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Ethylene-propylene copolymers by a supported Ziegler-Natta catalyst based on $TiCl_4/MgCl_2$

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Summary

Ethylene-propylene copolymers have been prepared by using Ziegler-Natta catalysts based on $TiCl_4$, $MgCl_2$, PCl_3 and $(n\text{-}Bu)_3PO_4$. The catalysts $TiCl_4/MgCl_2/PCl_3$ and $TiCl_4/MgCl_2/(n\text{-}Bu)_3PO_4$ were prepared by reacting $TiCl_4$ with pretreated $MgCl_2$. The support was prepared by ball milling of $MgCl_2$ with varied amounts of PCl_3 or $(n\text{-}Bu)_3PO_4$. The addition of PCl_3 has remarkably increased the $MgCl_2$ surface area in comparison with $(n\text{-}Bu)_3PO_4$. The effects of PCl_3 and $(n\text{-}Bu)_3PO_4$ on ethylene homopolymerization, ethylene-propylene copolymerization and on copolymer properties were evaluated. The catalyst system containing PCl_3 permitted to synthesize propylene-ethylene copolymers with up to 75 % (w/w) of propylene and provided control of copolymer crystallinity. The reduction of the copolymer molecular weight distribution suggested that PCl_3 acted as an internal donor, poisoning some active catalytic sites.

Introduction

Great efforts have been dedicated to the synthesis of elastomeric polyolefins by the application of heterogeneous Ziegler-Natta catalysts based on $TiCl_4/MgCl_2$. This is due, partially, to the high performance and versatility of magnesium chloride supported catalysts in the industrial production of isotactic polypropylene [1].Amorphous and elastomeric ethylene-propylene (E-P) copolymers have been produced by soluble vanadium catalysts, however, these catalytic systems show low activity, produce copolymers without control of the microstructure, and consequently the range of copolymer applications are limited [2,3]. By the application of titanium catalysts it is possible to produce E-P copolymers in particle form with high activity and consequently decreased production costs [4,5]. Although, titanium catalysts produce rubbery copolymers with undesirable crystallizable ethylene sequences [6 - 8], they have the advantage of being applied at high temperatures. It is well known that the properties of polyolefins depend on the catalyst type and on the production process [1,8,9]. The recent generation of supported Ziegler-Natta catalysts for polyolefin polymerization, e.g. $TiCl_4.MgCl_2$ internal electron donor (ID) / $AlEt_3$ (TEA), has been modified for the production of amorphous ethylene-propylene copolymers.

The performance of these highly active catalysts has been improved by using a proper support activated by a select internal electron donor, $TiCl_4$, and TEA as cocatalyst. It is well stablished that these heterogeneous catalysts in general have multiple active sites

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with different natures. As a result, E-P copolymers produced by these catalytic systems present a multiplicity of structures [6]. The role of the electron donor has been explained by the selective poisoning of non-stereospecific active centers or by the conversion of non-stereospecific active centers into stereospecific ones [9]. Ziegler-Natta supported catalysts based on $TiCl_4/MgCl_2$ are generally prepared by grinding. The grinding process is not easy to study or even to reproduce in devices of different designs. In the literature most of the studies describe surface area or X-ray diffraction variations during grinding which give information about the influence of grinding conditions, type and content of internal donor, on the size and shape of the catalytic particles and on some polymer characteristics [10]. Few papers in the literature discuss the influence of the type and content of IDs on the microstructure and chemical properties of E-P copolymers[11-15].

Some modifications have been proposed for supported catalysts based on $TiCl_4/MgCl_2$ to synthesize E-P copolymers combining specific properties such as narrow molecular weight distribution, amorphous structure, high comonomer content and high catalyst efficiency. These modifications include the addition of phosphorous compounds such as PCl_3, PCl_5 , $POCl_3$, $(n\text{-}Bu)_3PO_4$ [11], during the $MgCl_2$ milling. Although important studies have been carried out in this area, the control of the copolymer microstructure has not been attained yet [6,7,11,12,14-16]. The objective of these modifications is to obtain adequate heterogeneous catalytic systems, to produce copolymers with controlled molecular weight distribution, homogeneous composition, low crystallinity and thus to attain elastomeric copolymers with uniform properties [4,5-7,12,13,15]. Xingfa has applied directly PCl_3 in the synthesis of the $TiCl_4/MgCl_2$ catalyst and attained good results in regard to controlling of molecular weight distribution of E-P copolymers [12] . However the author did not discuss the catalyst performance in the controlling of the microstructure. Makino et al. [11] have used $(n\text{-}Bu)_3PO_4$ in the synthesis of catalyst based on $TiCl_4/MgCl_2$ and attained rubbery E-P copolymers with low crystallinity and high propylene incorporation.

