Synthesis and characterization of ethylene-1-hexene copolymers using homogeneous Ziegler-Natta catalysts

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SUMMARY

This study investigated the copolymerization of ethylene with 1-hexene using the homogeneous $Et[Ind]_2ZrCl_2$ and $[Ind]_2ZrCl_2$ catalysts. The $Et[Ind]_2ZrCl_2$ catalyst gave a higher catalytic activity than the $[Ind]_2ZrCl_2$ and also showed a better incorporation of 1-hexene for the same comonomer concentration in the feed. Thermal analysis (DSC) and viscosity measurements showed that an increase of the 1-hexene incorporated in the copolymer results in a decrease of the melting point, crystallinity and molecular weight of the polymer formed. The reactivity ratios for ethylene and 1-hexene confirmed the more successful incorporation of the comonomer for the polymerization catalyzed by $Et[Ind]_2ZrCl_2$.

INTRODUCTION

Copolymers of ethylene with higher olefins are important commercial products and industrial efforts have been directed towards finding novel and more efficient catalysts for the synthesis of desired products. Homogeneous Ziegler-Natta catalysts formed by the reaction of group(IV) metallocenes and methylaluminoxane (MAO) have been a research topic of growing interest in the last ten years. The objective of these investigations has been to find different types of homo and copolymers with special properties.

Several publications have been reported on the use of these catalyst systems for homo- and copolymerization of ethylene with α-olefins.[1-6] Moreover, only a few reports[7,8,9] discuss comparative results for ethylene copolymerization with different catalysts, which consider the relation between activity, comonomer incorporation and properties. This work presents results related to the copolymerization of ethylene-1-hexene using $Et[Ind]_2ZrCl_2$ and $[Ind]_2ZrCl_2$ $(Ind=\eta^5$-indenyl), which have not been compared before for this kind of polymerization. This study evaluates the effect of the ethane bridge in the incorporation.

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of the comonomer and in the properties of the obtained copolymer. Furthermore, it discusses the results for the activity, incorporation of 1-hexene, thermal analysis, molecular weight and molecular weight distribution.

EXPERIMENTAL

Polymerization

All operations were performed under argon atmosphere using standard Schlenck techniques. Toluene and 1-hexene were refluxed and freshly distilled under argon from metallic Na. Polymerization-grade ethylene was dried by passage through 4 A molecular sieves columns. Et[Ind]$_2$ZrCl$_2$ and [Ind]$_2$ZrCl$_2$ catalysts were prepared according to the literature[9,10]. Polymerizations were conducted at 60°C in a 1 l glass reactor equipped with a mechanical stirrer. The reactor was filled with toluene (0.3 l), comonomer and methylaluminoxane, thermostated, and saturated with ethylene by continuous addition of monomer. The monomer pressure was kept constant during the polymerization. Metallocene solution was injected into the reactor. The reaction was stopped through addition of acidic metanol solution. The polymer was subsequently filtered, washed with metanol, and dried in vacuum.

Characterization of the polymers

^{13}C-NMR, was employed to determine the compositions of the copolymers. These compositions were derived according to the literature[11]. The ^{13}C NMR spectra were recorded at 80°C using a VARIAN XL-200 spectrometer operating at 50.309 MHz. Sample solution of the copolymer was prepared with o-dichlorobenzene, benzene-d$_6$ (20% v/v) and chromium(III) acetylacetonate as paramagnetic substance to reduce relaxation times. Spectra were taken with 70° of flip angle, acquisition time of 1.5 s and a delay of 5.0 s . A Perkin-Elmer DSC-4 system measured the heat of fusion (ΔH_f) and melting temperature (Tm). The sample was first heated up to 180°C at 10°C/min., kept at 180°C for 2 minutes, cooled down to 40°C at 10°C/min. and, finally, recorded a DSC scan at 10°C/min. The crystallinity percentage was derived from ΔH_f by Xc = ΔH_f x 100/64.5[12]. Gel permeation chromatography using a WATERS-150C GPC and 1,2,4-trichlorobenzene as solvent at 140°C determined molecular weight and molecular weight distribution ($\overline{M}w/\overline{M}n$) of the polymers. The universal calibration curve of 18 polystyrene and 3 polyethylene monodisperse standards served to calculate the molecular weights. VISCOMATIC-MS-SOFICA viscosimeter[13,14] measured the intrinsic viscosity ([η]) of the polymer dissolved in decalin at 135°C.

