Microstructure Distribution of Polypropylenes Obtained in the Presence of Traditional Phthalate/Silane and Novel Diether Donors: A Tool for Understanding the Role of Electron Donors in $MgCl_2$-Supported Ziegler−Natta Catalysts

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ABSTRACT: Three diethers, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, and 2-ethyl-2-butyl-1,3-dimethoxypropane, differing in the bulkiness of the alkyl substituents in position 2, have been used as internal donors in $MgCl_2$−$TiCl_4$−diether/AlR_3 catalysts for the polymerization of propylene. The performance of the three diether-based catalysts is compared with that of a "traditional" $MgCl_2$-supported catalyst based on the phthalate/silane donor pair and with that of a "donor-free" catalyst by coupling the temperature rising elution fractionation (TREF) analysis with a study of the stereoregularity of the first monomeric unit insertion. On the basis of the experimental data obtained, the action mechanisms of the different donors are discussed taking into account the various models presented in the literature.

Introduction

After the discovery of $MgCl_2$-supported catalysts,[1] it was soon realized that to improve their stereospecificity some Lewis bases (donors) must be used.[2] Many efforts have been devoted to finding the best donors.[3] The evolution of the research and the main results obtained during 20 years can be summarized as follows: (i) When aromatic monoesters are used as internal donors, the isotactic index (II) is improved from 40% ($MgCl_2$−$TiCl_4$/AlR_3 catalyst) up to 60% ($MgCl_2$−$TiCl_4$−ethyl benzoate/AlR_3 catalyst). (ii) When aromatic monoesters are used both as internal and as external donors the II increases up to 95% ($MgCl_2$−$TiCl_4$−ethyl benzoate/AlR_3−methyl *p*-toluate catalyst).[4] (iii) Aromatic diesters as internal donors and silanes as external donors increase the II up to 97−99% ($MgCl_2$−$TiCl_4$−phthalate/AlR_3−alkoxy silane catalyst).[5] (iv) Diethers can be effectively employed as internal donors even in the absence of external donors and very high II's (97−99%) can be obtained ($MgCl_2$−$TiCl_4$−1,3-diether/AlR_3 catalyst).[6]

With the discovery of 1,3-diethers, a new and simplified generation of $MgCl_2$-supported catalysts was developed: actually, due to their chemical stability toward $TiCl_4$, AlR_3, and Ti-C and Ti−H bonds and to the fact that they are not extracted by the cocatalyst from the solid catalytic component, it has been possible, for the first time, to obtain very high performing catalysts by using only an internal donor.[7] Even if, from a scientific point of view, this is the main novelty introduced by diether donors, from an industrial point of view the diether-based catalysts have made it possible to increase the productivity two- or three-fold in comparison with the productivity of "traditional" catalysts based on the phthalate/silane donor pair.

Along with the very high activity and isospecificity, these catalysts generally show quite high rates in the chain transfer reaction with hydrogen (good hydrogen response) that makes them much more versatile in terms of obtainable polymer grades and/or in terms of usable technologies. In the literature, several papers deal with the functions carried out by donors: in fact, even if their main function is to control the catalyst stereospecificity, it is well known that they strongly affect the catalyst activity,[8] the first insertion[9] and the propagation[10] stereoregularity, and the molecular mass (MM) and the molecular mass distribution (MMD)[11] of the polymers produced.

Many efforts have been devoted to the comprehension of the mechanisms through which the donors interact with the other components of the catalyst. Several models have been proposed to describe the structure of the isospecific and of the aspecific centers and the function of the donors: among them, Corradini's model[12] is in good agreement with many experimental data but it seems too simplified when it describes the function of the donors. In fact, as already observed by other authors, this model does not explain some experimental data such as the variations of MM and MMD,[11] of tacticity distribution,[10] and of selectivity in the first monomeric unit insertion[9] observed when different donors are considered.

In this paper, a contribution to this debate through the discussion of the properties of polypropylenes (PP's) obtained with $MgCl_2$−diether-based catalysts will be given. The comparison among three diether-based catalysts, a phthalate/silane system, and a "donor-free" $MgCl_2$/$TiCl_4$ catalyst will be presented: our approach is mainly based on temperature rising elution fractionation (TREF) analysis of the obtained PP's, coupled with a study of the stereoregularity of the first monomeric unit insertion.