The purpose of this work is to investigate the influence of PCl_3 or $(n\text{-}Bu)_3PO_4$ addition during the $MgCl_2$ milling on the properties of E-P copolymers produced by the catalyst systems $TiCl_4$ / $MgCl_2$ / ID where ID is PCl_3 or $(n\text{-}Bu)_3PO_4$.

Experimental

Materials: Polymerization grade ethylene and propylene and argon were purified by passing the gases through columns of molecular sieve (3Å) and BASF catalyst for removal of water and oxygen, respectively. Extra pure grade titanium tetrachloride, from Riedel De Haën AG Seelze-Hanover (99,9 %), triethylaluminum (TEA) from Texas Alkyls Inc. (95,5 %), was used as a 1.6 M n-hexane solution. Commercial n-hexane was provided by Ibrasol. Phosphorous trichloride (PTC) purchased from Vetec S.A and tributyl phosphate (TBP) from Riedel De Haën AG Seelze-Hanover, were dried over preactivated molecular sieve (3Å) for at least 30 hr. Anhydrous magnesium chloride, provided by Toho Titanium, was ground with the electron donor (PTC or TBP) in a ball mill for 48 hours.

Catalyst preparation : The catalysts were obtained by impregnating ball milled $MgCl_2$ / PTC or TBP support with $TiCl_4$, at 85 °C, in a 250 mL glass reactor. The catalysts were characterized by chemical analysis. X-ray diffractograms of the catalyst supports were also made. The samples for X-ray analysis were prepared on a Mylar film. The range of 2Θ

angle employed was from 2° to 70° . The preparation and characterization of the support and catalyst have been described [13].

Polymerizations: The slurry ethylene polymerizations and ethylene-propylene copolymerizations were carried out in 150 mL of n-hexane in a 300 mL stainless steel Parr reactor, of semibatch type, equipped with temperature control. In the ethylene-propylene copolymerization the monomer mixture was separately prepared in a 1 L stainless steel cylinder, at 85 °C and 2 kgf/cm^2 of each monomer (total pressure of 4 kgf/cm^2). Then the monomer mixture was continuously fed into the reactor at 80 °C and the copolymerization was let to progress for 15 minutes. The monomer mixture composition was measured by gas chromatography before and after de copolymerization and the variation of the compostion in the cylinder was less than 10 %. Details of the polymerization procedure have been described [13].

Polymer characterization : The melting temperature(T_m) and enthalpy of fusion (ΔH_m) of the copolymers were determined by a Perkin-Elmer calorimeter (model DSC-7). The determination of glass transition temperature (T_g) was performed by a DuPont Thermal Analyzer, Model 910, according to ASTM D3418-82, at heating and cooling rates of 20 °C/ min. The copolymer cristallinity was estimated, in order to compare different samples, by taking the fusion enthalpy of 100 % crystalline high density polyethylene (286.32 J/g) as a standard value.

The crystallinity content (X_c) was calculated by using the expression [17]:
$\mathbf{X_c = (\Delta H_c / \Delta H_{PE}) . 100}$, where: ΔH_c = sample fusion enthalpy in J/g; ΔH_{PE} = 100 % crystalline fusion enthalpy of HDPE in J/g.

The propylene content, the diads EE, EP, PP, and the triads EEE, PPP, EPE, PEP, PEE, PPE, contents were measured by ^{13}C-NMR, in a 300 MHz. VARIAN spectrometer. The reactivity ratios were calculated by the expressions [6]:
$\mathbf{r_1 = 2. (EE)/ (EP). X}$ and $\mathbf{r_2 = 2. (PP). X / (EE)}$, where:
EE - diad ethylene-ethylene content in wt %;
EP - diad ethylene-propylene content in wt %;
PP - diad propylene-propylene in wt %;
X - ratio between ethylene and propylene concentrations in mol %.

