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Copolymerization of ethylene and 1-hexene with $Et(Ind)_2ZrCl_2$ in hexane

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Abstract

Copolymerizations of ethylene and 1-hexene were carried out in hexane at 60°C by using ethylenebis(indenyl)zirconium dichloride as catalyst and methylaluminoxane (MAO) as cocatalyst in presence of triisobutylaluminum (TIBA). The influence of the alkylaluminum concentration and Al_{TOTAL}/Zr molar ratio on the catalyst activity and comonomer incorporation are evaluated. Increasing the TIBA concentration, the MAO solubility augments in the polymerization milieu, as well as the catalyst activity and the comonomer incorporation. Increasing the Al_{TOTAL}/Zr molar ratio, catalyst activity becomes higher, while comonomer incorporation remained constant at around 8 wt% for molar ratios between 0 and 5000. For Al_{TOTAL}/Zr molar ratios higher than 5,000 comonomer incorporation increased gradually. Under the same experimental conditions dimethylsilylbis(indenyl)zirconium dichloride showed higher thermal stability and led to higher comonomer incorporation. © 2001 Published by Elsevier Science Ltd.

Keywords: Metallocene; MAO; Ethylene–1-hexene copolymerization

1. Introduction

Global linear low density polyethylene (LLDPE) consumption is increasing at impressive rates as people improve extrusion capabilities and search for greater product end-use performance and value. LLDPE is predicted to have the greatest increase in usage from greater than 9% increase from 1996 through 2005 to approximately 7% from 2005 through 2010 [1]. The driving force in the LLDPE growth can be attributed to metallocene-catalyzed LLDPE resins. The demand for metallocene-catalyzed polyethylene is predicted to increase 45%, i.e. from 220 to 970 kilotonnes, between 1996 and 2000 and eventually grow to 5,900 kilotonnes in the year 2010.

Properties of olefin copolymers are greatly influenced by various factors, e.g. molecular weight, molecular weight distribution, kind of comonomer, comonomer content and monomer sequence distribution. In turn, some of these properties are dependent on the nature of the catalyst and cocatalyst and on the polymerization conditions. Since the discovery of the metallocene/methylaluminoxane (MAO) catalyst system by Sinn and Kaminsky, a great amount of both industrial and academic research has been done. Such systems has been continuously reviewed in the literature [2–4]. The symmetry of the ligands in the coordination sphere around the metal center determines the stereospecificity of metallocene catalysts [5], affording polyolefins with almost all kinds of stereoregularities. Besides, metallocene catalysts produce polymers with narrow molecular weight distribution ($M_w/M_n \approx 2$), and uniform comonomer distribution.

A metallocene catalyst precursor can be activated with organoaluminoxanes, especially MAO, which provides maximum activity. The structure of MAO remains not completely elucidated, although it has been investigated by many cryoscopic, spectroscopic and other techniques [6–8]. Up to now, the most acceptable proposal for the active MAO consists of a cage-like structure. In such cages there are monomeric $AlMe_3$ molecules that provide the alkylation of the metallocene dichloride complex, and formal abstraction of a methyl anion from the transition metal to give a metallocene monomethyl cation that is stabilized by a bulky MAO anion [9].

Metallocene catalysts have high solubility in aromatic solvents like toluene due to the presence of the cyclopentadienyl rings. MAO is also very soluble in aromatic

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solvents (up to 30%), but it has very low solubility in aliphatic solvents (only 3 or 4%) [10]. However, aromatic solvents cannot be used in industrial processes due to their toxicity. The main problem concerning the use of an aliphatic hydrocarbon as the polymerization milieu is the low solubility of the catalyst components due to the low polarity of the solvent [11]. Commercial modified MAO (MMAO), prepared by controlled hydrolysis of mixture of trimethylaluminum (TMA) and triisobutylaluminum (TIBA) showed improved solubility in aliphatic solvents, keeping good polymerization efficiency. The introduction of TIBA in the polymerization milieu as the third catalyst component increases the solvent polarity, facilitating the MAO solubility and the formation and stabilization of the active species [12]. Moreover, it is worth mentioning that this approach searches for the replacement of the expensive MAO cocatalyst by cheaper alkylaluminum compounds.

