Activation Effect of Alkoxysilanes as External Donors in $MgCl_2$-Supported Ziegler-Natta Catalysts

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ABSTRACT: Three pairs of alkoxysilanes, (a) $Me(EtO)_3Si$, $Ph(EtO)_3Si$, (b) $Ph_2(MeO)_2Si$, $Ph_2(EtO)_2Si$, (c) $Ph_2(EtO)_2Si$, $Ph(EtO)_3Si$, differing only in one parameter, have been used as external donors with the catalysts $MgCl_2/TiCl_4$ and $MgCl_2/DIBP/TiCl_4$ (DIBP = diisobutyl phthalate), using selectively ^{13}C-enriched $AlEt_3$ as cocatalyst. The heptane-insoluble fractions of all the samples have been characterized by ^{13}C NMR analysis and gel permeation chromatography. The catalyst chemical modifications due to the external donors have been studied by GC analysis of the base content of the solid catalyst under the polymerization conditions. On the basis of all these data we can conclude that (i) all the alkoxy silane donors used, even those that do not produce any evident increase of isotactic productivity, interact with the isospecific centers making them more stereospecific and more active and (ii) it is possible to modulate the activation of the isospecific centers and the poisoning of the nonstereospecific ones by varying the number and the relative bulkiness of both hydrocarbon and alkoxy substituents. The mechanism of the activation effect is discussed.

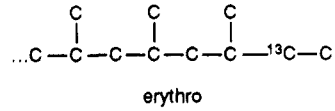
Introduction

The influence of external donors on high yield supported Ziegler-Natta catalysts can be explained by the coexistence of two concurrent effects (i) poisoning of the nonstereospecific sites and (ii) activation of the isospecific ones.[1] When the latter effect prevails over the former one can observe not only an increase of the isotacticity index of the polymer but also an increase of the absolute amount of isotactic polymer. In previous papers we have studied the activation mechanism by comparing the activation effects of three chemically different donors, ethyl benzoate, 2,2,6,6-tetramethylpiperidine, and phenyltriethoxysilane, on two catalysts containing ethyl benzoate and bis(2-ethylhexyl) phthalate as internal bases.[2-4] Our results showed that the activation effect of all three donors comes from their direct interaction (or from the interaction of the product of their coordination or reaction with the cocatalyst) with the active sites and that the effectiveness of the catalytic system strongly depends on the presence and the kind of internal base. However, many features of the actual activation mechanism are still not clear. In this paper we have compared the activation effect of alkoxysilanes having different structures with a catalyst containing diisobutyl phthalate as an internal base. The comparison of different alkoxysilanes may be useful to clarify some additional points since it is possible to change the size and the number of alkoxy and hydrocarbon substituents of alkoxysilanes without changing the kind of donor and, thus, to see the specific effect of each parameter. A systematic analysis on the influence of the structure of a number of alkoxysilanes with a catalyst containing diisobutyl phthalate as an internal base has been recently published by Harkonen at al.[5-7] and some characteristics needed for a high-performance alkoxysilane donor have been suggested. These authors have studied the correlation between the structure and the performance of the silane donors from the viewpoint of selective poisoning. In the present paper we will focus on the activation effect of silane donors and compare our and these authors' results to have a more complete picture of silane donor effect.

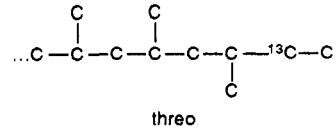
We have used the following pairs of alkoxysilanes that differ only in one parameter: (a) $Me(EtO)_3Si$, $Ph(EtO)_3Si$; (b) $Ph_2(MeO)_2Si$, $Ph_2(EtO)_2Si$; and (c) $Ph_2(EtO)_2Si$, $Ph(EtO)_3Si$ in the presence of the solid catalysts $MgCl_2/TiCl_4$ and $MgCl_2/DIBP//TiCl_4$ (DIBP = diisobutyl phthalate).

