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Polymerization Stereochemistry with Ziegler−Natta Catalysts Containing Dialkylpropane Diethers: A Tool for Understanding Internal/External Donor Relationships

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ABSTRACT: A study on a new generation of $MgCl_2$-supported Ziegler−Natta catalysts, which contain dialkylpropane diethers as internal donors and have the property of producing highly active and stereospecific catalysts without any external donor, has been performed. The behavior of three different diethers (2,2-diisobutyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, and 2-ethyl-2-butyl-1,3-dimethoxypropane) as internal donors is compared with the behavior of the same diethers when they are used as external donors with a catalyst containing diisobutyl phthalate as internal donor. The results obtained show that the same isospecific centers are produced when the same diether donor is present as an internal donor or replaces diisobutyl phthalate during polymerization when it is added as an external donor. The sum of the present results and of the previously obtained findings on traditional supported Ziegler−Natta catalysts has enabled us to reach some conclusions on the role and reciprocal behavior of internal and external donors.

Introduction

Right from the discovery of high-yield $MgCl_2$-supported Ziegler−Natta catalysts it was clear that (i) the presence of both an internal and an external donor is required in order to have an active and stereospecific catalyst and (ii) there exists some kind of interdependence between internal and external donors.[1] In fact the efficiency of a catalytic system was shown to be dependent on the choice of the specific pair of internal and external donors rather than on the single internal or external donor chosen. Ethyl benzoate/methyl *p*-toluate and diisobutyl phthalate/alkoxysilane or tetramethylpiperidine are commonly cited as examples of good internal/external donor pairs.[2] However, cross combinations of the same donors can produce inefficient catalysts from both activity and stereospecificity points of view.

A noticeable improvement in understanding the relationship between internal and external donors has been made possible by combining the chemical analysis of the catalyst and the polymerization stereochemistry.

The study of the chemical changes occurring in the solid catalyst when in contact, in the absence of the monomer, with $AlEt_3$ and the external donor showed that, under the polymerization conditions, a progressive decrease of the internal donor occurs along with the fixation of an increasing amount of the external one.[3−4] There is a clear correlation between the polymerization performance and the amount of external donor fixed to the catalyst. This fact accounts for the low performance afforded by the cross combinations ethyl benzoate/alkoxysilanes and diisobutyl phthalate/methyl *p*-toluate, both showing a limited incorporation of the external donor into the catalyst.[5] The diisobutyl phthalate/methyl *p*-toluate donor pair that shows the lowest external donor incorporation produces the poorest performance catalyst.

On the other hand, the study of polymerization stereochemistry has shown that all the external donors affect the stereospecificity of the isospecific centers and the variation produced depends on the kind of donor.[5−8] Different values of initiation and propagation stereoregularity have been observed by passing from ethyl benzoate to tetramethylpiperidine or to an alkoxysilane as external donors in the presence of the same internal donor. To go further into detail, within the same family of the alkoxysilane donors, with diisobutyl phthalate as an internal donor, widely different values of first-step stereoregularity are observed even by varying only one parameter, such as the size of the hydrocarbon or of the alkoxy substituents (e.g., $Me(EtO)_3Si < Ph(EtO)_3Si$ and $Ph_2(EtO)_2Si < Ph_2(MeO)_2Si$). These findings suggest that the external donor is absorbed in the vicinity of at least some isospecific centers in such a way as to modify their stereochemical behavior or to generate new isospecific centers having different stereospecificity. However, such a modification effect is always influenced by the kind of internal donor used. Indeed, these values, which are constant and reproducible with the same internal donor, vary widely if a different internal donor

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is used as well as if an internal donor is present or absent.