The soluble copolymer was isolated by Soxhlet extraction for 8 hours with n-hexane. The soluble content was calculated by using the relation: $\mathbf{S = C_s. 100 / C_t}$, where:
S - soluble copolymer content in wt %;
C_s - soluble copolymer weight in grams ;
C_t - total copolymer weight in grams.

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using a WATERS 150 C chromatograph. Complete description of copolymer characterizations has been presented [13].

Results And Discussion

$MgCl_2$ with high degree of disorder was obtained by ball milling, in the presence of PTC or TBP electron donors.

Table 1 shows the effect of PTC content on catalyst ($TiCl_4/MgCl_2$-PTC) characteristics and on catalyst performance in the ethylene homopolymerization. The PTC content was varied from 0 to 17.2 molar %.

The addition of PTC during $MgCl_2$ milling has, remarkably, increased the support surface area. The surface areas of $MgCl_2$-PTC supports are in the same order of magnitude as those obtained for supports prepared using ethyl benzoate as internal donor [15]. This result indicates that the complexation behavior of both electron donors relative to $MgCl_2$ must be similar. An increase of phosphorous content on the catalyst was observed when the amount of PTC added to the $MgCl_2$ milling was increased, but the magnesium and chloride contents remained pratically constant. The increase of phosphorous content, that was followed by a decrease of Ti in the catalyst, is an indication that the PTC incorporation occurred mainly on the catalyst surface. On the other hand, the decrease of Ti incorporation can be attributed to the decrease of free-chloride vacancies in the surface of milled $MgCl_2$, caused by PTC complexation. The decrease of catalytic activity when the PTC content was increased can be attributed to the decrease of catalytic sites, by the poisoning effect of PTC. Table 2 shows the influence of TBP addition, on catalyst ($TiCl_4/MgCl_2$-TBP) characteristics and on catalyst performance in ethylene homopolymerization. The addition of TBP did not promote the increase of the surface area of the support in relation to the support obtained without the electron donor. Probably this was due to the reaggregation of crystallites during milling. This conclusion is corroborated by the $MgCl_2$ X-ray diffractograms shown in Figure 1.

Figure 1 shows that the intensities of reflections at 15° (plane [003]), 30° (plane [101]) and 35° (plane[104]) diminished more strongly when PTC was added to $MgCl_2$ than in the case of TBP addition. One may conclude that the complexing power of PTC is probably higher than that of TBP's.

Table 2 shows a marked increase of phosphorous content on the catalyst when the amount of TBP added to $MgCl_2$ was increased, but the magnesium and chloride contents remained unchanged. The increase of phosphorous content was followed by an increase of Ti in the catalyst. Probably, a reaction between TBP and $TiCl_4$ has occurred and the generated products were impregnated on the catalyst crystal lattice. When the amount of TBP was increased a gradual decrease of catalytic activity occurred. That can be explained by the decrease of potential active site formation by the ID poisoning of the free-chloride vacancies on the support.

Effect of PTC and TBP on the copolymer properties

A decrease on the catalyst activity was observed in ethylene-propylene copolymerization as the amount of PTC added during the $MgCl_2$ milling was increased.
Table 3 shows the influence of PTC content on the properties of ethylene-propylene copolymers obtained with the $TiCl_4/MgCl_2$-PTC catalyst systems. The presence of PTC during the milling of $MgCl_2$ greatly affected copolymer properties. The incorporation of propylene increased when PTC was initially added to $MgCl_2$ milling, and then a slight decrease of propylene incorporation was observed when the amount of PTC was subsequently increased. There is strong evidence that PTC was incorporated in the catalyst system and influenced the insertion of propylene in the copolymer. The increase of PTC was followed by an increase in the T_g of the E-P copolymer, probably due to the increase of propylene incorporation as it is postulated in the literature [3]. The copolymer crystallinity was low and remained pratically constant when the PTC content was increased.