The present paper reports on the influence of the TIBA concentration and Al_{Total}/Zr molar ratio on the catalytic activity and the comonomer incorporation for the catalyst system ethylenebis(indenyl)zirconium dichloride ($Et(Ind)_2ZrCl_2$)–MAO/TIBA using hexane as solvent. A qualitative evaluation of the effect of TIBA addition on MAO solution was performed at different contact times and temperatures. For comparative reasons, dimethylsilylbis(indenyl)zirconium dichloride ($Me_2Si(Ind)_2ZrCl_2$) was also investigated. The resulting copolymers were evaluated by determining their melt flow indices (MFI), intrinsic viscosity(IV), melting and crystallization temperatures.

2. Experimental procedures

2.1. Materials

Polymerization grade ethylene 99.5% and nitrogen were purified by passing through pre-activated columns of alumina, molecular sieves (13 × 4 Å) and cupper catalyst (RIDOX 230). Hexane (Exxon Co./Ibrasol) was dried over pre-activated molecular sieves (13 × 4 Å). Toluene (Reagen) was dried with calcium chloride while 1-hexene (Ethyl Co.) with calcium hydride. Both were distilled and stored over molecular sieves (4 Å) and their humidity level was controlled below 20 ppm by a Karl Fischer equipment. MAO, TIBA, $Et(Ind)_2ZrCl_2$, and $Me_2Si(Ind)_2ZrCl_2$, generously supplied by Witco were used as received and all compounds were handled under Schlenk standard techniques.

2.2. Copolymerization procedure

Slurry copolymerizations of ethylene with 1-hexene were carried out in a 2 l steel jacketed Büchi reactor (2200 rpm) at 60 or 70°C. The reactor was initially purged with nitrogen flow at 70°C for 1 h and then cooled to 40°C. Hexane (1.0 l), 1-hexene (0.4 M), TIBA ($0.0–6.3 \times 10^{-3}$ M) and MAO (1.3×10^{-4} to 2.9×10^{-3} M) were charged to the reactor in this order under inert atmosphere. The catalyst solution (1.2×10^{-6} M) in toluene solution was charged and, after a pre-contacting time of 20 min, ethylene (6 bar) was admitted into the reactor which was then heated up to 60°C. One hour later, the non-reacted monomers were purged and the copolymer collected under acidified methanol. The suspension was stirred for 2 h, filtered and the copolymer dried at 60°C under vacuum.

2.3. Qualitative solubility test

In a 2.0 l Schlenk flask equipped with a mechanical stirrer, solvent, MAO and TIBA were introduced at the same order as in the copolymerization procedure. The system was kept in a glass thermostatized bath, in order to allow the visualization of the solution aspect.

2.4. Characterization of copolymers

The comonomer incorporation was evaluated by infrared technique by means of a Nicolet 710 FT-IR spectrometer. The polymers (0.2 g) were analyzed as films pressed at 10 MPa at 190°C for 30 s. The 1-hexene content measurement was based on 1377 cm^{-1} band height as function of the film thickness. Calibration curve was performed with standard samples provided by Montell Co. presenting 2–16 wt% 1-hexene content, which was previously determined by ^{13}C NMR.

Melt flow index (MFI) was determined in a Tinius Olsen MP 987 extrusion plastometer at 190°C. The 2.16 and 10.0 kg standard weights were employed. Intrinsic viscosity (IV) of samples (0.04 g) was determined in decahydronaphthalin at 135°C using a SOFICA-CINEVISCO viscometer.

Copolymer melting and crystallization temperatures, as well crystallinity were determined by differential scanning calorimeter (DSC) analysis using a DSC 2910 connected to a Thermal Analyst 2100 Integrator, at a heating rate of 10°C/min. The heating cycle was performed twice, but only the results of the second scan are reported, since the former is influenced by the mechanical and thermal history of the samples.

Molecular weight and molecular weight distributions were investigated with a Waters high-temperature GPC instrument, CV 150C, equipped with optic differential refractometer and three Styragel HT type columns (HT3, HT4 and HT6) with exclusion limit 10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 1 l/min. The analyses were performed at 140°C. The columns were calibrated with standard narrow molar mass distribution polystyrenes and then universally with linear low density polyethylenes and polypropylenes.