The following experimental methods have been used: (I) the analysis, through ^{13}C NMR, of the stereoregularity of the insertion of the first monomeric unit in the most isotactic fractions; (II) the GPC characterization of the most isotactic fractions; (III) the analysis, by GC, of the chemical changes occurring in the solid catalyst when contacted, in the absence of the monomer, with $AlEt_3$ and the external donor.

The stereoregularity of the insertion of the first monomeric unit 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, $Al(^{13}CH_2CH_3)_3$. When polymerization starts on the enriched titanium-$^{13}CH_2CH_3$, the two possible arrangements of the ethyl chain end groups of the isotactic fractions can be distinguished by ^{13}C NMR:[8,9]



erythro



threo

Erythro (or isotactic) is the stereoisomer in which the first two monomeric units have the same configuration and threo (or syndiotactic) that in which the first two monomeric units have the opposite configuration. The signals of the enriched methylene carbons of the erythro and threo stereoisomers are at 27.7_2 and 28.8_2 ppm, respectively, from hexamethyldisiloxane (HMDS).[8,9] 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

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Table I
Effect of the Size of the Hydrocarbon Group

catalyst[a]	donor	II[b]	IP[c]	isotactic fraction $10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	[mm][d]	[e][e]
$MgCl_2/TiCl_4$	0	44	2266	310	6.0	0.95	0.67
	$Me(EtO)_3Si$	78	2156	480	5.9	0.96	0.72
	$Ph(EtO)_3Si$	74	2523	450	5.6	0.97	0.78
$MgCl_2/DIBP/TiCl_4$	0	63	2080	255	5.2	0.96	0.73
	$Me(EtO)_3Si$	93	1926	375	7.1	0.98	0.82
	$Ph(EtO)_3Si$	96	2853	340	5.5	0.98	0.92

[a] Cocatalyst $Al(^{13}CH_2CH_3)_3/Zn(CH_2CH_3)_2$. [b] Isotacticity index, weight percent of heptane-insoluble fraction. [c] Isotactic productivity, yield in grams of isotactic polymer/(grams of Ti × hour). [d] Molar fraction of isotactic triads by NMR. [e] Extent of the first-step stereoregularity expressed as molar fraction of isotactic [e] placement of the first propene unit.

fraction [e] of the erythro placement represents the extent of the first-step stereoregularity. The first-step stereoregularity has been shown to supply more reliable information on the interactions between active sites and Lewis bases than the propagation stereoregularity[2-4] since it is more sensitive to the changes occurring in the active site's environment. In fact, during propagation, the bulkiness of the growing polymer chain plays the most important role on steric control and therefore the contributions of the other ligands to the stereoregulating capability of the isospecific centers are less evident.[10]

We have also performed the GPC analysis of the isotactic fractions to evaluate the influence of the different silane donors on molecular weights and molecular weight distributions.

Moreover we have studied the catalyst chemical modifications due to the alkyl silane donors by GC analysis of the base content in the solid catalyst, under the polymerization conditions. Noristi et al.[11,12] have shown that if an external donor is added with $AlEt_3$ to a catalyst containing an internal donor a progressive decrease of the internal donor is observed along with the fixation of increasing amounts of the external one. The performance of the catalyst system depends on the amount of the internal/external donor exchange.

The comparison of the stereochemical and GPC data with the data regarding the chemistry of the catalyst provides a more complete approach to the study of the mechanism of the Lewis base action.

