Role of the Pair of Internal and External Donors in $MgCl_2$-Supported Ziegler–Natta Catalysts

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ABSTRACT: Three different external donors, ethyl benzoate (EB), 2,2,4,4-tetramethylpiperidine (TMPip), and phenyltriethoxysilane (PTES), have been used with catalysts $MgCl_2/EB/TiCl_4$ and $MgCl_2/BEHP/TiCl_4$ (bis(2-ethylhexyl) phthalate (BEHP)), using selectively ^{13}C enriched $AlEt_3$ as cocatalyst. The heptane-insoluble–octane-soluble and octane-insoluble fractions of all the samples have been characterized by the gel permeation chromatography (GPC) and ^{13}C NMR analysis. The stereochemical and GPC data have been compared with the results of the study of the exchange between internal and external donors by GC analysis of the solid catalyst. On the basis of all these data, we can conclude that (i) the effectiveness of a catalytic system depends on the choice of the pair of internal and external donors rather than on the single internal and external donor, and (ii) while the amount of activation clearly depends on the external donor, the internal donor affects the stereoregularity.

Introduction

In previous papers we reported a stereochemical study of the Lewis base activation in high-yield supported Ziegler–Natta catalysts for isotactic propene polymerization.[1,2] Our approach consisted in finding the conditions in which different Lewis bases, used both as internal and external bases, produced an evident activation effect and then in evaluating, in such conditions, the variation in the initiation stereoregularity. The initiation stereoregularity is evaluated through ^{13}C NMR analysis of the stereochemical structure of the enriched chain end groups obtained in the presence of the selectively ^{13}C enriched cocatalyst $Al(^{13}CH_2CH_3)_3$.[3] We have shown that the extent of the first step stereoregularity is always lower than the propagation stereoregularity and varies from one catalyst to another, depending on the characteristics of each catalytic system, that is, on the size and on the relative positions of the active titanium ligands.[4-7] In particular we have observed that, in the $MgCl_2$-supported catalysts, the presence of either the internal or the external bases is accompanied by a change in the extent of the first-step stereoregularity and that different bases produce different variations.[1,2] On the basis of these findings and of our previous data we deduced that both the internal and the external bases are present in the environment of at least some of the isospecific centers and consequently the activation derives, at least partially, from a direct effect of the Lewis bases on the active sites. However, many problems are still open concerning the mechanism of the activation, the specific roles of the internal and external bases, the actual location of the base on the catalyst surface, and the role of the complex between the Lewis base and the aluminum alkyl cocatalyst.

In the present paper we have performed a wide and systematic study by comparing the effect of three different external donors, ethyl benzoate (EB), 2,2,6,6-tetramethylpiperidine (TMPip), and phenyltriethoxysilane (PTES), on two catalysts containing ethyl benzoate and bis(2-ethylhexyl) phthalate (BEHP), respectively, as internal bases. The stereochemical characterization of the most isotactic fraction was associated with the GPC characterization. Moreover, the stereochemical and gel permeation chromatography (GPC) data were compared with the results of the study of the exchange between internal and external bases by GC analysis of the base content of the solid catalyst.

The approach to the problem through different experimental investigations has allowed us to individuate some new aspects of the base activation effect concerning the behavior of the specific pairs of internal and external bases rather than the behavior of the single internal or external base and to determine some general trends in the Lewis base behavior.

Results and Discussion

(1) Propylene Polymerization with Different Pairs of Internal and External Bases. Three different bases, EB, TMPip, and PTES, have been used with both catalysts $MgCl_2/EB/TiCl_4$ and $MgCl_2/BEHP/TiCl_4$ (bis(2-ethylhexyl) phthalate (BEHP)) using selectively ^{13}C enriched $AlEt_3$ as cocatalyst. All the polymers were separated into isotactic and atactic fractions by extracting them with boiling heptane. The isotactic fractions were further extracted with boiling octane. The heptane-insoluble–octane-soluble and octane-insoluble fractions of all the samples were characterized by gel permeation chromatography and ^{13}C NMR analysis. All the results are shown in Table I (EB as an internal base) and Table II (BEHP as an internal base).