^{13}C NMR was employed to determine the composition and sequence distribution of the copolymers according to procedures in the literature [13]. The ^{13}C NMR spectra were recorded at 90°C using a Varian Inova 300 spectrometer operating at 75 MHz. Sample solutions of the copolymer were prepared in *o*-dichlorobenzene and benzene-d_6 (20 v/v). Spectra were taken with a 74° flip angle, an

Table 1
nfluence of the solvent on the catalyst activity in ethylene polymerization (polymerization conditions: $[Et(Ind)_2ZrCl_2] = 1.2 \times 10^{-6}$ M; Al/Zr = 2500; $T = 60$°C; $P_{ethylene} = 6$ bar; reaction time = 1 h)

Run no.	Solvent	Yield (g)	Catalyst activity (kg PE/g cat. h)
955	Toluene	49	116
953	Hexane	20	47

acquisition time of 1.5 s, and a delay of 4.0 s. Under these conditions the spectra are 90% quantitative if only carbon atoms that have a relaxation time (T_1) inferior to 2.0 s are taken into account [14].

3. Results and discussion

3.1. Influence of the TIBA concentration on catalyst activity

The intrinsic nature of the metallocene–MAO catalyst systems restricts their solubility in aromatic solvents. Table 1 shows the catalyst activity of $Et(Ind)_2ZrCl_2$/MAO system in toluene and hexane, under identical ethylene polymerization conditions.

According to Table 1, catalyst activity in hexane was shown to be ca. 60% lower than that observed in toluene. Similar results comparing aliphatic and aromatic solvents were already reported in the literature for homogeneous and supported metallocenes [15]. As already mentioned this reduction in activity can be attributed to the lower solubility of this system in aliphatic solvent. On the other hand, few, if any, commercial polymerization processes use toluene as a diluent. Aliphatic hydrocarbons, bulk monomers, and fluidizing gas streams are used in large-scale plants.

One approach to enhance the solubility consists in increasing the polarity of the polymerization milieu. In the present study, we evaluated the influence of increments of TIBA in MAO hexane solution on ethylene/1-hexene copolymerization. The MAO concentration (2.9×10^{-3} M) and Al_{MAO}/Zr ratio (2500) were kept constant. The TIBA/MAO molar ratio was varied from 0 to 2. The Al_{Total}/Zr molar ratio also changed, due to the variation on TIBA concentration.

Fig. 1 shows the variation of the catalyst activity and 1-hexene incorporation determined by FT-IR as function of TIBA concentration, using the catalyst system $Et(Ind)_2ZrCl_2$–MAO/TIBA. In the absence of TIBA, the catalyst activity was in the range of 50–100 kg LLDPE/g cat. h. Under identical experimental conditions, the catalyst activity exhibited in the copolymerization reaction was much higher than that observed in the case of homopolymerization of ethylene (see Table 1). This fact was already reported in the literature concerning Ziegler–Natta and metallocene/MAO catalyst systems and has been named as *comonomer effect* [16–18]. This phenomenon may have a simple physical explanation: the presence of α-olefin in the reaction milieu makes the polymer product more amorphous and soluble and thus increase the number of easily accessible polymerization centers.

Catalyst activity enhanced with increasing TIBA concentration. Preliminary tests showed that there was no catalyst activity when the polymerization was carried out in hexane cocatalyzed only by TIBA. Common alkylaluminum compounds do not usually activate metallocene