Experimental Section

Catalyst Synthesis and Polymerization Conditions. The catalyst preparations and the polymerization conditions

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Table 1. Propylene Polymerization with Different $MgCl_2$-Supported Catalysts[a]

cat.	H_2[b] (NL)	productivity (kg/g of cat.)	iso-PP product (kg/g of cat.)	iso-PP rel product	XI[c] (%)	IV[d] (dL/g)	M_w (10^{-3})	M_w/M_n	T_m[e] °C
$MgCl_2-TiCl_4$−DIBDMP/$AlEt_3$	1.7	80	78	7.8	97.5	1.69	350	6.2	162
$MgCl_2-TiCl_4$−DCPDMP/$AlEt_3$	1.7	50	49	4.9	97.3	1.86	380	6.6	163
$MgCl_2-TiCl_4$−EBDMP/$AlEt_3$	1.7	35	32	3.2	92.3	1.69	340	6.6	159
$MgCl_2-TiCl_4$−DIBP/$AlEt_3$−PES	1.7	40	39	3.9	97.3	1.89	430	7.6	162
$MgCl_2-TiCl_4/AlEt_3$	1.0	24	10	1	41.7	1.47[f]	332[f]	9.3[f]	158

[a] The solid catalytic components were prepared according to ref 6; polymerization conditions not reported in the table: 4 L reactor, C_3H_6 = 1.2 kg, Ti = 6 × 10^{-3} mmol, $AlEt_3$ = 7 mmol, PES = 0.7 mmol, 70 °C, 2 h. [b] Hydrogen added in polymerization. [c] Xylene-insoluble polymer fraction at 25 °C. [d] Intrinsic viscosity measured in tetralin at 135 ± 0.1°C. [e] Melting temperature (second fusion; rate 10 °C/min). [f] Referred to the XI fraction.

are reported in Table 1. The synthesis of $Al(^{13}CH_2CH_3)_3$ (90% enriched) and of selectively enriched samples was performed as described in previous papers.[9]

SEC Analyses. The molecular mass distribution (MMD) of each sample was determined from SEC elution curves obtained with a Waters 200 chromatograph (solvent = *o*-dichlorobenzene; T = 135 °C; solution concentration (w/v) = 0.25%) using four columns packed with silanized silica with pore sizes between 150 and 3500 Å. Broad molecular weight polyolefinic standards were used for the calibration.

TREF Analyses. The fractionation of the polymers was carried out by dissolving 1 g in *o*-xylene at 135 °C and slowly cooling (20 h) to 25 °C in a column loaded with glass beads. Elution with *o*-xylene (600 mL/h) was first carried out at 25 °C to obtain the xylene-soluble ("atactic") fraction. Elution was then continued while increasing the temperature from 25 to 95 °C to yield a single fraction mainly consisting of the "stereoblock" isotactic fraction. Finally, the temperature was increased from 95 to 120 °C at a rate of 3 °C/h, collecting individual fractions at temperature intervals of 1 °C. The polymer fractions were recovered by precipitation in acetone, filtered on a 0.5 μm PTFE filter, and dried under vacuum at 70 °C. All the recoveries were above 97%.

DSC Analyses. Thermograms were recorded at a heating rate of 10 °C/min using a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated by measurements of the melting points of indium and lead.

NMR Analyses. The NMR samples were prepared by dissolving ca. 100 mg of the polymer in 2 mL of $C_2D_2Cl_4$, (which 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 in the PFT (pulsed Fourier transform) mode at 107 °C. In all measurements, CPD (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.

Results and Discussion

Three 1,3-diethers, 2,2-diisobutyl-1,3-dimethoxypropane (DIBDMP), 2,2-dicyclopentyl-1,3-dimethoxypropane (DCPDMP), and 2-ethyl-2-butyl-1,3-dimethoxypropane (EBDMP), differing in the bulkiness of the alkyl substituents in position 2 (Figure 1), have been used as internal donors in $MgCl_2-TiCl_4$−diether/AlR_3 catalysts for the polymerization of propylene. In Table 1, the productivities and the main characteristics of the polymers produced by the three diether-based catalysts are compared with the data of a highly isospecific catalyst based on a phthalate/silane donor pair and of a "donor-free" catalyst reported as reference points. The presence and the structure of the diether donors influence the activity, the isospecificity, the chain transfer with hydrogen of the catalyst, and the MMD and the melting temperature of the corresponding polymers.

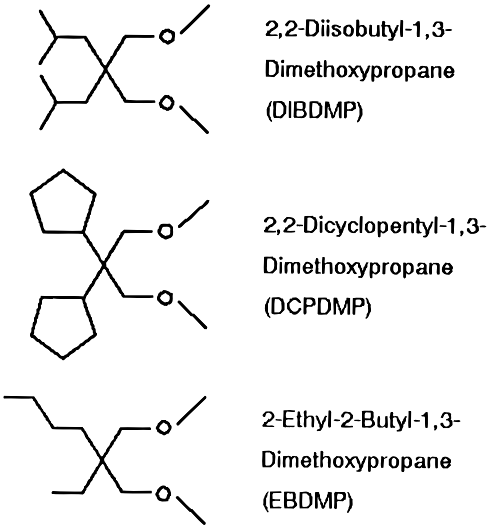

Figure 1. Differently hindered 1,3-diethers used as internal donors.

