

Optimization of olefin copolymerization: effects of reaction parameters on catalytic activity and properties

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ABSTRACT

The copolymerization of ethylene with 1-hexene using $\text{Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$ as catalyst was studied by multivariate methods. Three complete factorial designs were performed to study the influence of 1-hexene concentration, reaction temperature and $[\text{Al}]/[\text{Zr}]$ ratio on catalytic activity, copolymer viscosity, crystallinity and melting point. Since the $[\text{Al}]/[\text{Zr}]$ ratio has a small effect on the catalytic activity, a fourth design with 1-hexene and temperature was developed, giving higher catalytic activities. Temperature and 1-hexene concentration were the main effects found in the system. A second order effect arising from 1-hexene versus $[\text{Al}]/[\text{Zr}]$ ratio was also detected. Polymer viscosity, crystallinity and melting points decreased with 1-hexene concentration. Viscosity decreased with temperature whereas crystallinity increased when the temperature was raised from 30 to 60° C.

INTRODUCTION

The copolymerization of ethylene with α -olefins via metallocene catalysts permits the synthesis of linear low density polyethylene (LLDPE), a product of great industrial interest due to its special properties.

The single site characteristic of metallocene catalysts make it possible to control molecular weight, stereoregularities and comonomer incorporation, maintaining narrow molecular weight and composition distributions. The catalyst system, the comonomer type and incorporation and the reaction process, among other variables, are essential to obtain polyolefins with good properties¹⁻⁵.

Many studies related to catalytic system have been made, but little has been done on reaction parameters and their effect on the properties. In previous papers⁶⁻¹¹ we have reported on the effects of some parameters on the copolymerization of ethylene with α -olefins. Our study was aimed at establishing correlations between the reaction parameters and the properties of the products obtained.

The knowledge of the olefin copolymerization reaction parameters is extremely important, since microstructure and properties are dependent on such factors. On the other hand, polymerization systems working with condensed and gaseous media at the same time, using complex catalysts, require a high number of experiments in order to improve data reproducibility. In this work factorial designs¹² were used to optimise the catalytic activity using the system $\text{Et}[\text{Ind}]_2\text{ZrCl}_2/\text{MAO}$. The influence of 1-hexene

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concentration, temperature and [Al]/[Zr] ratio on viscosity, crystallinity and melting point of the copolymers was also studied.

EXPERIMENTAL PROCEDURE

Polymerizations were performed according to our previous works^{8,10}.

Differential scanning calorimetry (DSC) measurements were made with a Polymer Laboratories DSC instrument. Each sample was heated from 40 °C to 140 °C at a heating rate of 10 °C/min, and maintained at this temperature for 2 min, cooled to 40 °C at 10 °C/min and finally reheated at the same rate. The values presented for the melting point were observed in the second scan. The percentage crystallinity was derived from ΔH_f by $X_c = \Delta H_f \times 100/64.5$ ¹⁴. A Viscomatic-MS-Sofica viscosimeter was used to measure the intrinsic viscosity ($[\eta]$) of the polymer dissolved in decalin at 135°C.

RESULTS AND DISCUSSION

To study the effect of comonomer concentration, temperature and [Al]/[Zr] ratio on the catalytic activity and on copolymer properties, three factorial designs (D-1, D-2 and D-3) at two levels (- and +) were developed. **Table 1** shows the experimental conditions for the three designs used in this work. **Table 2** shows the results of catalytic activity, viscosity, crystallinity and melting point obtained for the three designs. From these results it is possible to calculate the main effects and the interaction effects of each one of the variables using the Yates algorithm¹².

Table 1: Experimental conditions for the three factorial designs (D-1, D-2 and D-3) showing the low (-) and high (+) levels of the factors under analysis.

Factor =>	[1-hexene] (mol/l)		Temperature (°C)		[Al]/[Zr]	
Design	-	+	-	+	-	+
D-1	0	0.08	30	60	1750	2000
D-2	0.08	0.19	60	70	2000	2200
D-3	0.19	0.26	50	60	2200	2400

Table 2: Activity, crystallinity, melting point and viscosity for the three full factorial designs. The last line presents the average value for the eight runs from each design.