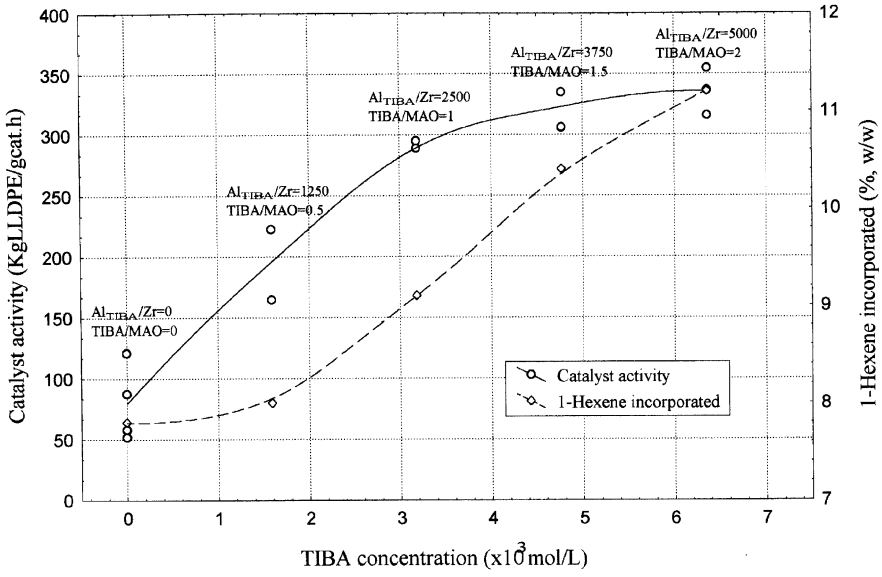

Fig. 1. Variation of catalyst activity and comonomer incorporation as function of the TIBA concentration for the copolymerization of ethylene and 1-hexene using $Et(Ind)_2ZrCl_2$–MAO/TIBA system. Polymerization conditions: hexane = 1 l; $[Et(Ind)_2ZrCl_2] = 1.2 \times 10^{-6}$ M; $Al_{MAO}/Zr = 2500$; [1-hexene] = 0.4 M; $P_{ethylene} = 6$ bar; $T = 60$°C; $t = 1$ h.

Table 2
Qualitative evaluation of MAO solubility in hexane in presence of TIBA (catalyst components addition order: 1 l hexane; $T = 40$°C, TIBA; after 6 min MAO; m.r. = molar ratio)

[TIBA] ($\times 10^3$ M)	[MAO] ($\times 10^3$ M)	TIBA/MAO (m.r.)	t (min)	T (°C)	Aspect
2.9	2.9	1	20	40	Cloudy
4.3	2.9	1.5	20	40	Decreasing cloudiness
5.8	2.9	2	20	40	With increasing
11.6	2.9	4	20	40	TIBA concentration
2.9	2.9	1	20	40	Cloudy
			30	40	Decreasing cloudiness with
			40	40	Increasing contact time
2.9	2.9	1	20	40	Cloudy
			20	50	Decreasing cloudiness with
			20	60	Increasing temperature

catalysts. Polymerizations carried out with TIBA/MAO in molar ratio varying from 1.5 to 2.0 gave catalyst activity values in the range of 300–350 kg LLDPE/g cat. h. The presence of TIBA in the polymerization milieu increased the catalyst activity at least by 200%.

In order to verify MAO solubility in hexane, we performed a qualitative evaluation by adding TIBA into a flask containing MAO in hexane. Table 2 reports the solution aspect at different TIBA increments, reaction time and temperature. As we increased the TIBA/MAO ratio from 1 to 4, the transparency of the solution increased suggesting an enhancement in MAO solubility. Similar behavior was observed with increasing time. In other words, it seems that contact time might be important to guarantee a higher activity. Besides based exclusively on MAO solubility aspect higher temperature might afford higher catalyst activity.

The increase in catalyst activity can be explained, taking into account that increasing TIBA concentration in the polymerization milieu, MAO solubility in hexane also enhances due to an increase in solvent polarity, which guarantees then a higher MAO concentration in the solution, available for stabilizing the active species. However, we cannot neglect that TIBA is often used also as a scavenger of impurities. Therefore, the increase in catalyst activity could also partly result from a decreased concentration of catalyst poisons.

According to Fig. 1, comonomer incorporation did not change significantly (≈8 wt%) as TIBA concentration was varied from zero to 1.6×10^{-3} M. For TIBA concentrations up to 6.3×10^{-3} M the comonomer incorporation increased gradually, reaching the maximum of 11 wt%. Copolymerizations at 1.2×10^{-6} M of catalyst and higher TIBA concentrations could not be carried out, since the reaction temperature could not be controlled leading to melting polymer inside the reactor.

Table 3 reports melt flow index (MFI), ratio of melt flow indices ($I_{10}/I_{2.16}$), intrinsic viscosity (IV), melting (T_{m2}) and crystallization (T_c) temperatures and crystallinity of the resulting copolymers. Copolymers with comonomer content between 7.8 and 11.2 wt% showed MFI (2.16 kg at 190°C) between 0.44 and 1.60 g/10 min., and IV values around 1.4 dl/g. Melting and crystallization temperature, as well as crystallinity remained roughly constant, respectively at 109, 96°C and 35%.

The MFI, $I_{10}/I_{2.16}$ and IV of the obtained copolymers were sensitive to the presence of TIBA. The dependence of molecular weight of copolymer on the TIBA concentration can be explained in terms of chain transfer reaction to TIBA. Similar behavior was already observed in the case of propylene syndiotactic polymerization with TIBA [19].