Table 1: Influence of PTC addition in the $MgCl_2$ milling on the catalyst ($TiCl_4/MgCl_2$ -PTC) characteristics and catalyst performance in the ethylene polymerization

Catalyst (Code)	PTC content (mol %)	Support specific area (m^2/g)	Catalyst Ti content (wt %)	Catalyst P content (ppm)	Catalyst Cl content (wt %)	Catalyst Mg content (wt %)	Reaction run (Code)	Catalyst activity (Kg pol/ g.Ti.h)
G12	0.0	17	1.00	0	71	23	HP156	40
G14PTC	3.2	45	1.15	1700	68	22	HP165	42
G16PTC	6.5	47	1.04	2100	67	22	HP188	36
G15PTC	9.8	47	1.14	2400	67	23	HP158	26
G13PTC	13.4	50	0.92	2700	68	24	HP159B	22
G17PTC	17.2	41	0.72	3200	69	24	HP186	17

Polymerization conditions: Temperature = 85 °C; ethylene pressure = 3.0 kgf/cm^2; Al/Ti molar ratio = 15; [Ti] = 0.01mg/ml; co-catalyst: TEA; polymerization time = 15 min; polymerization solvent: n-hexane

The low crystallinities are probably due to the high propylene incorporation in the copolymer, as indicated by T_g.The copolymer polydispersion showed a decrease when the PTC amount was increased. The lowest polydispersion was attained with the catalyst prepared with 9.8 mol % of PTC . Higher amounts of PTC did not alter the copolymer polydispersion. This behaviour indicates that PTC poisoned some catalyst sites acting as ID and it has remained in the catalyst bulk, since phosphorous was detected on the catalyst (Table 1). Table 4 shows the effect of TBP content on the properties of ethylene-propylene copolymers obtained with the catalyst systems ($TiCl_4/MgCl_2$-PTC). The catalyst activity decreased markedly when the amount of TPB added during $MgCl_2$ milling was increased (Table 4). The catalytic activity was more influenced by the presence of the TBP in milling than by the presence of PTC (Table 3). The highest values of catalytic activity were attained by the catalyst prepared with PTC. The presence of TBP affected the propylene incorporation, the Tg of the copolymer, and copolymer molecular weight Mw. The values of copolymer polydispersion were slightly lower than that of the copolymer produced with the catalyst prepared without electron donor (G12).

Effect of TBP on the ethylene-propylene copolymer microstructure

Table 5 shows the effect of the TBP content on the diad and triad distribution of ethylene-propylene copolymers obtained with the catalyst $TiCl_4/MgCl_2$-TBP. The addition of TBP has strongly affected the diad and triad content. The EEE triad proportion incresead from 6.4 wt % to 23.9 wt % and PPP triad decreased from 53.1 wt % to 18.5 wt % when the TBP content increased from 0.0 to 5.6 mol %. For the same variation of TBP, the EE diad content increased from 11.2 wt % to 37.0 wt % and PP diad showed an marked decrease from 65 wt % to 26.5 wt %.These results show that there was an increase of the ethylene blocks and a decrease of propylene blocks in the copolymer chains. The EPE* (EPE + PEP) random triad increased from 13.5 wt % to 24.0 wt % when the TBP content was increased from 0.0 to 5.6 mol %. This result means that the copolymer structure has changed from a PPP block structure to a more random enchainment. These results show that TBP, or a possible compound derived from a reaction between $TiCl_4$ and TBP, has changed the nature of catalyst sites.

Table 2: Influence of TBP addition in the MgCl$_2$ milling on the catalyst characteristics (TiCl$_4$/MgCl$_2$-TBP) and catalyst performance in the ethylene polymerization

Catalyst (Code)	TBP content in milling (mol %)	Support specific area (m^2/g)	Catalyst Ti content (wt %)	Catalyst P content (ppm)	Catalyst Cl content (wt %)	Catalyst Mg content (wt %)	Reaction run (Code)	Catalyst activity (Kg pol/ g.Ti.h)
G12	0.0	17	1.00	0	71	23	HP156	40
G9TBP	2.6	16	2.90	6500	67	24	HP135	36
G8TBP	4.6	2	2.42	11000	67	24	HP153	31
G7TBP	5.6	20	4.09	13000	64	24	HP216	20

Polymerization conditions: see in Table 1.