RESULTS AND DISCUSSION

Catalytic Activity

Figure 1 shows the results of the activity for the two catalysts studied. The catalytic activity for Et[Ind]$_2$ZrCl$_2$ presents higher values compared to the [Ind]$_2$ZrCl$_2$ catalyst in all the 1-hexene concentrations. One reason for this behaviour may be that the ethane bridge produces a greater angle of coordination, which facilitates the access of

the monomer to the metal center, increasing the rate of polymerization. This type of catalyst also presents a different activity behaviour with respect to the increase of 1-hexene concentration in the feed. The increase of 1-hexene concentration in the feed enhances the activity in the $Et[Ind]_2ZrCl_2$ system whereas it does not seem to affect the activity of the $[Ind]_2ZrCl_2$ system.
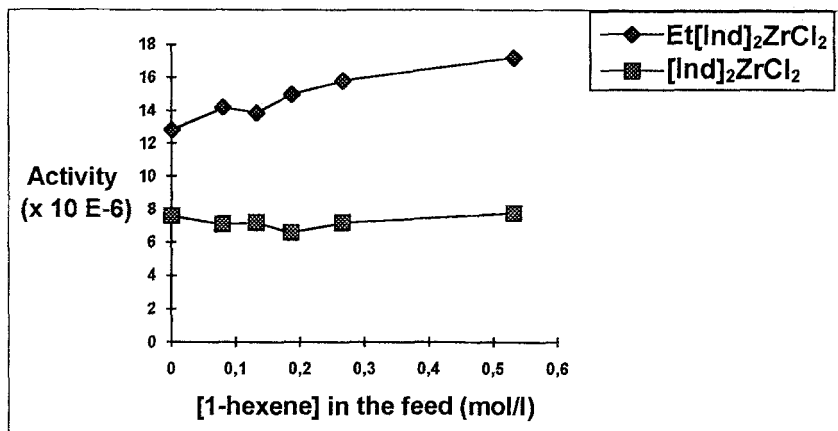

FIGURE 1: Relationship between ethylene/1-hexene copolymerization activity[a] with concentration of 1-hexene in the feed for $Et[Ind]_2ZrCl_2$ and $[Ind]_2ZrCl_2$ catalysts[b].
[a] Activity = g polymer (mol Zr x h x atm)$^{-1}$
[b] Polymerization:$[Zr]=2.0 \times 10^{-6}M$,$[Al]/[Zr]=1750$,$T=60°C$, $t=30min.$, $P_{[E]}=1.6$ bar.

Ethylene-1-Hexene Copolymer
Table 1 shows how the 1-hexene content in the copolymer changes with the concentration of the comonomer in the feed. As the 1-hexene concentration in the feed is increased, the incorporation of the comonomer increases as well. Significant differences in the content of 1-hexene incorporated can be observed when employing different catalysts with the same feed concentration. The bridged catalyst $Et[Ind]_2ZrCl_2$ adds a higher extent of 1-hexene to the copolymer than $[Ind]_2ZrCl_2$. The bridge in the $Et[Ind]_2ZrCl_2$ catalyst permits an easier approximation of the comonomer to the active center, thus increasing the rate of the insertion.
Table 2 shows the values for the reactivity ratios for the two catalysts systems obtained by using ^{13}C-NMR[14] and Fineman-Ross[7] methods. Both methods present similar results showing a satisfactory correlation between both techniques.
By comparing the values of r_E for the two catalysts, one observes that the $Et[Ind]_2ZrCl_2$ preferentially incorporates 1-hexene as its r_E value is smaller. The very low r_H values confirm that HH blocks were not formed.

TABLE 1- 1-Hexene content in the copolymers.

[1-hexene] in the feed (mol/l)	1-hexene content in the copolymer (mol%)	
	Et[Ind]$_2$ZrCl$_2$	[Ind]$_2$ZrCl$_2$
0.000	0.0	0.0
0.027	< 1.0	< 1.0
0.080	1.9	< 1.0
0.133	4.8	< 1.0
0.187	5.3	1.1
0.267	7.6	4.5
0.533	11.6	6.0
0.800	18.0	-

TABLE 2- Comparative results of reactivity ratios obtained for ethylene-1-hexene copolymerization by using Fineman-Ross[7] and ^{13}C-NMR[14] methods[a].

Catalyst type	Fineman-Ross			^{13}C-NMR	
	r_E	r_H	$r_E.r_H$	r_E	r_H
Et[Ind]$_2$ZrCl$_2$	31.0	0.013	0.40	36.0	~ 0
[Ind]$_2$ZrCl$_2$	88.0	0.005	0.46	86.7	~ 0

[a] Polymerization:[Zr]=2.0x10^{-6}M,[Al]/[Zr]=1750,T=60°C, t=30min., P$_{[E]}$=1.6 bar.