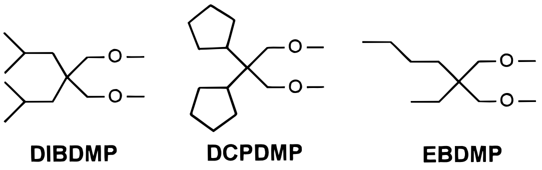
At this point the difficulty in understanding the kind of interdependence between internal and external donors derives from the fact that it has not yet been actually possible to get definitive evidence of the presence or absence of the internal donors in the neighborhood of the isospecific sites. A close interaction between internal donor and isospecific centers has been suggested on the basis of the results of stereoselective polymerization of 3,7-dimethyl-1-octene with $MgCl_2$-supported highly active catalytic systems in the presence of optically active internal and/or external donor.[9] On the other hand, according to a widely accepted hypothesis, the internal donor is not present at all in the neighborhood of the isospecific centers.[10−12] The internal donor should play its role during the preparation of the solid catalyst when it competes with $TiCl_4$ for coordination to the $MgCl_2$ support and shields the faces of the support where only aspecific centers could be formed from $TiCl_4$ coordination. A stereochemical analysis of the effect of different internal donors in the absence of any external donor has been performed, analogous to that one performed for the external donors.[1b] However, due to the fact that, during polymerization, the internal donors commonly used react with the aluminum alkyl in different ways and are abstracted from the catalyst in different amounts, it has not been possible to have conclusive findings on their direct effect on the stereochemistry of monomer insertion.

This last difficulty could now be overcome due to the recent discovery of 1,3-dimethoxypropane internal donors.[13] These donors are known as having the property that, when used as internal donors, produce highly active and stereospecific catalysts without any external donor.[14−16] Indeed, they offer the advantage that (i) in comparison to all the other internal donors, they are not extracted from the catalyst by $AlEt_3$ and (ii) in comparison to the external donors commonly used, they can be used both as internal and as external donors. Thus such donors offer the unique opportunity of studying the behavior of the same donor in both roles and so will allow us to give conclusive answers to the above mentioned open questions.

Results and Discussion

We have compared three different diethers: 2,2-diisobutyl-1,3-dimethoxypropane (DIBDMP), 2,2-dicyclopentyl-1,3-dimethoxypropane (DCPDMP), and 2-ethyl-2-butyl-1,3-dimethoxypropane (EBDMP).

Chart 1



Two of them, diisobutyl- and dicyclopentyldimethoxypropane, which bear branched and bulky hydrocarbon groups, are reported to be good diether donors while the last one, which bears linear and less bulky substituents, is reported to be a lower performance donor.

First we have analyzed their behavior as internal donors in the absence of any external donor. As in all our previous research on the action mechanism of the donors, the present research basically consists of the analysis of the donor effect on first-step stereoregularity. The use of selectively ^{13}C-enriched triethylaluminum as cocatalyst allows us to determine the stereoregularity of the insertion of the first propene unit from the stereochemical structure of the resulting enriched chain end groups.[17−21] We express the extent of first-step stereoregularity as molar fraction [*e*] of the erythro (or isotactic) placement of the first propene unit. As we have shown in our previous work,[17,21] first-step stereoregularity is more influenced than propagation stereoregularity by the sterical environment of the active center which could be affected by the presence of the donor in the active center neighborhood.

Table 1. Effect of Diethers Used as Internal Donors

			isotactic fraction	
catalyst[a]	II[b]	IP[c]	[*mm*][d]	[*e*][e]
$MgCl_2$/DIBDMP/$TiCl_4$	91	3810	0.97	0.83
$MgCl_2$/DCPDMP/$TiCl_4$	90	3440	0.98	0.86
$MgCl_2$/EBDMP/$TiCl_4$	80	2010	0.96	0.72

[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 per grams of Ti × hour. [d] Molar fraction of isotactic triads by NMR. [e] Extent of first-step stereoregularity expressed as molar fraction of isotactic [*e*] placement of the first propene unit.