Results and Discussion

1. Effect of the Size of the Hydrocarbon Group. Table I shows the stereochemical data of the samples prepared with a pair of alkoxy silanes that differ only in the size of the hydrocarbon substituents. The effect on the molecular weight, the isotacticity index, and the isotactic productivity is shown as well. The stereochemical data regard the samples prepared with selectively ^{13}C-enriched cocatalyst $Al(^{13}CH_2CH_3)_3$ and $Zn(CH_2CH_3)_2$. The addition of $ZnEt_2$ to the cocatalyst reduces the molecular weights, thus making the chain end groups more detectable. This action, which produces a change of the fraction distribution,[13] does not appreciably affect the [e] values of the heptane-insoluble fractions. The other data (average of three to five runs) regard samples prepared with conventional $AlEt_3$ without $ZnEt_2$. Figures 1 and 2 show the molecular weight distribution curves of the heptane-insoluble fractions of the samples obtained with all the alkoxy silanes considered with $MgCl_2/TiCl_4$ (Figure 1) and $MgCl_2/DIBP/TiCl_4$ (Figure 2). Table II shows the base content of the solid catalysts after treatment with $AlEt_3$ and $AlEt_3$/alkoxy silane mixtures.

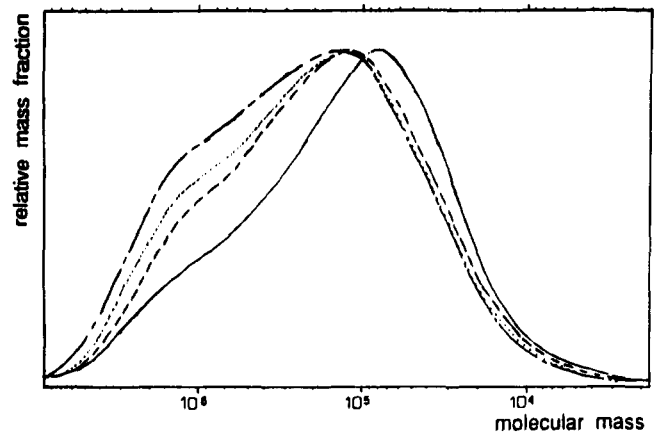

Figure 1. Molecular weight distribution curves of heptane-insoluble fractions of the samples obtained with $MgCl_2/TiCl_4$ without any external base (—) and with $Ph_2(EtO)_2Si$ (- - -), $Ph(EtO)_3Si$, $Ph_2(MeO)_2Si$ (· · ·), and $Me(EtO)_3Si$ (– – –) as external bases.

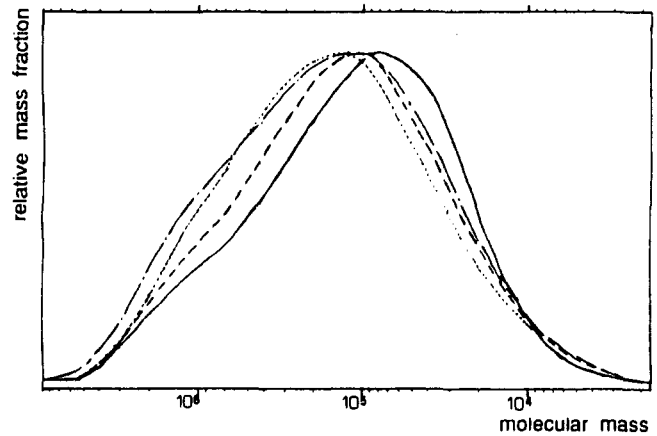

Figure 2. Molecular weight distribution curves of heptane-insoluble fractions of the samples obtained with $MgCl_2/DIBP/TiCl_4$ without any external base (—) and with $Ph_2(EtO)_2Si$ (- - -), $Ph(EtO)_3Si$, $Ph_2(MeO)_2Si$ (· · ·), and $Me(EtO)_3Si$ (– – –) as external bases.

Table II
Base Content of the Catalysts Treated with TEA/External Base Mixtures[a]

catalyst	treatment		base content: internal, mmol/100 g	base content: external, mol/100 g
$MgCl_2/TiCl_4$	none			
	contact with	$TEA/Me(EtO)_3Si$		13
		$TEA/Ph(EtO)_3Si$		6
$MgCl_2/DIBP/TiCl_4$	none		54	
	contact with	TEA	2	
		$TEA/Me(EtO)_3Si$	1	35
		$TEA/Ph(EtO)_3Si$	2	30

[a] TEA = $AlEt_3$.