Properties of the copolymers
The DSC curves for the copolymers obtained using the two catalysts with the same concentration of 1-hexene (0,267 M) in the feed are shown in Figure 2. It can be seen that the shape of the curves is different for the two catalysts. The Et[Ind]$_2$ZrCl$_2$ catalyst presents a broader curve. This confirm a branching increase due to a better comonomer incorporation. Figure 3 shows the thermal behaviour of the copolymers obtained with Et[Ind]$_2$ZrCl$_2$ catalyst. When the concentration of 1-hexene in the feed is increased, one can observe a decrease of the melting point and a broadening of the shape of the curve.
Table 3 shows that the melting point and cristallinity decrease with the increase of 1-hexene in the copolymer. The presence of the comonomer in the main chain of polyethylene produces branching that changes the size of the crystals and decreases the crystallinity. The broadening of the curve found for higher content of 1-hexene can be due to factors like different size of crystals and imperfections in the crystalline lattice.

Table 4 shows the relationship between viscosity, molecular weight and molecular weight distribution with the 1-hexene incorporated. The viscosity decreases when the concentration of the comonomer in the feed increases. For Et[Ind]$_2$ZrCl$_2$ the majority of these viscosity values were lower when compared with those obtained for the copolymer by using [Ind]$_2$ZrCl$_2$.

In this type of polymerization monomer and comonomer transfer reactions and β-hydride elimination may take place. The later process has a higher rate when more 1-hexene is incorporated, because the β-hydrogen in the comonomer is more labile than in ethylene.

The molecular weight distribution is higher than normally expected for this kind of catalyst. This may be due to dynamic dissociation/association of MAO and changes in its state of coordination (monodent, bident, etc.). The [Ind]$_2$ZrCl$_2$ catalyst presents broader molecular weight distributions than the Et[Ind]$_2$ZrCl$_2$ catalyst. In the [Ind]$_2$ZrCl$_2$ system the indenyl ligands are free to assume various coordination geometries since they are not constrained by a bridge as in Et[Ind]$_2$ZrCl$_2$. Another possible cause for these higher values may be the dissociation and recomplexation of the indenyl ligands with the metal.[15]
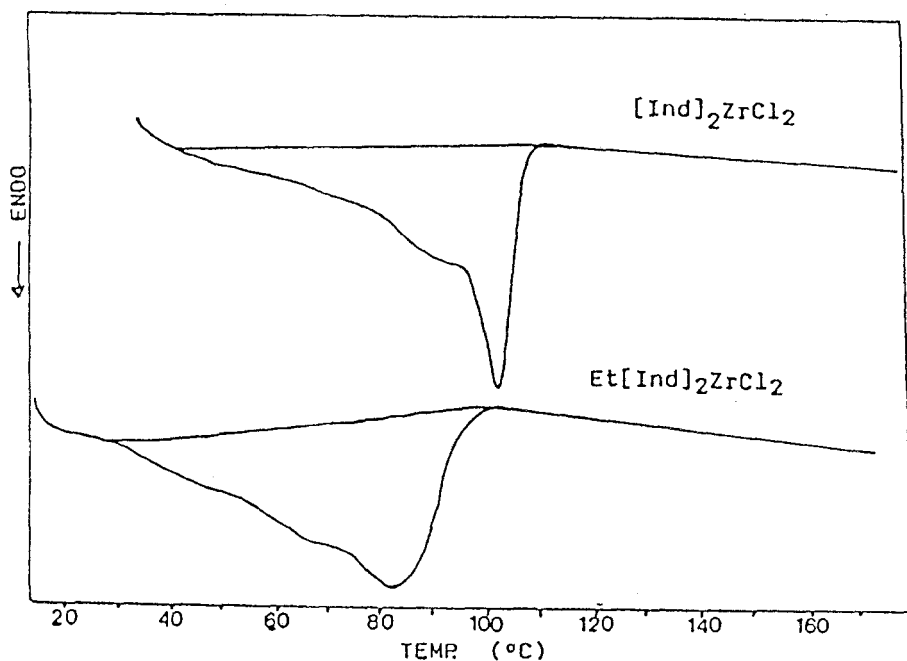