Run	[1-H] (mol/l)	T (°C)	[AZ]	Activity x 10 ⁻⁸ (g/nzr.h.bar)			Viscosity (dl/g)			Crystallinity (%)			Melting Point (°C)		
				D-1	D-2	D-3	D-1	D-2	D-3	D-1	D-2	D-3	D-1	D-2	D-3
1	-	-	-	3	14	14	2.52	1.89	1.45	61.3	48.3	28.0	134.7	116.5	98.8
2	+	-	-	0	20	17	2.09	1.62	1.52	32.8	22.4	23.3	119.3	113.2	83.9
3	-	+	-	9	10	15	2.6	1.36	1.35	63.6	41.4	28.9	135.1	113.4	96.8
4	+	+	-	18	14	20	1.5	1.16	1.49	35.7	26.9	30.6	114.4	104.4	97.5
5	-	-	+	4	23	9	3.05	2	1.79	58.4	53.5	41.6	135.1	123.6	107.7
6	+	-	+	1	15	22	2.3	1.35	1.64	34.2	28.9	27.8	113.7	96.8	99.7
7	-	+	+	17	14	14	2.66	1.56	1.49	64.1	44.4	42.1	134	119.9	105
8	+	+	+	14	14	14	1.89	1.28	1.26	48.3	41.2	29.4	116.5	109.5	101.9
Average				8	16	16	2.32	1.52	1.49	49.8	38.4	31.5	125.4	112.2	98.9

Catalytic activity

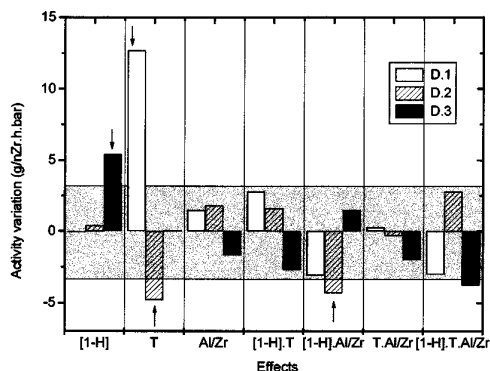
Figure 1 presents the calculated significant factor effects on catalytic activity. Two methods were applied to evaluate the significance of these effects. The first considers the third order interaction as extremely improbable in such system, so it may be used as an estimation of the experimental error. Thus, Figures 1, 3, 4 and 5 show a horizontal bar representing the error calculated from the three third order interaction effects (D-1, D-2 and D-3). The second method to evaluate the standard error was the inverse Yates algorithm, where the small effects (first, second or third order) are

neglected. In the Figures 1, 3, 4 and 5, these results are indicated by arrows close to the bars. In general, there is good agreement between the two methods.

In the first design (D-1) it is found that temperature increase between 30 and 60°C was the only significant (and positive) effect on catalyst activity. The increase in [1-hexene] and in [Al]/[Zr] ratio have no effect on catalyst activity under the experimental conditions used for this factorial. The overall average activity in this design was 8×10^6 g/n_z.h.bar. From these results the second design (D-2) was developed, increasing the temperature from 60 to 70 °C, since this increase has been shown to be positive on the activity in the first design. The [Al]/[Zr] ratio and the [1-hexene] were also increased in this second design, considering the possibility of a second order interaction (negative) between these two factors in the first design (close to the experimental error). The results

of D-2 indicate two significant effects: temperature and the second order interaction between [1-hexene].[Al]/[Zr], both of which are negative on the activity. The overall average activity for the eight runs increases to 16×10^6 g/n_z.h.bar, indicating that the changes in the experimental conditions were correct. These two significant effects allow the following comments: first, the new temperature range is too high to maximise the copolymerization reaction, meaning that probably there is a deactivation of the catalyst site above 60° C. Second place, the second order interaction of [1-hexene] and [Al]/[Zr] also decrease activity. Probably the [1-hexene] increase in the medium blocks some catalyst sites, thereby diminishing their activity. From these second design results (D-2), a third design (D-3) was developed, decreasing the temperature and increasing the [1-hexene] and the [Al]/[Zr].

Figure 1: Main and interaction effects of catalyst activity from the three designs (D.1, D.2 and D.3). The grey region indicates experimental error from the third order interaction. The arrows point to the significant effects from the inverse Yates algorithm.



The experimental results of D-3 point to only one significant effect, due to [1-hexene] which is positive. Apparently, [1-hexene] plays an important role for the catalyst activity only in the highest range under analysis (0.19-0.26 mol/l). This behaviour may be due to the fact that polyethylene homopolymers and copolymers with low comonomer incorporation are insoluble in the medium and the reaction may be controlled by diffusion. When [1-hexene] in the medium increases, more comonomer is incorporated in the copolymer, and since the copolymer is soluble in the medium, the reaction is no longer controlled by diffusion and the activity increases.

From these sets of results a fourth experiment (D-4) was designed to explore only [1-hexene] and temperature, at a constant [Al]/[Zr], showing no effect on the activity in the range studied. Since the overall activity results of D-3 (16×10^6 g/n_z.h.bar) were similar to those of D-2 (16×10^6 g/n_z.h.bar), it is supposed to be close to the maximum. In this way D-4 is a central composite design to explore this

region with respect to its curvature. **Table 3** shows the experimental conditions and response for the central composite design. From the three central points (runs 5-7) the experimental error can be estimated for all as a standard deviation equal to 3.5 (18.4%). **Table 4** presents the effects calculated from the results of **Table 3**.