Table 3
Influence of the comonomer content in ethylene/1-hexene copolymers produced with $Et(Ind)_2ZrCl_2$–MAO/TIBA catalyst systems at different TIBA concentration (polymerization conditions: $[Et(Ind)_2ZrCl_2] = 1.2 \times 10^{-6}$ M; [1-hexene] = 0.4 M; Al/Zr = 2500; $T = 60$°C; $P_{ethylene} = 6$ bar; reaction time = 1 h)

Run no.	[TIBA] ($\times 10^3$ mol/l)	Comonomer incorporation (%)	MFI (2.16/10.0 kg) (g/10 min)	$I_{10}/I_{2.16}$	Intrinsic Viscosity (dl/g)	T_{m2}/T_c (°C)	Crystallinity (%)
1111	0	7.8	0.44/10.1	23.0	1.53	110/94	38
1110	1.6	8.0	0.44/10.5	23.9	1.50	111/98	35
1095	2.9	9.1	0.61/9.7	15.9	1.47	108/93	33
1097	2.9	10.0	1.00/15.7	15.7	1.41	109/94	34
1101	4.7	10.4	0.91/11.4	12.5	1.42	108/93	30
1104	6.3	11.2	1.60/19.8	12.4	1.34	109/96	32

3.2. Influence of the Al_{Total}/Zr molar ratio

The influence of the Al_{Total}/Zr molar ratio on the catalyst activity and comonomer incorporation was also investigated. The 1-hexene concentration was kept constant at 0.4 M and TIBA/MAO molar ratio equals to 2. It is worth mentioning that the Al_{Total}/Zr was reached reducing the amount of both cocatalysts. In fact, considering the optimal conditions observed under the previous conditions (Fig. 1), the molar ratio Al_{Total}/Zr corresponds to 7800, which represents a very high Al/Zr ratio and it is not interesting from the economic point of view.

Fig. 2 shows the variation of the catalyst activity and comonomer incorporation as function of the Al_{Total}/Zr molar ratio in the polymerization milieu. Catalyst activity increases with cocatalyst concentration. Even copolymerization reactions using the lowest tested cocatalyst concentrations, like $Al_{TIBA}/Zr = 230$ and $Al_{MAO}/Zr = 110$, showed a relatively high catalyst activity (≅100 kg PE/g cat. h), which corresponds to 42 tonnes PE/mol Zr h. This catalyst activity is comparable to that observed with supported conventional Ziegler–Natta catalysts (2 wt% Ti). In such cases, catalyst activity is around 3–20 kg PE/g cat. h, which corresponds to 7–48 tonnes PE/mol Ti h.

Comparing copolymerization results of catalyst system in absence of TIBA (Fig. 1, $Al_{Total}/Zr = 2500$, TIBA/MAO = 0) with those in the presence of TIBA (Fig. 2, $Al_{Total}/Zr = 2400$, TIBA/MAO = 2), we can observe that catalyst activity increased ca. 100% with partial replacement of MAO by TIBA. Such results combine two advantages. First, the reduction of the expensive MAO amount by mixing with TIBA; and secondly, the use of aliphatic solvent (which is not toxic), keeping relatively high productivity.

The comonomer incorporation was around 8 wt% for Al_{Total}/Zr molar ratio up to 5000. For higher values of Al_{Total}/Zr molar ratio the comonomer incorporation increased gradually to 11 wt%.

Table 4 shows the influence of the comonomer incorporation on the MFI, $I_{10}/I_{2.16}$, IV, T_{m2} and T_c and crystallinity of the copolymers produced. Judging from data presented in Table 4, changing the Al_{Total}/Zr molar ratio from 340 to 7800 the rheological properties of those resins seem to vary, in spite of being impossible to establish a trend between Al_{Total}/Zr and $I_{10}/I_{2.16}$. It is worth mentioning that rheological properties are the most important factor in polymer processing.

Molecular weight (M_w) and molecular weight distribution (M_w/M_n) of the same samples were determined by GPC. A slight reduction in molecular weight was observed with increase in the Al_{Total}/Zr ratio, probably due to chain transfer reaction to alkylaluminum during the polymerization reaction. Values of M_w/M_n are close to that usually reported for these single site catalysts, i.e. close to 2.0.