We can observe that (i) $Me(EtO)_3Si$ and $Ph(EtO)_3Si$ produce a noticeable increase of the first-step stereoregularity both with and without the internal base. This increase is always higher with $Ph(EtO)_3Si$ bearing the bulkier substituent. It is worthwhile to observe that the propagation stereoregularity is nearly the same in all the isotactic fractions independently of the size of the hydrocarbon substituent.

(ii) Both alkoxy silanes are absorbed to a greater extent on the catalyst containing the internal base; $Me(EtO)_3Si$ bearing the smaller substituent is more absorbed than $Ph(EtO)_3Si$ on both solid catalysts.

Table III
Effect of the Size of the Alkoxy Group

catalyst[a]	donor	II[b]	IP[c]	isotactic fraction $10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	[mm][d]	[e][e]
$MgCl_2/TiCl_4$	0	44	2266	310	6.0	0.95	0.67
	$Ph_2(MeO)_2Si$	81	2505	440	5.7	0.96	0.80
	$Ph_2(EtO)_2Si$	72	2750	435	5.9	0.96	0.79
$MgCl_2$/DIBP/ $TiCl_4$	0	63	2080	255	5.2	0.96	0.73
	$Ph_2(MeO)_2Si$	97	3474	360	6.5	0.98	0.91
	$Ph_2(EtO)_2Si$	94	2886	295	5.4	0.97	0.87

[a] Cocatalyst $Al(^{13}CH_2CH_3)_3/Zn(CH_2CH_3)_2$. [b] Isotacticity index, weight percent of heptane insoluble fraction. [c] Isotactic productivity, yield in grams of isotactic polymer/(grams of Ti × hour). [d] Molar fraction of isotactic triads by NMR. [e] Extent of the first-step stereoregularity expressed as molar fraction of isotactic [e] placement of the first propene unit.

Table IV
Base Content of the Catalysts Treated with TEA/External Base Mixtures[a]

catalyst	treatment		base content: internal, mmol/100 g	base content: external, mmol/100 g
$MgCl_2/TiCl_4$	none			
	contact with	$TEA/Ph_2(MeO)_2Si$		7
	contact with	$TEA/Ph_2(EtO)_2Si$		3
$MgCl_2$/DIBP/ $TiCl_4$	none		54	
	contact with	TEA	2	
	contact with	$TEA/Ph_2(MeO)_2Si$	2	30
	contact with	$TEA/Ph_2(EtO)_2Si$	3	16

[a] TEA = $AlEt_3$.

(iii) While the isotactic productivity due to $Ph(EtO)_3Si$ is proportional to the amount of its absorption (in fact its activation effect is higher with the catalyst containing the internal base), with $Me(EtO)_3Si$ the isotactic productivity is always very low and nearly independent of its absorption on the solid catalyst.

(iv) Both alkoxy silanes produce a noticeable increase of the molecular weight and such an increase seems more related to the amount of the base absorbed than to the effect of the base itself on the isotactic productivity.

The fact that both silanes increase the first step stereoregularity of the most isotactic fractions shows that both donors (even $Me(EtO)_3Si$, which does not produce any apparent activation effect) are present in the environment of the isospecific centers. In fact the bulkier $Ph(EtO)_3Si$ makes the first step more stereospecific than $Me(EtO)_3Si$. The presence of both donors in the isospecific site environment is also confirmed by the noticeable increase of $\bar{M}_W$ that they produce. Therefore, both donors can activate the stereospecific centers. However, $Me(EtO)_3Si$, bearing a small alkyl substituent, is not selective in poisoning (as is shown by its strong absorption) and this poisoning always prevails over the activation of the isospecific centers. $Ph(EtO)_3Si$, bearing a bulky alkyl substituent, poisons selectively the nonstereospecific centers: therefore its activation always prevails over the poisoning and is proportional to its absorption on the catalyst surface. The fact that the activation is more pronounced with $MgCl_2/DIBP/TiCl_4$ than with $MgCl_2/TiCl_4$ can be accounted for by the fact that $AlEt_3$ removes a large quantity of the internal donor[1c] and thus can make more active sites available for complexation with the external donor.

