, a toluene solution containing the desired amount of the metallocene and the other half of MAO were added. After 10 minutes of contact, the final solution was injected into the reactor saturated with ethylene under 2bar at the experiment temperature. The reaction was carried out for 1 hour. The polymerization rate was determined from the consumption rate of ethylene monomer measured by a hot-wire flowmeter (model 5850D from Brooks Instruments Div.) connected to a personal computer through an A/D converter. The polymerization was terminated by adding a dilute solution of hydrochloric acid in ethanol. The polymer was washed up with plenty of ethanol and vacuum dried at 60°C.

The reactions with hydrogen were carried out by the same procedure. The hydrogen was introduced at the experiment concentration before the ethylene monomer.

Polymer characterization

All the polymers were characterized by the melting temperature (T_m), crystallinity degree (x_c), average molecular weight (M_w) and polydispersity (M_w/M_n) determinations. The differential scanning calorimetry analyses (DSC) were used to determine the melting

temperature and crystallinity degree. The analyses were carried out in the range temperature from 50 to 250°C by a heating rate of the 10°C/min. The crystallinity degree were determined using $\Delta H_{\text{ethylene}}^{\circ} = 292\text{J/mol}$. Size exclusion chromatography (SEC) analyses were made in a Waters 150CV plus equipment at 135°C using a set of $\mu\text{Styragel}$ HT6E, HT3, HT4 columns from Waters, monodisperse polystyrene as calibration standard and trichlorobenzene as solvent.

Results and discussion

Table 1 shows the experimental planning and the results obtained for catalyst activity and polymer characteristics such as melting temperature (T_m), crystallinity (x_c), weight-average molecular weight (M_w) and polydispersity (M_w/M_n) obtained using the biscyclopentadienyl hafnium di(2-methyl-2-adamantolate)/MAO polymerization system.

Table 1: Experimental planning and results of ethylene polymerization with $\text{Cp}_2\text{Hf}(\text{OMAd})_2/\text{MAO}$ ^a

Experiment	T_p (°C)	H_2 (%)	activity (kgP/[Hf]h)	T_m (°C)	x_c (%)	$M_w \cdot 10^{-3}$	M_w/M_n
1	100 (+1)	7 (+1)	950	134	82	42	2.1
2	100 (+1)	0 (-1)	1724	135	71	151	2.0
3	50 (-1)	7 (+1)	320	134	70	121	2.6
4	50 (-1)	0 (-1)	194	135	58	784	2.0
5	75 (0)	3.5 (0)	1530	134	73	157	2.3
6	75 (0)	3.5 (0)	1500	135	71	204	2.3
7	75 (0)	3.5 (0)	1380	134	64	253	2.4

^a Polymerization conditions: toluene = 100ml; [Hf]= $5 \cdot 10^{-5}$ mol; [Al]/[Hf]= 2000; ethylene pressure = 2bar

Table 2: Parameters of the experimental error for the $\text{Cp}_2\text{Hf}(\text{OMAd})_2/\text{MAO}$ system.

Parameters	activity (kgP/[Hf]h)	T_m (°C)	x_c (%)	$M_w \cdot 10^{-3}$	M_w/M_n
x1	1530	134	73	157	2.3
x2	1500	135	71	204	2.3
x3	1380	134	64	253	2.4
\bar{x}	1470	134.2	69	205	2.3
x max.	1667	135.9	81	324	2.5
x min.	1273	132.5	58	85	2.2
outlier max.	1633	135.6	79	303	2.5
outlier min.	1307	132.8	60	106	2.2

The polymerization results were investigated by a statistical treatment using the Statistica program. By the central point (5, 6 and 7 experiment), the experimental error was calculated. The results are shown in Table 2.

In Table 2, x_1 , x_2 and x_3 are the results obtained in the experiments 5, 6 and 7 respectively. The \bar{x} is the arithmetic mean of x_1 , x_2 and x_3 . The mean range was obtained by the student test.

The model obtained for the catalyst activity (a) was: $a = 540T - 673([H_2])^2 - 225T[H_2] + 1470$ (correlation index $R^2 = 0.997$ and $s^2 = 614.13$). This model was obtained with normalized variable (+1 to -1) for polymerization temperature and hydrogen concentration and is represented by the Figure 2.