Effect of PTC on the ethylene-propylene copolymer microstructure

The effect of PTC content on the microstructure of the ethylene-propylene copolymer produced with the TiCl$_4$/MgCl$_2$-PTC catalyst is shown in Table 5. The ethylene-propylene copolymer produced with the catalyst without electron donor showed the highest proportion of PP diad and PPP triads. These sequences diminished when PTC was added to the MgCl$_2$. The PPP triad content decreased from 53.1 wt % to 11.2 wt %, when the content of PTC was varied from 0.0 mol % to 17.2 mol % respectively. The PP diad content decreased from 65.0 wt % to 35.9 % wt % when the PTC content was increased from 0.0 mol % to 13.4 mol %. As it is observed in Table 5 the addition of PTC caused an increase in the proportions of EEE triad and EE diad to a determined value and then remained constant after subsequent additions of PTC. The EPE* (EPE+PEP) random triads increased from 13.5 wt % to 24.3 wt %, when the PTC content was varied from 0.0 mol % to 17.2 mol %. One may conclude that the copolymer changed from a PPP block structure to a more random one. That conclusion is corroborated by the $r_1 \bullet r_2$ value (Table 4).

Table 3 : Effect of PTC content on the properties of the ethylene-propylene copolymer

Catalyst (Code)	PTC content (mol %)	Catalyst activity (Kg pol/ g.Ti.h)	Copolymer propylene content (wt %)	Soluble content (%)	T$_G$ (°C)	X$_c$ (%)	$\bar{M}n$ (x10^{-3})	$\bar{M}w$ (x10^{-3})	$\bar{M}w/\bar{M}n$	$r_1 \cdot r_2$
G12	0.0	16.3	58.1	70	-51	0.9	5.7	91.0	15.9	5.13
G14PTC	3.2	9.5	78.4	93	-39	0.8	22.4	95.4	8.9	4.86
G16PTC	6.5	9.1	75.1	86	-38	0.7	8.2	60.7	7.4	2.80
G15PTC	9.8	8.2	75.7	93	-40	0.4	10.5	59.3	5.7	2.17
G13PTC	13.4	8.6	73.5	94	-31	0.1	8.5	86.7	9.6	2.81
G17PTC	17.2	9.6	71.9	88	-31	0.1	17.4	169.2	9.7	5.95

Polymerization conditions: Temperature = 85 °C;; Al/Ti molar ratio = 15; [Ti] = 0.01mg/ml; co-catalyst: TEA; polymerization time = 15 min; polymerization solvent: n-hexane; ethylene pressure = 2.0 kgf/cm^2; propylene pressure = 2.0 Kgf/cm^2

Table 4: Effect of TBP content on the properties of ethylene-propylene copolymer

Catalyst (Code)	TBP content (mol %)	Catalytic activity (Kg pol/ g.Ti.h)	Copolymer propylene content (wt %)	Soluble content (%)	T_G (°C)	X_c (%)	$\bar{M}n$ ($x10^{-3}$)	$\bar{M}w$ ($x10^{-3}$)	$\bar{M}_w / \bar{M}n$	$r_1 . r_2$
G12	0.0	16.3	58.1	70	-51	0.9	5.7	91.0	15.9	5.13
G9TBP	2.6	6.5	75.7	90	-46	0.0	4.1	50.6	12.3	2.87
G8TBP	4.6	8.4	76.5	97	-42	0.1	5.3	73.4	13.8	2.98
G7TBP	5.6	6.1	70,6	55	-46	3.6	3.9	50.1	12.8	2.92

Polymerization conditions: see in Table 3.