2. Effect of the Size of the Alkoxy Group. Table III shows the polymerization data of the samples prepared with a pair of alkoxy silanes differing only in the size of the alkoxy groups. Table IV shows the base content of the solid catalysts after treatment with $AlEt_3$ and an $AlEt_3$/alkoxy silane mixture. The molecular weight distribution curves are shown in Figures 1 and 2.

Table V
Effect of the Number of Alkoxy Groups

catalyst[a]	donor	II[b]	IP[c]	isotactic fraction $10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	[mm][d]	[e][e]
$MgCl_2/TiCl_4$	0	44	2266	310	6.0	0.95	0.67
	$Ph_2(EtO)_2Si$	72	2750	435	5.9	0.97	0.79
	$Ph(EtO)_3Si$	74	2523	450	5.6	0.96	0.78
$MgCl_2$/DIBP/ $TiCl_4$	0	63	2080	255	5.2	0.96	0.73
	$Ph_2(EtO)_2Si$	94	2886	295	5.4	0.98	0.87
	$Ph(EtO)_3Si$	96	2853	340	5.5	0.98	0.92

[a] Cocatalyst $Al(^{13}CH_2CH_3)_3/Zn(CH_2CH_3)_2$. [b] Isotacticity index, weight percent of heptane-insoluble fraction. [c] Isotactic productivity, yield in grams of isotactic polymer/(grams of Ti × hour). [d] Molar fraction of isotactic triads by NMR. [e] Extent of the first-step stereoregularity expressed as molar fraction of isotactic [e] placement of the first propene unit.

Table VI
Base Content of the Catalysts Treated with TEA/External Base Mixtures[a]

catalyst	treatment		base content: internal, mmol/100 g	base content: external, mmol/100 g
$MgCl_2/TiCl_4$	none			
	contact with	$TEA/Ph_2(EtO)_2Si$		3
	contact with	$TEA/Ph(EtO)_3Si$		6
$MgCl_2$/DIBP/ $TiCl_4$	none		54	
	contact with	TEA	2	
	contact with	$TEA/Ph_2(EtO)_2Si$	3	16
	contact with	$TEA/Ph(EtO)_3Si$	2	30

[a] TEA = $AlEt_3$.

$Ph_2(MeO)_2Si$, bearing less bulky alkoxy groups with respect to $Ph_2(EtO)_2Si$, gives a better equilibrium between selective poisoning and activation, especially with the catalyst containing the internal base (Table III). In this case we observe the highest values of isotactic productivity (IP) and isotacticity index (II) ever observed. Table IV shows that $Ph_2(MeO)_2Si$ is more absorbed than $Ph_2(EtO)_2Si$ on both catalysts. The extent of the first-step stereoregularity [e] and the molecular weights always increase as long as the amount of donor absorbed increases. The difference between the effects produced by the two silanes both on the first-step stereoregularity and on the molecular weights is more remarkable with the catalyst containing the internal base in which the amount of external donor absorbed varies to a greater extent.

It is possible to account for the fact that the higher first-step stereoregularity is given on the one hand by the donor bearing the smaller alkoxy group and on the other by the donor bearing the bulkier hydrocarbon group (see previous section). In fact the less bulky $Ph_2(MeO)_2Si$ has a greater complexing capability and is present on more active centers, as is shown by its strong absorption on the catalyst. The extent of the first-step stereoregularity that we observe is the average of the first-step stereoregularity values of all the kinds of isospecific centers present in the system. Therefore it depends both on the amount of the effect of the donor on the steric control of the active center and on the number of active centers on which such an effect is exerted.