Table 2. Base Content of the Catalysts Treated with $AlEt_3$/External Donor Mixtures

		base content (mmol/100 g)	
catalyst	treatment	internal	external
$MgCl_2$/DIBP/$TiCl_4$	none	49	
	contact with $AlEt_3$/DIBDMP	0.7	47
	contact with $AlEt_3$/DCPDMP	0.2	49
	contact with $AlEt_3$/EBDMP	0.4	57

Table 1 reports polymerization results as well as stereochemical data of the polypropene samples. As expected, a lower yield and isotacticity index are obtained with EBDMP. The propagation stereoregularity [*mm*] of the isotactic fraction is slighty lower as well. Such a small difference in propagation stereoregularity is strongly enphasized in first-step stereoregularity [*e*]. Indeed a rather low first-step stereoregularity is observed with EBDMP, only slightly higher than that observed in the absence of any donor (with the simple $MgCl_2/TiCl_4$, $[e] = 0.67$)[8]. On the other hand, with the two bulky donors, rather high and similar values of first-step stereoregularity are observed, not so far from the values observed with some good internal/external donor pairs.[5,8] Only trace amounts of diether internal donors are displaced from the catalyst surface during polymerization.[14] Thus such a dependence of first-step stereoregularity on the donor molecular features of the diether substituents is in good accordance with the presence of the internal donors in the isospecific center environment and of their direct influence on the polymerization stereochemistry.

To get evidence of the mechanism of internal/external donor interdependence, we have used the same diethers as external donors in the presence of the catalyst containing diisobutyl phthalate as an internal donor. The behavior of the phthalate/diether system is identical to that of the “traditional” phthalate/silane system, from the point of view of the chemical changes occurring in the catalyst during polymerization. Table 2 shows that when the catalyst containing diisobutyl phthalate is in

Table 3. Effect of Diethers Used as External Donors

catalyst[a]	external donor	II[b]	IP[c]	isotactic fraction [mm][d]	isotactic fraction [e][e]
$MgCl_2$/DIBP/$TiCl_4$	DIBDMP	89	1720	0.97	0.83
	DCPDMP	93	2100	0.98	0.85
	EBDMP	89	1420	0.97	0.75

[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 x hour. [d] Molar fraction of isotactic triads by NMR. [e] Extent of first-step stereoregularity expressed as molar fraction [e] of isotactic placement of the first propene unit.

contact with the three triethylaluminum/diether donor combinations, under the polymerization conditions, a nearly complete displacement of the phthalate occurs along with the fixation of considerable amounts of diether. The trend of diether incorporation into the catalyst is the same observed for alkoxysilane donors;[8] that is, the donor bearing the smaller substituents (EBDMP) is the most extensively and likely the least selectively incorporated. On the basis of these data, the stereochemical results shown in Table 3 are particularly significant. Indeed, by comparing the correspondent stereochemical values of Tables 1 and 3, similar, in one case (DIBDMP) identical, values of first-step stereoregularity are observed when the diethers are present as internal donors (Table 1) and when they are added with the cocatalyst (Table 3). If we consider the total dependence of the stereochemistry of first monomer insertion on the steric environment of the active centers, we can draw the conclusion that the same isospecific centers are formed in both cases. These stereochemical data are in close agreement with other experimental data regarding the same DIBDMP used both as internal donor and as external donor in combination with DIBP by Albizzati et al.[15] According to their data, the two catalytic systems produce polypropene samples whose characteristics (chain transfer reaction with hydrogen, molecular weight, molecular weight distribution, and tacticity distribution) are nearly identical and only differ in their activity, which is always noticeably lowered by using the diether as external donor.

From these findings it seems also possible to draw more general conclusions on the reciprocal behavior of the internal and external donors. We can rationalize the interactions among the catalytic system components with the following reaction model:

$$\text{Cat}\cdot\text{ID} + \text{AlEt}_3 = \text{Cat-[ ]} + \text{AlEt}_3\cdot\text{ID} \qquad (1)$$

$$\text{ED} + \text{AlEt}_3 = \text{AlEt}_3\cdot\text{ED} \qquad (2)$$

$$\text{Cat-[ ]} + \text{ED} = \text{Cat}\cdot\text{ED} \qquad (3)$$

$$\text{Cat-[ ]} + \text{AlEt}_3\cdot\text{ED} = \text{Cat}\cdot\text{AlEt}_3\cdot\text{ED} \qquad (4)$$

$$\text{Cat-[ ]} + \text{AlEt}_3\cdot\text{ED} = \text{Cat}\cdot\text{ED} + \text{AlEt}_3 \qquad (5)$$

where Cat-[ ] is a free site, ID is an internal donor, and ED is an external donor.