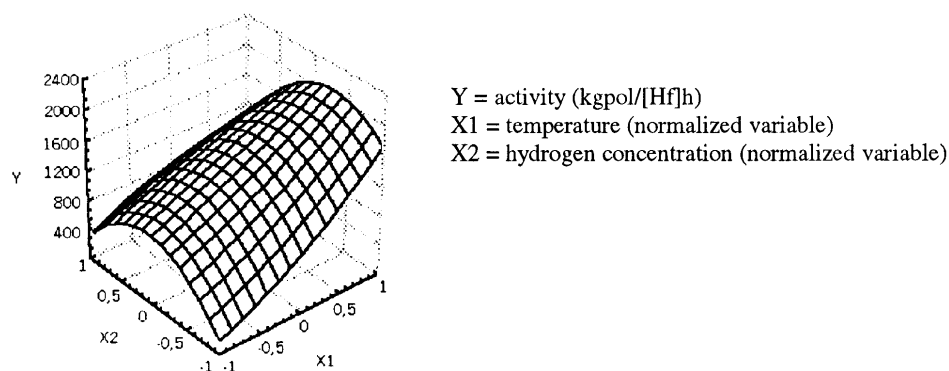


Figure 2: Graphic representation of the catalyst activity model for the $Cp_2Hf(OMAd)_2/MAO$ system

The model obtained for weight-average molecular weight was expressed by the equation: $M_w = 23.13 + \exp(4.78 - 0.87T - 0.98[H_2])$ ($R^2 = 0.997$ and $s^2 = 301.45$). This model was obtained with normalized variable (+1 to -1) for polymerization temperature and hydrogen concentration and is represented by the Figure 3.

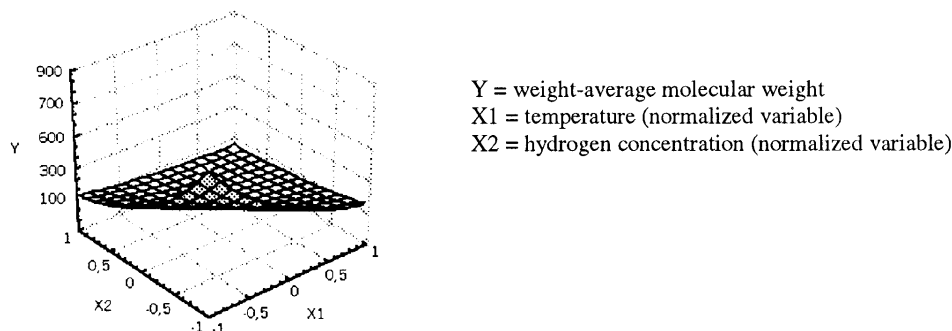


Figure 3: Graphic representation of the polyethylene weight-average molecular weight model for $Cp_2Hf(OMAd)_2/MAO$ system

The model can be also obtained for the crystallinity (x_c) and polydispersity (M_w/M_n), but the experimental and instrumental errors did not allow satisfactory results.

The Fischer test (F) can be applied to show the concordance between the experimental and the model results (Eq. 1). With the degrees of freedom of the central point ($v=3- 1=2$)

and the model ($v=7-1=6$) we have the range where F values are true ($F_{\min} = 0.025$ and $F_{\max} = 39.33$).

$$F = s_{\text{model}}^2 / s_{\text{exper}}^2 \quad \text{Eq.1}$$

In Eq. 1, s_{model}^2 is the variance obtained for the model and s_{exper}^2 is the one obtained with the experimental points (Table 3). Table 4 shows the results of the Fisher test.

Table 3: Variance and variance range for the the $\text{Cp}_2\text{Hf}(\text{OMAd})_2/\text{MAO}$ system.