Table 3: Experimental conditions and activities for the central composite design (D-4).

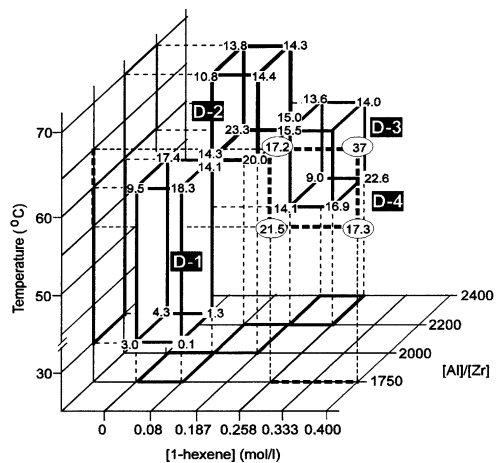
Run	[1-hexene] (mol/l)	Temperature (°C)	Activity x 10 ⁶ (g/n _{Zr} .h.bar)
1	10	55	21
2	15	55	17
3	10	65	17
4	15	65	36
5	12.5	60	15
6	12.5	60	19
7	12.5	60	24

Table 4: Effects calculated from the central composite design (D-4).

Factor	β coefficient \pm Standard Error (x 10 ⁶ (g/n _{Zr} .h.bar))
Curvature	2.9 \pm 3.5
[1-hexene]	3.9 \pm 2.3
Temperature	4.0 \pm 2.3
[1-hexene] . Temperature	5.8 \pm 2.3

The **Figure 2** presents all results in a three-dimensional plot, showing global activity values as a function of experimental conditions.

Figure 2: Plot of D-1, D-2, D-3 and D-4 showing activities at the vertices of each design (D-4 values are circled).



From the data shown in **Table 4** it is observed that the system does not have a conclusive curvature, since this value and the β coefficient are smaller than the experimental error. On the other hand, both [1-hexene] and temperature have significant main effects, and show a second order interaction between these variables. This last conclusion does not allow the expression of such results in a final equation, since the second order interaction requires additional experiments to apply the correct second

order analysis. However, in this D-4 design the highest value for the activity is reached, indicating a good performance of the optimisation.

The first and second order interaction effects of [1-hexene], temperature and [Al]/[Zr] on copolymer properties were calculated and they are shown in **Figures 3, 4 and 5**.

Figure 3: Main and interaction effects for viscosity changes from the three designs (D-1, D-2 and D-3). The gray range indicates experimental error from the third order interaction. The arrows point to the significant effects estimated from the Yates algorithm.

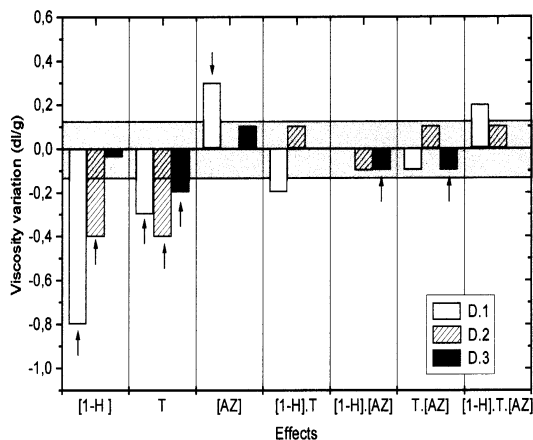
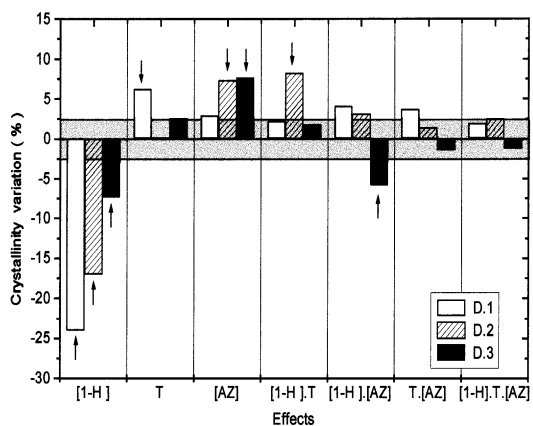


Figure 4: Main and interaction effects for crystallinity variations from the three designs (D-1, D-2 and D-3). The gray range indicates experimental error from the third order interaction. The arrows point to the significant effects estimated from the Yates algorithm.