3. Effect of the Number of Alkoxy Groups. Table V shows the polymerization data of the samples prepared with a pair of alkoxy silanes differing only in the number of the alkoxy groups. Table VI shows the base content of the solid catalysts after treatment with $AlEt_3$ and an $AlEt_3$/alkoxy silane mixture. The molecular weight distribution curves are shown in Figures 1 and 2.

We can see that $Ph(EtO)_3Si$ produces a higher isotacticity index than $Ph_2(EtO)_2Si$ with both catalysts. With the catalyst containing the internal base, $Ph(EtO)_3Si$ also produces a noticeably higher first-step stereoregularity (Table V). $Ph(EtO)_3Si$ is more absorbed than $Ph_2(EtO)_2Si$ on both catalysts (Table VI). The increase of the isotacticity index shows that the presence of more alkoxy groups makes the alkoxy silane more effective in selective poisoning. This occurs since the hydrocarbon group is large enough (see section 1). The increased complexing capability of the donor, due to the higher number of alkoxy groups, also makes it more effective in activating the isospecific centers, as it is shown by the greater increase of $\bar{M}_W$ produced by $Ph(EtO)_3Si$ and by the high value of [e] with the catalyst containing the internal base.

Conclusion

All the results reported above along with other authors' results allow us to trace some general trends of the mechanism of the alkoxysilane effect. According to Iiskola et al., one alkoxy group of the alkoxysilane immediately coordinates with $AlEt_3$ and no donor remains in the free form under the polymerization conditions.[14] Therefore, we can neglect the donor/$AlEt_3$ equilibrium and only discuss the interactions of the donor/$AlEt_3$ complex with the catalyst. This donor/$AlEt_3$ complex has two functions:

(i) If it still contains a free alkoxy group, it can deactivate the active centers. Such a deactivation is selective only when the hydrocarbon groups are bulky enough.[5-7]

(ii) It activates some centers, making them more stereospecific and more active. Such an activation always occurs, even when, due to the low selectivity of the poisoning, there is no increase of isotactic productivity.

Among the alkoxy silanes bearing hydrocarbon substituents large enough to give selective poisoning, the activation increases with the complexing capability of the donor, that is, when the size of alkoxy groups is lower and the number of alkoxy groups is higher. Therefore it is possible to modulate the activation of isospecific sites and the poisoning of the nonstereospecific ones by varying the number and the relative bulkiness of both hydrocarbon and alkoxy substituents.

In order to account for the way in which the alkoxysilane/aluminum alkyl complex produces the activation effect we will consider the equilibria present in solution. If the equilibria involving the free aluminum alkyl both in the formation of the donor/aluminum alkyl complex and in the titanium alkylation are neglected, the following reaction models may coexist in solution:

$$\text{Cat ID} + AlEt_3 \rightleftarrows \text{Cat-[]} + AlEt_3\,\text{ID} \quad (1)$$

$$\text{Cat-[]} + AlEt_3\,\text{ED} \rightleftarrows \text{Cat ED} + AlEt_3 \quad (2)$$

$$\text{Cat-[]} + AlEt_3\,\text{ED} \rightleftarrows \text{Cat}\,AlEt_3\,\text{ED} \quad (3)$$

where Cat-[] = free site, ID = internal donor, and ED = external donor.

Equilibrium 1 is always present, even in the absence of the external donor. Equilibria 2 and 3 represent two different ways in which the donor/aluminum alkyl complex can act. According to equilibrium 2, the complex releases the donor that would be absorbed to the catalyst surface in the free form. According to equilibrium 3 the complex itself would be coordinated to the catalyst surface.

We cannot distinguish between equilibria 2 and 3 since our data only show that the silane donor is located in the neighborhood of the isospecific sites in such a way as to produce a sterical interaction with the incoming monomer.