Parameters	activity (kgP/[Hf]h)	T_m (°C)	x_c (%)	$M_w * 10^{-3}$	M_w/M_n
s^2	6300	0.48	22	2304	0.0
s^2 max.	12830957	977.6	45485	4693143	6.8
s^2 min.	2508	0.19	9	917	0.00132

Table 4: Results of the Fischer test for activity and average molecular weight in the hafnocene adamantolate/MAO system

Variable	s_{model}^2	s_{exper}^2	F^a
a(kgP/[Hf]h)	614.13	6300	10.26
M_w	301.45	2304	7.64

^a dimensionless

This test showed that the model and the experimental data are in agreement. All of these analyses were also carried out for the hafnocene dichloride. Table 5 shows the results of the experimental planning.

Table 5: Experimental planning and results of ethylene polymerization with biscyclopentadienyl hafnium dichloride/MAO ^a

Experiment	T_p (°C)	H_2 (%)	activity (kgP/[Hf]h)	T_m (°C)	x_c (%)	$M_w * 10^{-3}$	M_w/M_n
1	100 (+1)	7 (+1)	2100	-	-	46	2.2
2	100 (+1)	0 (-1)	2480	133.3	79	134	2.4
3	50 (-1)	7 (+1)	720	-	-	180	2.7
4	50 (-1)	0 (-1)	760	131.6	58	665	2.8
5	75 (0)	3.5 (0)	2520	-	-	160	2.3
6	75 (0)	3.5 (0)	2560	-	-	117	2.1
7	75 (0)	3.5 (0)	2520	-	-	195	2.6

^a Polymerization conditions: toluene= 100ml; [Hf]= $5 * 10^{-5}$ mol; [Al]/[Hf]= 2000; ethylene pressure= 2bar

In order to compare the results obtained by both systems, the error was determined only for activity and average molecular weight. Table 6 shows the parameters of experimental error.

Table 6: Parameters of the experimental error for the biscyclopentadienyl hafnium dichloride/MAO system.

Parameters	Activity (kgP/[Hf]h)	$M_w * 10^{-3}$
x1	2520.00	160.00
x2	2520.00	117.00
x3	2560.00	195.00
\bar{x} sample	2533.33	157.33
\bar{x} max.	2590.71	254.39
\bar{x} min.	2475.96	60.27
outlier max.	2580.67	237.42
outlier min.	2485.99	77.24

The experimental planning gave a mathematical model for activity graphically showed in Figure 4. The expression of activity (a) for the dichloride system is: $a = 775T - 1018([H_2])^2 - 85T[H_2] - 105T^2[H_2] + 2533$ ($R^2 = 1.00$ and $s^2 = 842.05$). This model was also obtained with normalized variables (+1 to -1) for polymerization temperature and hydrogen concentration.

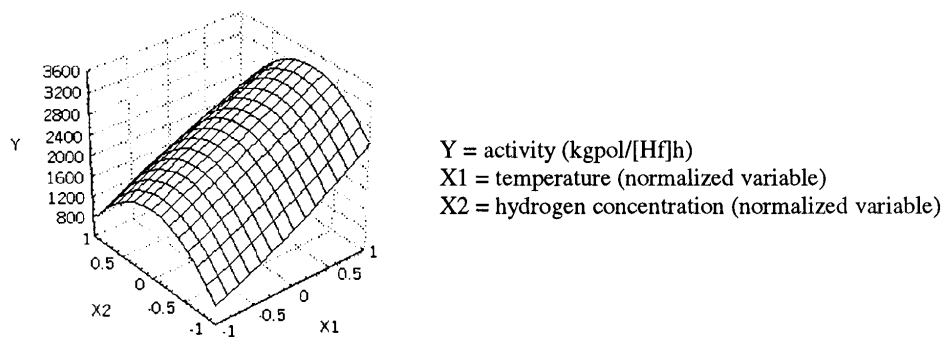


Figure 4: Graphic representation of the activity model for Cp_2HfCl_2/MAO system

The obtained model for M_w represented in Figure 5 is described by the follow expression: $M_w = -166.25T - 143.75[H_2] + 99.25T[H_2] + 98,92T^2 + 157,33$ ($R^2 = 0.99$ and $s^2 = 204.885$).

The Fischer test (F) applied to this case showed also an agreement with experimental data and the model was obtained. The degrees of freedom were obtained in the same way. So the interval which F is true ($F_{\min} = 0.025$ and $F_{\max} = 39.33$) is also the same. Table 7 shows the variance data and Table 8 the results.