Equilibrium 1 is always present, even in the absence of the external donor. The free site produced could be aspecific or already stereospecific. Equilibrium 2 is always present also: indeed ED and $AlEt_3$ are known to form an acid/base adduct which subsequently, according to the ED nature, gives rise to addition or even exchange products. Moreover, the possibility of formation of the complex between $AlEt_3$ and the external donors is important in order to reduce the concentration of the free donor which can act as a poison.[1b,22] Therefore, we can neglect the interactions of the free donor with the catalyst (eq 3) and only consider those of the donor/aluminum alkyl complex. In principle it could react with the free site in two different ways. According to equilibrium 4, the complex itself would be coordinated to the catalyst surface. According to equilibrium 5, the complex releases the donor which is absorbed in the free form. The data obtained indicate equilibrium 5 as the likely one. Indeed, the fact that the same first-step stereoregularity value is obtained when the same diether donor is present as internal donor or is added as external donor with diisobutyl phthalate (DIBP) as internal one strongly suggests that the same kind of isospecific center is created in both cases. If this is the case, the position in which first the internal and then the external donor is absorbed should be, at least for some active centers, close enough to the active titanium to affect the stereochemistry of the monomer insertion. Other considerations also seem to disfavor the hypothesis that the whole complex takes part in the formation of the isospecific active centers (equilibrium 4) as has been proposed.[23−25] Polypropene samples have been prepared in the presence of ^{13}C selectively enriched aluminum alkyls bearing, besides the ^{13}C-enriched ethyl group, alkyl groups of different sizes: $Al(^{13}CH_2CH_3)(iC_4H_9)_2$ and $Al(^{13}CH_2CH_3)(CH_3)_2$.[26] The analysis of first-step stereoregularity has shown that the mechanism of steric control on the first monomer insertion is completely independent of the steric bulkiness of the aluminum alkyl cocatalyst. This supports the hypothesis that the role of the aluminum alkyl is that of activating the catalyst by alkylating the surface titanium complexes and, in the presence of the donors, of favoring the exchange of the internal and external donors, but it does not participate directly in the active center structure. The substitution between internal and external donors is also supported by the results of a molecular mechanics study of the interaction between a donor molecule and the catalyst surface.[27] Similarities of occupied volume and point charge position are observed between DIBP internal base and the most probable conformations of the most active alkoxysilanes. Analogous steric equivalence is observed between DIBP, 2,2,6,6-tetramethylpiperidine and the most probable conformations of the best 1,3-dimethoxypropane donors.

The actual presence of the internal donor itself when, as in the case of the diethers, it remains fixed in the catalyst during polymerization, or of the external donor, once it has replaced the internal one, in the vicinity of the active titanium, likely accounts for the increase of catalyst activity produced by the donors. Other interpretations (such as selective poisoning of the aspecific centers or prevention of aspecific center formation), which certainly are not to be ruled out, only account for the increase of the isotacticity index. On the basis of our experimental data we cannot say how such an activation, which accompanies the stereochemical variations, occurs; that is, we cannot distinguish whether the donors turn the aspecific centers into isospecific ones or whether they make the centers, which are already isospecific, more stable or more active. Support for the former explanation comes from some recent calculations about diethers/$MgCl_2$ support interactions.[27] Such theoretical results lead to active titanium environment models according to which the donor molecules turn the aspecific $TiCl_4$ reliefs into isospecific ones by giving to the titanium atom the required chirality according to Corradini's model.

A last consideration regards the noticeably lower yield obtained when the diethers are added as external donors (Table 3) than when they are present as internal donors (Table 1). With the two good diethers the yields are about half the corresponding yields shown in Table 1. Evidently when the diethers are added as external donors, they have some poisoning effect on both aspecific and isospecific centers. The same effect is observed by increasing the concentration of external donor with the catalytic system $MgCl_2$/phthalate/$TiCl_4$−$AlEt_3$/silane[28] beyond certain values.