A summary of all the significant effects is presented in Table 5, making it possible to find the best correlations and trends. The following comments are possible from these tendencies, considering that the experimental values of [1-hexene] and [Al]/Zr always increase from D-1 to D-3, while the temperature increases from D-1 to D-2 and decreases from D-2 to D-3.

Viscosity

Analyzing the variable effects on the viscosity it can be seen that [1-hexene] produces a negative effect in all designs (from D-1 to D-3). This can be explained by the fact that [1-hexene] in the medium increases the termination reactions, thereby decreasing the molecular weight of the copolymers (molecular weight and viscosity are directly correlated by the Mark-Kuhn-Houwink equation¹⁵).

Figure 5: Main and interaction effects for melting point changes from the three designs (D-1, D-2 and D-3). The gray range indicates the experimental error from the third order interaction. The arrows point to the significant effects estimated from the Yates algorithm.

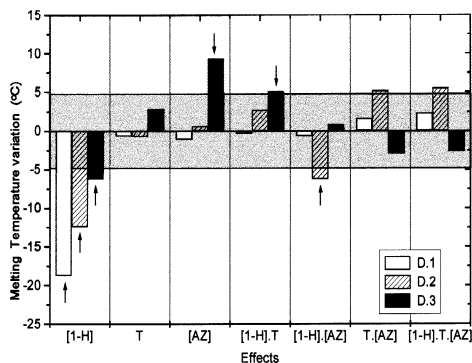


Table 5: Summary of trends of all significant effects on the activity, viscosity, crystallinity and melting point. The arrows indicate a weak (\uparrow) or strong ($\uparrow\uparrow$) increase or decrease in polymer properties.

Effects	Trends								
	Viscosity			Crystallinity			Melting Point		
	D-1	D-2	D-3	D-1	D-2	D-3	D-1	D-2	D-3
[1-H]	$\downarrow\downarrow$	\downarrow		$\downarrow\downarrow$	$\downarrow\downarrow$	\downarrow	$\downarrow\downarrow$	$\downarrow\downarrow$	\downarrow
T		\downarrow		\uparrow					
[AZ]			\downarrow		\uparrow	\uparrow			\uparrow
[1-H].T					\uparrow	\uparrow			\uparrow
[1-H].[AZ]				\uparrow		\downarrow		\downarrow	
T.[AZ]									\uparrow
[1-H].T.[AZ]									\uparrow

Temperature also produces a negative effect on the viscosity or molecular weight. The reactions carried out at lower temperatures give products with higher molecular weights, as had already been reported¹⁶. Propagation and termination rates are both affected by temperature, but termination reactions need higher activation energies than propagation, so that, at lower temperatures, propagation is favored over termination, and the molecular weights become higher.

The [Al]/[Zr] only affects viscosity when it increases from 1750 to 2000. This is a small effect, and it may be associated with the fact that MAO hinders some termination reactions, thus increasing molecular weight. In relation to the interaction effects, no significant values were found for viscosity.

Crystallinity and melting point

The increase in [1-hexene] also had a negative effect on crystallinity and melting point. This is indirect evidence that 1-hexene is progressively incorporated in the polymer when its concentration in the system increases.

Temperature presents a significant positive effect only when it is increased substantially (from 30 to 60°C). This effect may be related to chain length; as has been discussed above, molecular weight decreases with temperature. The copolymers obtained at 60°C have lower molecular weight than those obtained at 30°C, and copolymers with lower molecular weight present higher crystallinities^{17,18}.

The reaction temperature did not affect the melting points.

The [Al]/[Zr] has a significant positive effect on crystallinity (D-2 and D-3) and on the melting point (D-3). It is possible that the [MAO] increase (the catalyst concentration is kept constant) could influence comonomer distribution in the chain, thereby affecting crystallinity. With respect to interaction effects, there is a positive one on crystallinity due

to the interaction between [1-hexene] and temperature (D-2), and a negative effect due to the interaction between [1-hexene] and [Al]/[Zr] (D-3). However, it is not possible to reach conclusions about such effects due to their small difference when compared to the error estimations.

CONCLUSIONS

The maximum catalytic activity between 50-60°C indicates that the propagation rate increases with temperature, but above 60°C catalyst deactivation becomes more important than propagation. Increasing [1-hexene] the catalyst activity increases only above a determined comonomer concentration probably due to diffusion effects: at low [1-hexene] polyethylene is insoluble but by increasing [1-hexene] the copolymer becomes soluble in the medium, thus increasing the reaction rate. The [Al]/[Zr] does not affect the activity but has a positive effect on properties, increasing viscosity (D-1), crystallinity (D-2 and D-3) and melting point (D-3). Three second order interaction effects are observed between [1-hexene] and [Al]/[Zr]. Temperature has one conclusive effect on polymer viscosity, suggesting a molecular weight lowering when temperature is raised.

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