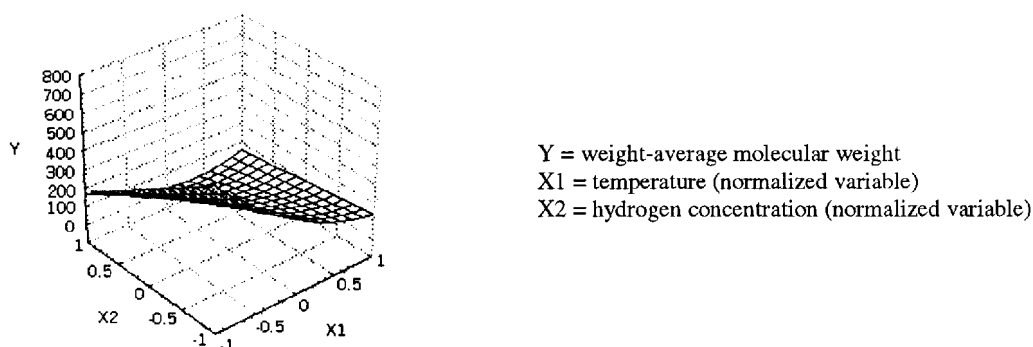


Figure 5: Graphic representation of the molecular average weight model for $\text{Cp}_2\text{HfCl}_2/\text{MAO}$ system

Table 7: Variance and variance range for the biscyclopentadienyl hafnium dichloride/MAO system.

Parameters	Activity (kgP/[Hf]h)	$M_w \cdot 10^{-3}$
s^2 sample	533.33	1526.33
s^2 max.	1086218.6	3108621.86
s^2 min.	212.31	607.61

Table 8: Results of Fischer test to activity and molecular average weight in the hafnocene dichloride/MAO system

Variable	s^2_{model}	$s^2_{\text{exper.}}$	F^a
$a(\text{kgP}/[\text{Hf}]\text{h})^2$	842.05	533.33	0.63
M_w	204.88	1526.33	7.45

^a dimensionless

This test showed that also for dichloride catalyst the model and the experimental data are in agreement. In both cases, we observed that the systems are similar and their equations describes similar curves. In the observed range of conditions, the catalysts are very thermally stable and activity increases when temperature is increased. A curious effect is observed for the hydrogen concentration. The models show a optimum concentration at about 3.5% (normalized variable = 0). Excess of hydrogen causes the decrease of the catalyst activity. Although the curve of activity *versus* hydrogen concentration are very similar for both catalyst, the representative equations are not the same. For example, in the alcoholate catalyst system the temperature did not show a quadratic interaction as in the case of the dichloride one.

Hafnocene/MAO systems generally produce polymers with higher average molecular weight than the corresponding zirconocene ones. As shown by our results, in absence of hydrogen and at lower temperatures the hafnocene adamantolate/MAO system produced polymers with M_w in the same range of the analogous hafnocene dichloride in the same polymerization condition. At higher temperatures, chain transfer reactions occur faster,

but it seems that the voluminous group do not have any influence on the average molecular weight as well.

The models obtained with the experimental planning for the average molecular weight were different for both catalysts but showed that the systems are extremely sensible to polymerization temperature and hydrogen. For the alcoholate system an exponential expression was obtained while for the dichloride hafnocene an expression that indicates a linear and quadratic behavior for X2 (hydrogen concentration) and X1 (polymerization temperature) variables was attained, respectively.

Alkylation of metallocenes by MAO leads to different A1 by-products. It is probable that in the case of alcoholates, the well accepted ionization process responsible for the active specie formation does not necessarily proceed by way of the dialkyl intermediate complex. It is possible that $\text{Cp}_2\text{HfMe(OR)}$ might be more readily ionized by MAO to form a ion-pair $[\text{Cp}_2\text{HfMe}] [\text{MAO-OR}]$. It is well-established that the nature of the counter-ion can influence the catalyst behavior. (17-19) So, the differences observed indicate that although the systems are close in structure, regarding metal type and π ligand, the presence of a voluminous alcoholate as σ ligand probably lead to this different ion-pair when activated by MAO.

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