FIGURE 2: DSC curves for copolymers obtained with Et[Ind]$_2$ZrCl$_2$ and [Ind]$_2$ZrCl$_2$ using the same concentration of 1-hexene (0.267 M) in the feed.
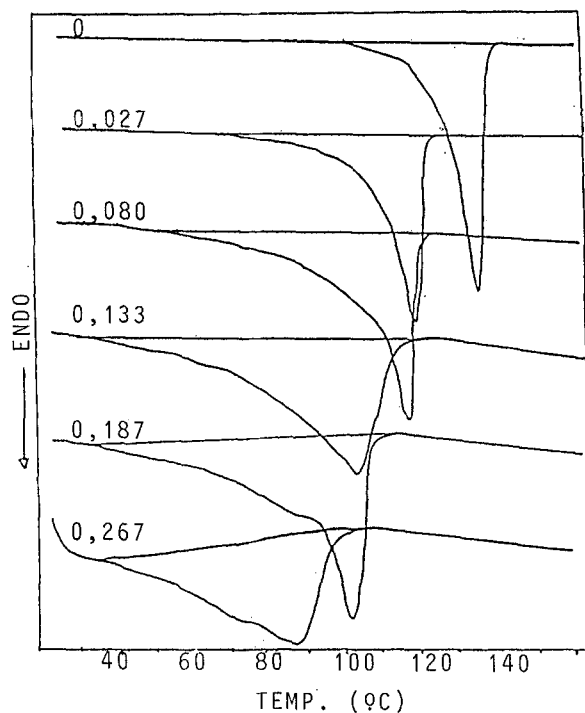
FIGURE 3: DSC curves for copolymers obtained with Ėt[Ind]₂ZrCl₂ for different 1-hexene concentration in the feed.

$$\text{Et[Ind]}_2\text{ZrCl}_2$$

TABLE 3- Properties of the ethylene-1-hexene copolymers[a].

Et[Ind]$_2$ZrCl$_2$				[Ind]$_2$ZrCl$_2$			
[1-hexene] in the feed (mol/l)	M.P. (°C)	Xc (%)	1-hexene incorporated (mol %)	[1-hexene] in the feed (mol/l)	M.P. (°C)	Xc (%)	1-hexene incorporated (mol %)
0	136	74	0	0	137	76	0
0.027	117	48	<1.0	0.027	130	57	<1.0
0.080	115	37	1.9	0.080	123	51	<1.0
0.133	101	28	4.8	0.133	116	43	<1.0
0.187	99	23	5.3	0.187	118	49	1.1
0.267	83	14	7.6	0.267	109	34	4.5
0.533	70	-	11.6	0.533	100	23	6.0

a)Polymerization:[Zr]=2.0x10^{-6}M,[Al]/[Zr]=1750,T=60°C, t=30min., P$_{[E]}$=1.6 bar.

TABLE 4- Correlation between the 1-hexene concentration in the feed and in the copolymer with viscosity, molecular weight and molecular weight distribution (Mw/Mn) of the copolymers obtained with Et[Ind]$_2$ZrCl$_2$ and [Ind]$_2$ZrCl$_2$.

	Et[Ind]$_2$ZrCl$_2$				[Ind]$_2$ZrCl$_2$			
[1-hexene] in the feed (mol/l)	1-hexene incorp. (mol %)	[η] (dl/g)	$\overline{M}w$ (10^{-5})	$\overline{M}w/\overline{M}n$	1-hexene incorp. (mol %)	[η] (dl/g)	$\overline{M}w$ (10^{-5})	$\overline{M}w/\overline{M}n$
0	0	3.1	-	-	0	4.2	-	-
0.027	<1.0	2.3	-	-	<1.0	4.6	-	-
0.080	1.9	1.8	1.1	2.7	<1.0	2.8	2.2	3.4
0.133	4.8	1.4	-	-	<1.0	2.5	-	-
0.187	5.3	1.4	0.9	2.4	1.1	2.6	2.1	3.4
0.267	7.6	1.2	-	-	4.5	0.9	-	-
0.533	11.6	1.1	-	-	6.0	0.7	-	-

CONCLUSION

- Indenyl zirconium catalysts efficiently produce ethylene-1-hexene copolymers. When higher activities are required Et[Ind]$_2$ZrCl$_2$ must be used.
- The use of Et[Ind]$_2$ZrCl$_2$ catalyst gives higher contents of 1-hexene incorporated.
- The type of catalyst and comonomer concentration in the feed can regulate the molecular weight and molecular weight distribution.
- Thermal analysis shows that higher 1-hexene content in the copolymer produces different size of crystallites and imperfections in the crystalline lattice.

ACKNOWLEDGMENT

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