3.3. Influence of the nature of the bridge and copolymerization temperature

The bridging unit of *ansa*-bisindenyl zirconium dichloride complexes has an important influence on the catalytic properties of these complexes [20,21]. An increase in the *bite angle* is achieved by changing the ethylene bridge by the *silyl* one. A bigger *bite angle* is supposed to increase the catalyst activity because of an unforced monomer

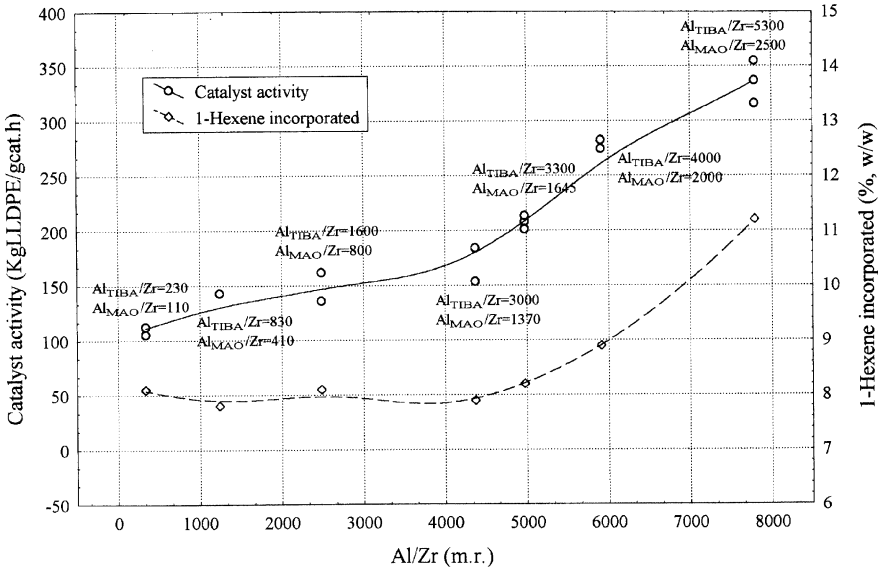

Fig. 2. Variation of catalyst activity and comonomer incorporation as function of the Al_{Total}/Zr molar ratio for the copolymerization of ethylene and 1-hexene using $Et(Ind)_2ZrCl_2$–MAO/TIBA system. Polymerization conditions: hexane = 1 l; $[Et(Ind)_2ZrCl_2] = 1.2 \times 10^{-6}$ M; TIBA/MAO = 2; [1-hexene] = 0.4 M; $P_{ethylene} = 6$ bar; $T = 60°C$; $t = 1$ h.

Table 4
Influence of the comonomer content in ethylene/1-hexene copolymers produced with $Et(Ind)_2ZrCl_2$–MAO/TIBA catalyst systems produced with different Al_{Total}/Zr molar ratios (polymerization conditions: $[Et(Ind)_2ZrCl_2] = 1.2 \times 10^{-6}$ M; [1-hexene] = 0.4 M; TIBA/MAO = 2; $T = 60°C$; $P_{ethylene} = 6$ bar; reaction time = 1 h; nd = non determined)

Run no.	Al_{Total}/Zr (molar ratio)	Comonomer incorporation (wt%)	MFI (2.16/10.0 kg) (g/10 min)	$I_{10}/I_{2.16}$	Intrinsic Viscosity (dl/g)	T_{m2}/T_c (°C)	Crystallinity (%)	M_w (10^5)	M_w/M_n
1144	340	8.1	3.1/23.0	7.4	1.38	110/96	35	nd	nd
1147	1240	7.8	1.6/14.8	9.3	1.43	111/97	39	7.8	2.5
1128	2400	8.1	0.4/12.8	32.0	1.43	109/95	37	7.9	2.6
1131	4370	7.9	0.4/12.8	32.0	1.42	109/95	38	nd	nd
1133	4370	8.2	1.0/14.3	14.3	1.44	109/95	37	nd	nd
1135	6000	8.9	0.6/13.7	22.8	1.42	108/93	34	6.5	2.2
1104	7800	11.2	1.6/19.8	12.4	1.34	109/96	32	5.8	2.3

Table 5
Influence of the nature of the bridge and reaction temperature on catalyst activity, on comonomer incorporation and on ethylene/1-hexene copolymers properties (polymerization conditions: $[Et(Ind)_2ZrCl_2] = 1.2 \times 10^{-6}$ M; [1-hexene] = 4 M Al/Zr = 5000; TIBA/MAO = 1; $P_{ethylene} = 6$ bar; reaction time = 1 h)