The hypothesis that the free donor is absorbed in the space left free by the internal base in the vicinity of the active titanium (equilibrium 2) is supported by the results of a theoretical study[15] based on a modeling representation of the interaction between the base and the catalytic surface. In addition, a stronger affinity of the external donor to the catalyst surface with respect to the internal one would account for the fact that the internal donor removal is favored by the addition of the silane donor.[11]

Other experimental findings concerning both silanes and other donors support the hypothesis that the complex itself is absorbed in the active-site environment (equilibrium 3). In fact only when a sufficient amount of base/metal alkyl complex is present the activation effect is observed.[16] If the complex is not allowed from a chemical[17] or sterical[18,5-7] viewpoint, a low increase (if any) of isotactic productivity is observed.

Further work should be done to clarify the detailed mechanism of the activation effect of alkoxysilanes.

Experimental Section

Reagents. The catalyst containing diisobutyl phthalate as internal base (Ti = 3.6%, DIBP = 16%) and the catalyst without internal base (Ti = 3.3%) were kindly supplied by Himont, Centro Ricerche G. Natta, Ferrara, Italy. $Al(^{13}CH_2CH_3)_3$ was prepared by reaction of $CH_3{}^{13}CH_2Li$ with $AlCl_3$ as reported in the literature.[19]

Polymerizations. Five polymerization runs were carried out with each catalytic system, in a glass reactor containing 100 mL of heptane as a solvent. The Lewis base (base/Al = 0.1 mr), $AlEt_3$ (Al/Ti = 100 mr), and the solid catalyst (25–35 mg) were added in the order given. The reactor was filled with propylene and the polymerizations were performed under atmospheric pressure for 1 h at 60 °C. Under the same conditions single polymerization runs were performed, using $Al(^{13}CH_2CH_3)_3$ (90% enriched) and $ZnEt_2$ (Al/Zn = 3 mr) as cocatalyst. Polymers were fractionated with boiling heptane by conventional methods. Isotacticity index, isotactic productivity, and molecular weight are average values deduced from the samples prepared with the conventional cocatalyst. The stereochemical data ([e] and [mm]) regard the samples prepared with the enriched cocatalyst.

GPC Analysis. The polydispersity and $\bar{M}_w$ of all the heptane-insoluble fractions were determined by gel permeation chromatography in o-dichlorobenzene at 135 °C, using a Waters 150-C gel permeation chromatograph equipped with four Styragel HT 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.

Treatment and Analysis of the Solid Catalyst. Three grams of catalyst was placed in a glass reactor equipped with a stirrer and immersed in a thermostatic bath. The temperature was set at 60 °C; then 950 mL of hexane and the solution of $AlEt_3$ or the $AlEt_3$/silane mixture was added in the said order, reaching 1 L total volume. All the operations were carried out under nitrogen. After stirring for 1 h at 60 °C, the solid was rapidly filtered, washed several times with hexane, and dried under vacuum. The base content was then determined by GC, after having dissolved the catalyst in a solvent properly chosen so as to avoid donor decomposition. Suitable solvents were EtOH for ethoxysilanes, MeOH for methoxysilanes, and acetone for the internal base. The analysis was performed with a Carlo Erba 2350 gas chromatograph equipped with a flame ionization detector and using He as carrier gas. The column (2–3 mm) was filled with Chromosorb W plus SE 30 as stationary phase for the analysis of silanes, and with GasChromQ plus SilGum for the analysis of the internal base.

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References and Notes

(1) (a) Pino, P.; Guastalla, G.; Rotzinger, B.; Mulhaupt, R. In *Transition Metal Catalyzed Polymerization: Alkenes and Dienes*; Quirk, R. P., Ed.; Harwood: New York, 1983; p 435. (b) Kashiwa, N. In *Transition Metal Catalyzed Polymerization: Alkenes and Dienes*; Quirk, R. P., Ed.; Harwood: New York, 1983; p 379. (c) Barbè, P. C.; Cecchin, G.; Noristi, L. *Adv. Polym. Sci.* **1986**, 81,

(2) Sacchi, M. C.; Shan, C.; Locatelli, P.; Tritto, I. *Macromolecules* **1990**, *23*, 383.