Taking the experiments without any external base as starting points, we can observe that the addition of the external base always produces an increase in isotactic productivity,[9] with the extent depending on the base. Moreover, while in the experiments without any base the heptane-insoluble fraction is completely octane soluble (EB as an internal base, Table I) or a relatively low octane-insoluble fraction is present (BEHP as an internal base, Table II), when the external base is added, an octane-insoluble fraction is always present, and this can reach more than 50% of the overall isotactic polymer. All the octane-insoluble fractions are characterized by higher $\bar{M}_w$ and lower $\bar{M}_w/\bar{M}_n$ values with respect to the correspond-

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Table I
Effect of Different Bases on the Catalyst $MgCl_2/EB/TiCl_4$[a]

Be[b]	Y[c]	II[d]	IP[e]	Fr[f]	wt %	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	[mm][g]	[e][h]
0	65	45	2199	E-8	45	200	4.7	0.95	0.76
				I-8	0				
EB	38	94	2685	S-8	40	218	5.7	0.96	0.75
				I-8	54	491	2.9	0.99	0.94
TMPip	69	91	4721	S-8	41	207	4.5	0.96	0.75
				I-8	50	531	3.2	0.99	>0.95
PTES	46	94	3251	S-8	47	323	5.5	0.96	0.84
				I-8	47	573	2.9	0.99	>0.95

[a] Cocatalyst $Al(^{13}CH_2CH_3)_3$. [b] External base. [c] Yield in grams of polymer/(grams of catalyst·hour). [d] Isotacticity index, weight percent of heptane-insoluble fraction. [e] Isotactic productivity, yield in grams of isotactic polymer/(grams of Ti·hour). [f] Fraction: S-8, octane-soluble fraction; I-8, octane-insoluble fraction. [g] Molar fraction of isotactic triads by NMR. [h] Extent of the first-step stereoregularity expressed as molar fraction of isotactic (e) placement of the first propene unit.[8]

Table II
Effect of Different Bases on the Catalyst $MgCl_2/BEHP/TiCl_4$[a]

Be[b]	Y[c]	II[d]	IP[e]	Fr[f]	wt %	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	[mm][g]	[e][h]
0	62	73	1489	S-8	49	250	4.5	0.94	0.68
				I-8	24	497	3.0	0.95	0.83
EB	75	76	1875	S-8	66	195	3.5	0.93	0.71
				I-8	10	449	2.8	0.98	0.89
TMPip	66	91	1976	S-8	47	260	4.4	0.92	0.62
				I-8	44	493	2.9	0.96	0.82
PTES	65	94	2010	S-8	45	238	4.9	0.97	0.77
				I-8	49	467	2.8	0.96	0.93

[a] Cocatalyst $Al(^{13}CH_2CH_3)_3$. [b] External base. [c] Yield in grams of polymer/(grams of catalyst·hour). [d] Isotacticity index, weight percent of heptane-insoluble fraction. [e] Isotactic productivity, yield in grams of isotactic polymer/(grams of Ti·hour). [f] Fraction: S-8, octane-soluble fraction; I-8, octane-insoluble fraction. [g] Molar fraction of isotactic triads by NMR. [h] Extent of the first-step stereoregularity expressed as molar fraction of isotactic (e) placement of the first propene unit.[8]

Table III
Base Content of the Catalysts Treated with $AlEt_3$/External Base Mixtures[a]

catalyst	treatment contact with	base content, mmol/100 g internal	base content, mmol/100 g external
$MgCl_2/EB/TiCl_4$ ([Ti] = 1.7%)	none	58	
	$AlEt_3$	10	
	$AlEt_3$/MPT (3/1)	27	21
	$AlEt_3$/PTES (3/1)	18	27
	$AlEt_3$/TMPip (3/1)	15	34
$MgCl_2/DIBP/TiCl_4$ ([Ti] = 2.4%)	none	44	
	$AlEt_3$	6	
	$AlEt_3$/MPT (10/1)	8	6
	$AlEt_3$/PTES (10/1)	3	41
	$AlEt_3$/TMPip (10/1)	5	22

[a] Abbreviations: DIBP, diisobutyl phthalate; EB, ethyl benzoate; MPT, methyl *p*-toluate; PTES, $PhSi(EtO)_3$; TMPip, 2,2,6,6-tetramethylpiperidine. Contact conditions: $T = 50$ °C; time, 1 h; catalyst concentration, 4 g/L, [Al]/[Ti] = 20 mr; solvent, hexane.

ing octane-soluble fractions (Figure 1), as has been shown by other authors.[10,11] The NMR data show that all the octane-insoluble fractions have a higher stereoregularity of both propagation [mm] and initiation [e] with respect to the octane-soluble ones (Figure 2).