Table 5 : Effect of ID content on the diad and triad distribution of the ethylene-propylene copolymers

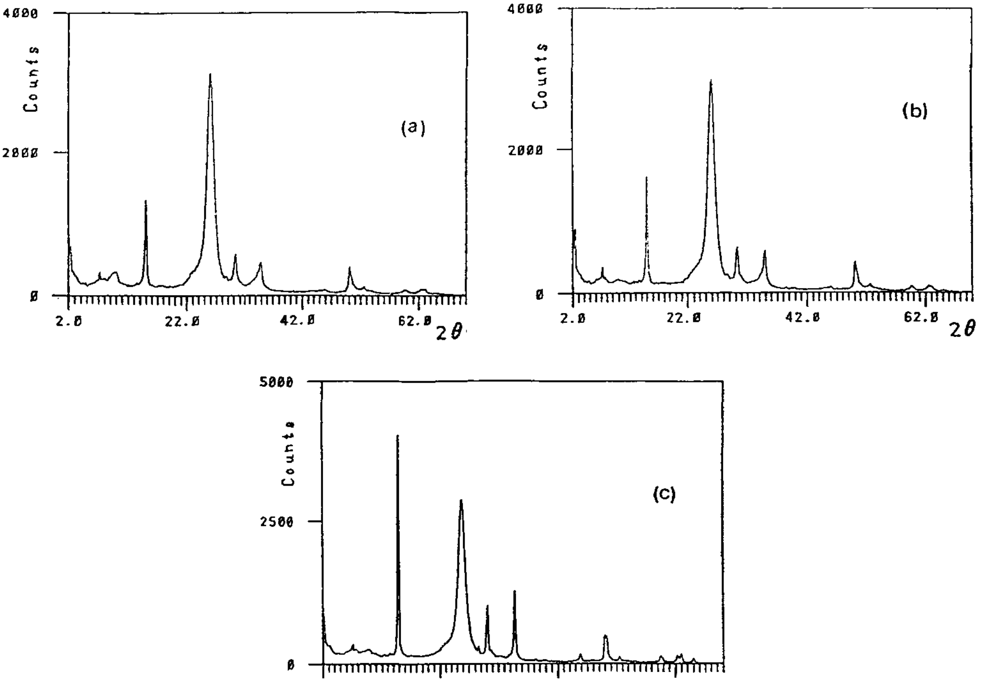
Catalyst (Code)	ID content (mol %)	EEE triad content (wt %)	PPP triad content (wt %)	EPE* triad content (wt %)	PEE triad content (wt %)	PPE triad content (wt %)	EE diad content (wt %)	PP diad content (wt %)	PE diad content (wt %)
G12	0.0	6.4	53.1	13.5	13.8	13.2	11.2	65.0	23.8
G9TBP	3.2	23.9	18.5	24.0	16.2	34	38.7	25.8	35.5
G8TBP	6.5	11.5	32.2	20.2	22	16.9	18.8	46.8	34.3
G7TBP	9.8	19.7	16.1	15.4	19.9	23.9	29.3	36.2	34.5
G14PTC	3.2	12.4	27.5	24.0	20.2	19.5	22.5	40.8	36.0
G16PTC	6.5	13.0	25.5	23.0	19.3	19.1	22.9	40.7	36.0
G15PTC	9.8	13.4	24.3	23.5	22.0	16.9	23.0	37.2	39.8
G13PTC	13.4	14.9	22.8	24.3	20.7	20.9	28.7	35.9	38.0
G17PTC	17.2	13.7	25.4	24.3	22.4	14.2	28.0	43.4	28.0

Polymerization conditions: see in Table 3.

Conclusion

PTC showed a better performance than TBP as ID, probably, the complexing power of PTC is higher than that of TBP. The catalytic activity in ethylene-propylene copolymerization was more affected by the variation of TBP content than by the PTC content.The highest values of catalytic activity were attained for polymers produced with the catalyst prepared with PTC. The copolymerization of ethylene-propylene with the $TiCl_4/MgCl_2$ /PTC system resulted in high propylene incorporation in the copolymer, high content of soluble copolymer, and very low crystallinity. The copolymer polydispersion was much more sensitive to PTC content than to TBP content.The copolymer microstructure was affected by the addition of PTC and TBP to the $MgCl_2$ milling. These compounds changed the copolymer structure from a PPP block one to a more random one.

Figure 1: X-ray diffractograms of $MgCl_2$ supports obtained (a) with PTC, (b) with TBP and (c) without electron donor addition



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