(3) Sacchi, M. C.; Tritto, I.; Shan, C.; Noristi, L. In *Catalytic Olefin Polymerization*; Keii, T., Soga, K., Eds.; Kodansha: Tokyo, 1990; p 185.

(4) Sacchi, M. C.; Tritto, I.; Shan, C.; Mendichi, R.; Noristi, L. *Macromolecules* **1991**, *24*, 6823.

(5) Harkonen, M.; Seppala, J. V.; Vaananen, J. In *Catalytic Olefin Polymerization*; Keii, T., Soga, K., Eds.; Kodansha: Tokyo, 1990; p 87.

(6) Seppala, J. V.; Harkonen, M.; Luciani, L. *Makromol. Chem.* **1989**, *190*, 2535.

(7) Seppala, J. V.; Harkonen, M. *Makromol. Chem.* **1991**, *192*, 2857.

(8) Zambelli, A.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1982**, *15*, 211.

(9) Zambelli, A.; Locatelli, P.; Sacchi, M. C.; Tritto, I. *Macromolecules* **1982**, *15*, 831.

(10) Sacchi, M. C.; Locatelli, P.; Tritto, I. *Makromol. Chem.* **1989**, *190*, 139.

(11) Noristi, L.; Barbè, P. C.; Baruzzi, G. *Makromol. Chem.* **1991**, *192*, 1115.

(12) Barbè, P. C.; Noristi, L.; Baruzzi, G. *Makromol. Chem.* **1992**, *193*, 229.

(13) The addition of $ZnEt_2$ to the cocatalyst, due to its high chain-transfer ability, reduces the molecular weights and increases the concentration of polymer chain end groups. In the presence of $ZnEt_2$, due to the lowering of the molecular weights, some of the isotactic chains become heptane soluble, thereby producing a decrease of the percent of heptane-insoluble fraction, usually considered the isotacticity index.

(14) Iiskola, E.; Sormunen, P.; Garoff, T.; Vahasarja, E.; Pakkanen, T. T.; Pakkanen, T. A. In *Transition Metals and Organometallics as Catalysts for Olefin Polimerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; p 113.

(15) Scordamaglia, R.; Barino, L. Private communication.

(16) Sacchi, M. C., Tritto, I.; Locatelli, P. *Prog. Polym. Sci.* **1991**, *16*, 331.

(17) Tritto, I.; Sacchi, M. C.; Locatelli, P. In *Transition Metal Catalyzed Polymerization: Ziegler–Natta and Metathesis Polymerization*; Quirk, R. P., Ed.; Cambridge University Press, 1988; p 255.

(18) Pino, P.; Cioni, P.; Wei, J.; Rotzinger, B.; Arizzi, S. In *Transition Metal Catalyzed Polymerization: Ziegler–Natta and Metathesis Polymerization*; Quirk, R. P., Ed.; Cambridge University Press: 1988; p 292.

(19) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, 1972.

Registry No. DIBP, 84-69-5; $MgCl_2$, 7786-30-3; $TiCl_4$, 7550-45-0; $Me(EtO)_3Si$, 2031-67-6; $Ph(EtO)_3Si$, 780-69-8; $Al(^{13}CH_2CH_3)_3$, 97-93-8; $Zn(CH_2CH_3)_2$, 557-20-0; $Ph_2(MeO)_2Si$, 6843-66-9; $Ph_2(EtO)_2Si$, 2553-19-7; polypropylene (homopolymer), 9003-07-0; polypropylene (isotactic homopolymer), 25085-53-4.