All these data suggest that in the presence of the external base a new kind of isotactic site, capable of producing more stereoregular polypropene and characterized by higher stability and/or propagation rate, is formed.

However, the behavior of each base with the two different solid catalysts is not the same: e.g., the greatest improvement of isotactic productivity is produced by TMPip with the catalyst containing EB and by PTES with the catalyst containing BEHP; moreover, EB is a relatively efficient isotacticity improver with the former and an inefficient one with the latter (when BEHP is the internal base the amount of the more stereoregular octane-insoluble fraction is even lower than in the absence of the external base). The NMR data show that the stereospecificity of both initiation [e] and propagation [mm] are higher in the series of experiments with EB as an internal base than in those with BEHP. It is interesting to observe that all the [e] values are widely different from each other and depend both on the characteristics of the external base, as we have already shown,[1] and on those of the specific combination of external and internal bases. In particular, with EB as an internal base, both TMPip and PTES produce catalytic sites having an initiation stereoregularity nearly as high as the propagation stereoregularity while different and lower [e] values are observed when the same two bases are used with BEHP as an internal base.

As to the octane-soluble fractions, they are roughly characterized by relatively low $\bar{M}_w$ and high $\bar{M}_w/\bar{M}_n$ values and the [mm] are slightly lower than in the corresponding octane-insoluble fractions. The presence of isospecific centers having different propagation stereoregularity has been shown by other authors.[12] The [e] values are different and mostly higher than those of the octane-soluble fractions of the corresponding catalysts without external base. It seems likely that these fractions are produced by a mixture of active sites of different kinds containing and not containing the internal and/or the external bases. The fact that TMPip produces a slight decrease of the [e] values of the octane-soluble fractions of both catalysts is not easy to account for.

(2) Study of the Interactions between the Solid Catalysts and the External Bases. Trying to better understand the activation mechanism, we have also studied the reaction exchange of catalyst components that takes place when the solid catalyst makes contact with the cocatalyst solution. It is known that when the solid catalyst is placed in contact with a solution containing both $AlEt_3$ and an external base a partial replacement of the internal base by the external one occurs.[13] Table III shows the base content of both $MgCl_2/EB/TiCl_4$ and $MgCl_2/DIBP/TiCl_4$ catalysts after treatment with $AlEt_3$ or $AlEt_3$/external base mixtures. The contact conditions were close

Table IV

base	TMPip	EB/MPT	PTES	DIBP
solvent	CH_2Cl_2/NaOH/MeOH	EtOH/MeOH[a]	EtOH	$(CH_3)_2CO$
column	4 mm/3 mm	2 mm/3 mm	2 mm/3 mm	2 mm/3 mm
packing	Chromosorb W	Chromosorb W	Chromosorb W	GasChrom Q
stationary phase	Aniarex Co 880	Aniarex Co 880	SE 30 (5%)	SilGum (5%)
column temp, °C	150	140	150	200
gas pressure, atm	0.7	1.0	1.5	1.0

[a] EtOH for EB, MeOH for MPT.

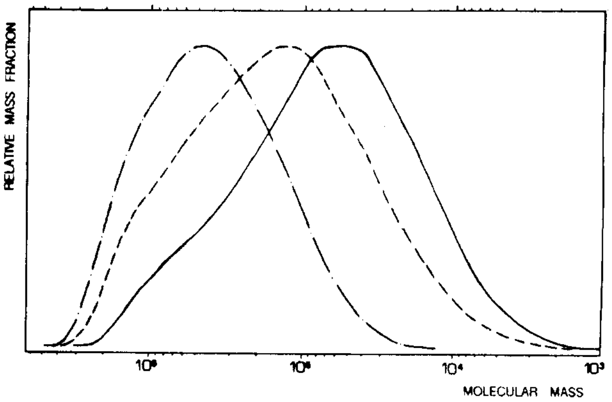

Figure 1. Molecular weight distribution curves of the heptane-insoluble fraction of the sample obtained with $MgCl_2/EB/TiCl_4$ without any external base (—) and of the heptane-insoluble–octane-soluble (- - -) and the octane-insoluble (– · –) fractions of the sample obtained with $MgCl_2/EB/TiCl_4$ with PTES as an external base.