Bridge	Ethylene (Et)		Dimethylsilyl (Me_2Si)	
Run no.	1031	1028	1043	1046
Temperature (°C)	60	70	60	70
Yield (g)	146.1	120.0	30.8	52.0
Activity (kg LLDPE/g cat. h)	292.2	240.0	61.6	104.0
Comonomer incorporation (wt%)	9.9	10.1	11.4	12.0
MFI (2.16/10.0 kg) (g/10 min)	1.1/13.4	0.5/7.5	1.6/11.3	1.0/10.0
$I_{10}/I_{2.16}$	12.2	15.0	7.1	10.0
IV (dl/g)	1.43	1.40	1.43	1.58
T_{m2}/T_c (°C)	109/93	106/92	99/85	98/85
Crystallinity (%)	30	27	25	24

Table 6
Chemical composition and triad sequence distribution of the ethylene/1-hexene copolymers obtained with $Et(Ind)_2ZrCl_2$–MAO/TIBA system

Run no.	T (°C)	^{13}C NMR										FT-IR	
		[HHH] (mol%)	[EHH] (mol%)	[EHE] (mol%)	[EEE] (mol%)	[HEH] (mol%)	[HEE] (mol%)	[H] (mol%)	[E] (mol%)	n_E (unities)	n_H (unities)	[H] wt%	[H] mol%
1031	60	0.0	0.0	3.8	88.5	0.0	7.7	3.8	96.2	25.0	1.0	9.9	3.5
1033	70	0.0	0.0	3.8	88.5	0.0	7.7	3.8	96.2	25.1	1.0	10.1	3.6

entrance, as well as the comonomer incorporation. However, electronic and kinetics factor must also be taken into account.

Table 5 reports catalyst activity, 1-hexene incorporation and resulting copolymer properties, using $Et(Ind)_2ZrCl_2$ and $Me_2Si(Ind)_2ZrCl_2$. Comparing both catalysts, $Et(Ind)_2ZrCl_2$ was shown to be the most active. The lowest catalyst activity exhibited by $Me_2Si(Ind)_2ZrCl_2$ can be in part attributed to the higher comonomer incorporation, which in turn is due to the bigger *bite angle* of the catalyst, conferred by the silyl bridge. Propagation chain constants involving 1-hexene insertion are about 60 lower than those concerning ethylene insertion [22]. Therefore, yield is reduced as higher comonomer insertion takes place.

The increase in copolymerization temperature leads to an increase in catalyst activity in the case of $Me_2Si(Ind)_2ZrCl_2$, while a small reduction in the case of $Et(Ind)_2ZrCl_2$. The stability of active species is believed to be substantially dependent on the rigidity of the framework [23]. Then, the higher activity exhibited by the former catalyst can be in part attributed to the nature of the bridge.

The increase of copolymerization temperature from 60 to 70°C did not affect the comonomer incorporated content, and consequently the MFI, IV and thermal properties of the resulting copolymers (Table 5).

In our copolymerization procedure, 1-hexene is fed before the catalyst and 20 min. before ethylene. As a consequence, we cannot neglect the possibility that part of the 1-hexene might be polymerized to poly-1-hexene. Under these experimental conditions, no 1-hexene homopolymer was observed. In order to check that possibility, we performed ^{13}C NMR of polymers produced by $Et(Ind)_2ZrCl_2$ both at 60 and 70°C. Table 6 reports on the microstructure of

the copolymers. For comparative reasons, data obtained by FT-IR measurements were also included. The absence of [HHH] triads suggests that if 1-hexene homopolymerization takes place, this is negligible.

4. Conclusions

In $Et(Ind)_2ZrCl_2$–MAO/TIBA catalyst system the addition of TIBA in an aliphatic solvent lead to an enhancement of catalyst activity as well as 1-hexene incorporation. This fact may be in part attributed to an increase in MAO solubility in the polymerization medium. Under our experimental conditions we could observe that Al_{Total}/Zr molar ratio between 5000 and 8000, both catalyst activity and 1-hexene incorporation increased.

The addition of TIBA in the polymerization milieu, having an aliphatic solvent seems to be a potential solution to overcome the problem of using aromatic solvents in industrial processes.

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