Conclusions

Due to the peculiar characteristics of the 1,3-dimethoxypropane donors, it has been possible to study the polymerization stereochemistry (i) in the actual presence of three different internal donors and (ii) by using the same donors in the role of internal or of external ones. The results obtained enabled us to reach some conclusions on the role and the reciprocal behavior of internal and external donors.

(i) As it was observed for the external donors, the internal donors also produce a modification of the stereochemical behavior of the isospecific centers which depends on the donor molecular features. This is in accordance with the presence of the internal donors in the vicinity of the titanium centers and with their direct influence on polymerization stereochemistry.

(ii) The same isospecific centers are obtained when the same diether donor is present as an internal donor or replaces DIBP during polymerization when it is added as an external donor. This means that each donor has a characteristic closeness with respect to the active titanium and has a typical effect on polymerization stereochemistry.

(iii) As to the reciprocal interdependence between internal and external donors we cannot say that the external donor is absorbed exactly in the space left free by the internal one. However, it is likely that the abstracted internal donor leaves the catalyst surface modified in such a way that only an external donor having analogous steric features and point charge distribution can be absorbed in the titanium environment in an effective way.

(iiii) All our stereochemical data concerning both diether donor and "traditional" internal/external donor pairs are accounted for by the results of a molecular mechanics study according to which the donors have several possibilities of coordinating near activable titanium atoms and so of sterically establishing the right chirality for isotactic polymerization for those sites which are potentially aspecific.

Experimental Section

Reagents. The catalysts containing diisobutyl phthalate as internal base (Ti, 3.6%; DIBP, 16%) and the catalysts containing 2,2-diisobutyl-1,3-dimethoxypropane (Ti, 3.1%; DIBDMP, 15.5%), 2,2-dicyclopentyl-1,3-dimethoxypropane (Ti, 3.3%; DCPDMP, 18.6%), and 2-ethyl-2-butyl-1,3-dimethoxypropane (Ti, 3.3%; EBDMP, 20.7%) were kindly supplied by Montell Italia, 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.[28]

Polymerizations. All the polymerizations were carried out in a glass reactor containing 100 mL of heptane as a solvent. The external donor, if any (donor/Al = 0.1 *mr*), $AlEt_3$ (Al/Ti = 100), and the solid catalyst (25−35 mg) were added in the order given. The polymerizations were performed at 60 °C, at amospheric monomer pressure, for 1 h. At least three experiments were performed with each catalytic system; single experiments were performed under the same conditions using $Al(^{13}CH_2CH_3)_3$ (90% enriched) and $ZnEt_2$ as cocatalysts. The addition of $ZnEt_2$ reduces the molecular weights, thus making the chain end groups more easily detectable. Polymers were fractionated with boiling heptane by conventional methods. The stereochemical data (first-step and propagation stereoregularity) are deduced from ^{13}C NMR spectra of the selectively enriched samples, while isotacticity index and isotactic productivity are average values regarding the samples prepared with conventional catalysts.

NMR Analysis. The NMR samples were prepared by dissolving ∼100 mg of the polymer in 2 mL of $C_2D_2Cl_4$ (that is also used as a lock solvent) in a 10-mm-o.d. tube and hexamethyldisiloxane (1%) as an internal chemical shift reference. All the spectra were obtained by using a Bruker AM-270 spectrometer operating at 67.89 MHz PFT (pulsed Fourier transform) mode at 107 °C. In all measurements, composite pulse decoupling was used to remove $^{13}C-^{1}H$ couplings, the pulse angle was 90°, the pulse repetition time was 27 s, and 4500 free induction decays were stored in 32 000 data points using a spectral window of 4950 HZ.

Catalyst Analysis. The content of Ti was measured by atomic absorption spectroscopy. The content of Lewis base was determined by gas chromatography after dissolution of the catalyst in properly selected solvents. The treatment of the catalysts in the polymerization conditions in the absence of monomer was performed as described in ref 8.

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