as possible to the polymerization conditions (see the Experimental Section). Methyl *p*-toluate (MPT) was used instead of ethyl benzoate as an external base in order to recognize the internal–external base exchange when EB is the internal base. The use of a catalyst containing diisobutyl phthalate (DIBP) as an internal base instead of BEHP should not change the results, since it is likely that both diesters have similar behavior. The data of Table III show that the diester can be removed from the catalyst by this treatment to a higher extent than EB, either with or without external base. We can also observe that in both series of experiments the best catalytic systems (that is, those that give the highest isotacticity index and isotactic productivity) are those in which the external base is able to be absorbed on the solid catalyst to the largest extent. Moreover, the external bases have different behavior depending on the solid catalyst they are in contact with. In fact, MPT, which can be noticeably absorbed on the first catalyst, is hardly absorbed on the other one and PTES and TMPip show opposite trends of absorption in the two series of experiments.

Conclusions

The stereochemical and GPC results obtained confirm that the isotactic activation effect of the external base comes from its direct interaction with the active sites. Moreover, all the data observed clearly show that the effectiveness of a catalytic system depends more on the specific pair of internal and external bases than on the single internal or external base. In particular, the stereoregularity of both initiation and propagation depends more on the kind of internal base than on the choice of the external base. On the other hand, the choice of the external base clearly influences the amount of activation, which has been shown to be proportional to the capability of the external base being fixed on the solid catalyst by replacing the internal base. The fact that with a diester as an internal base the [e] values of the octane-insoluble fractions are lower than with EB could be accounted for by the greater room available due to replacement of the diester.

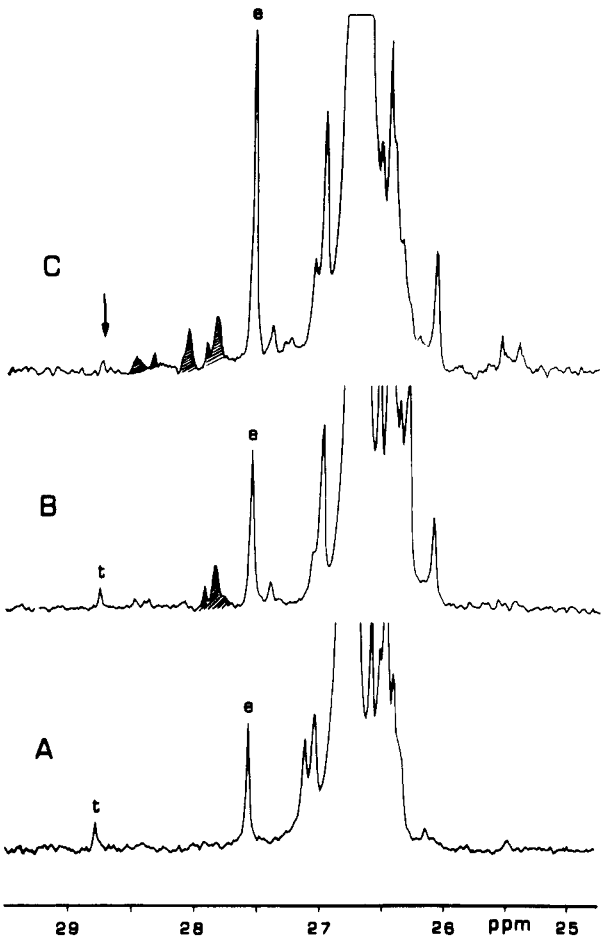

Figure 2. Methylenic chain end group region of the ^{13}C NMR spectra of the heptane-insoluble fraction of the sample obtained with $MgCl_2/EB/TiCl_4$ without any external base (A) and of the heptane-insoluble–octane-soluble (B) and the octane-insoluble (C) fractions of the sample obtained with $MgCl_2/EB/TiCl_4$ with PTES as an external base.

Experimental Section

Reagents. The catalyst containing ethyl benzoate as an internal base ([Ti] = 1.33%, [EB] = 10.5%) was kindly supplied by Dr. Albizzati of Istituto G. Donegani, Novara, Italy. The catalyst containing bis(2-ethylhexyl) phthalate as an internal base ([Ti] = 3.04%, [DEHP] = 17.9%) was prepared from soluble $MgCl_2$, 2-ethylhexanol, phthalic anhydride, and $TiCl_4$ according to patent literature.[14] $Al(^{13}CH_2CH_3)_3$ was prepared by reaction of $CH_3{}^{13}CH_2Li$ with $AlCl_3$ as reported in the literature.[15]

Polymerizations. All the polymerizations were carried out in a glass reactor containing 50 mL of heptane as a solvent. $Al(^{13}CH_2CH_3)_3$ ([Al]/[Ti] = 20 mr), the Lewis base ([base]/[Al] = 0.3 mr with the catalyst containing EB, and [base]/[Al] = 0.1 mr with the catalyst containing BEHP), and the solid catalyst (0.2 g) were added in the order given. The reactor was filled with propylene, and the polymerizations were performed under atmospheric pressure for 1 h at room temperature. The polymers were fractionated with boiling solvents by conventional methods.

GPC Analysis. The polydispersity and $\bar{M}_w$ of all the heptane-insoluble–octane-soluble and octane-insoluble fractions were determined by gel permeation chromatography in *o*-dichlorobenzene at 135 °C, using a Waters 150-C gel permeation chromatograph equipped with Ultrastyragel columns (10^6-, 10^5-, 10^4-, and 10^3-Å pore size).

NMR Analysis. The NMR samples were prepared by dissolving ca. 100 mg of polymer in 1 mL of 1,2,4-trichlorobenzene in a 10-mm-o.d. tube. $C_2D_2Cl_4$ (0.5 mL) was added as a lock solvent, and hexamethyldisiloxane (1%) was used as an internal chemical shift reference. All the spectra were obtained by using a Bruker AM-270 spectrometer operating at 67.89 MHz in PFT mode, at a temperature of 115 °C.

Analysis of the Solid Catalysts. A 4-g sample of solid catalyst was placed in the reactor under nitrogen and the temperature was raised to 50 °C. Then 950 mL of hexane and the solution of $AlEt_3$ or of the $AlEt_3$/external base mixture were added in the order given, reaching 1-L total volume. The reaction mixture was stirred for 1 h at 50 °C, filtered, washed several times with hexane at the same temperature, and dried under vacuum. The amount of base contained in the samples so obtained was determined by GC, using a Carlo Erba 2350 chromatograph equipped with a flame ionization detector and He as carrier gas. Proper solvents, columns, and conditions were used for each base as reported in Table IV. The experimental error is less than 5%. For further experimental details see ref 16.

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References and Notes

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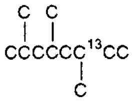
(3) When polymerization starts on the enriched titanium–$^{13}CH_2$-CH_3, the two possible arrangements of chain end groups are distinguished by ^{13}C NMR:[4,5]

$\mathrm{C\overset{C}{C}C\overset{C}{C}C\overset{C}{C}{}^{13}CC}$

erythro



$\mathrm{C\overset{C}{C}C\overset{C}{C}C\underset{C}{C}{}^{13}CC}$

threo

Erythro (or isotactic) is the stereoisomer in which the two first monomeric units have the same configuration and threo (or syndiotactic) that in which they have the opposite configuration. If e and t are the integrated peak areas of the enriched methylene resonances assigned respectively to the erythro and threo placements of the first propene unit, the molar fraction [e] of the erythro placement represents the extent of the first-step stereoregularity. In our previous papers the extent of the first-step stereoregularity was expressed as molar ratio (e/t) between the erythro and threo placements.

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(8) It must be said that the [e] values of the octane-insoluble fractions are evaluated with a higher error than those of the octane-soluble ones and of the heptane-insoluble fractions.[1,2] Indeed, due to the high molecular weight and the high first-step stereoregularity of these fractions, the smaller peak of the erythro resonance in some cases can be hardly detected.

(9) The increase of isotactic productivity due to the external bases in the series of experiments with BEHP as an internal base (Table II), as well as the differences among the isotactic productivities due to the three different bases, would be more remarkable if different polymerization conditions had been used (higher temperature, higher Al/Ti ratio, etc.). The actual conditions, equal to those of the previous papers, allow us to compare all our results.

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Registry No. EB, 93-89-0; TMPip, 768-66-1; PTES, 780-69-8; BEHP, 117-81-7; DIBP, 84-69-5; MPT, 99-75-2; $MgCl_2$, 7786-30-3; $TiCl_4$, 7550-45-0; $AlEt_3$, 97-93-8; polypropylene, 9003-07-0.