In comparison with the "traditional" $MgCl_2$-supported catalyst based on the diisobutyl phthalate/phenyltriethoxysilane donor pair (DIBP/PES), two of the diether-based catalysts (DIBDMP and DCPDMP) show a similar isospecificity and a higher activity (2 times higher in the case of the DIBDMP donor), while the third diether-based catalyst (EBDMP) shows lower activity and isospecificity but a similar hydrogen response.

As far as the MMD of the polymers is concerned, the three diether-based catalysts, in comparison with the "traditional" one, produce PP's with a narrower distribution. The effects of the presence and type of donor become more evident in terms of stereospecificity, activity, MMD, and hydrogen response if we compare the data regarding all the donor-based catalysts with the "donor-free" one. In particular, the "atactic" (XS) fraction is extremely high (58%) and regarding the hydrogen response, it can be observed that, even if in polymerization a lower hydrogen concentration was used, the intrinsic viscosity (IV) of the isotactic fraction of the PP obtained with the "donor-free" catalyst is slightly lower.

Finally, it can be observed that the melting temperatures (T_m), mainly related to the microtacticity of the polymers, are rather different: the phthalate/silane and two diether-based catalysts produce PP's which have the same T_m while the donor-free and the less stereospecific EBDMP-based catalysts produce PP's which have similar and lower T_m's (4−5 deg below).

In order to better characterize the polymers, a TREF analysis was performed in the temperature range between 100 and 125 °C: the results obtained are reported in Tables 2 and 3 and plotted in Figure 2. In Table 2, the ^{13}C-NMR stereosequence distributions of the fractions obtained with the TREF analysis of the PP prepared with the DIBDMP-based catalyst are reported: the atactic PP is collected in the fraction eluted

Table 2. ^{13}C NMR Stereosequence Distributions of TREF-Fractionated PP from DIBDMP-Based Catalyst

T_{el} °C	mmmm (%)	mmmr (%)	rmmr (%)	mmrr (%)	mrmm + rmrr (%)	mrmr (%)	rrrr (%)	rrrm (%)	mrrm (%)
25	22.0	11.7	3.0	15.1	11.2	0.3	16.4	9.4	8.2
26−99	86.3	4.8	0.5	4.0	1.0	0.3	0.6	0.7	1.8
100−105	93.8	2.6	0.2	1.9	0.4	0.1	0.1	0.2	0.7
106−108	94.5	1.9	0.3	1.8	0.4	nd	nd	0.1	0.9
109	96.7	1.3	0.2	1.1	0.1	nd	nd	nd	0.6
110	97.0	1.1	0.3	0.9	0.2	nd	nd	nd	0.5
111	97.5	0.9	nd	0.7	nd	nd	nd	nd	0.4
112	98.5	0.6	nd	0.6	nd	nd	nd	nd	0.3

[a] nd = not detectable (or too weak for integration).

Table 3. TREF Results and Characterization of the Fractions

	DIBDMP-based cat.				DCPDMP-based cat.			EBDMP-based cat.			DIBP/PES-based cat.			"donor-free" cat.		
T_{el} (°C)	wt %	mmmm (%)	T_m (°C)	IV (dL/g)	wt %	T_m (°C)	IV (dL/g)	wt %	T_m (°C)	IV (dL/g)	wt %	T_m (°C)	IV (dL/g)	wt %	T_m (°C)	IV (dL/g)
25	2.5				2.7			7.7			2.7			58.3		
26−99	18.0	86.3	157	0.67	20.0	156	0.72	39.4	156	0.99	21.1	156	0.67	31.1	155	1.03
100	0.3				0.4			0.5			0.5			0.2		
101	0.3				0.6			0.6	158		0.6			0.4		
102	0.5				0.8			2.1			1.4			0.8	157	1.42
103	0.7				0.9	158		5.4		1.41	0.9	160		1.2		
104	1.4	93.8			1.0			11.1			1.0			1.5		
105	1.6				1.3			14.0	161	1.98	1.4			1.6	160	2.11
106	2.0		161	0.98	2.0		1.05	11.9			2.4		1.06	1.7		
107	2.8	94.5			2.4	161		6.7		3.46	2.1	162		1.9	161	3.56
108	3.9				2.5			0.3			6.6			1.1		3.90
109	8.5	96.7			4.4			0.2			7.9			0.2		
110	16.9	97.0	163	1.58	9.3	162	1.64	0.1			7.7		1.70	0.0		
111	16.3	97.5			14.9			0.0			12.4					
112	12.7	98.5	164	2.49	16.6	164	2.42				11.4	164	2.47			
113	9.1				10.4						9.7					
114	2.5		165	3.50	8.0	166	3.60				8.5		3.82			
115	0.0				1.8		3.81				1.7	165				
>115					0.0						0.0					
whole	100	92.1	162	1.69	100	163	1.86	100	159	1.69	100	162	1.89	100	158	1.11

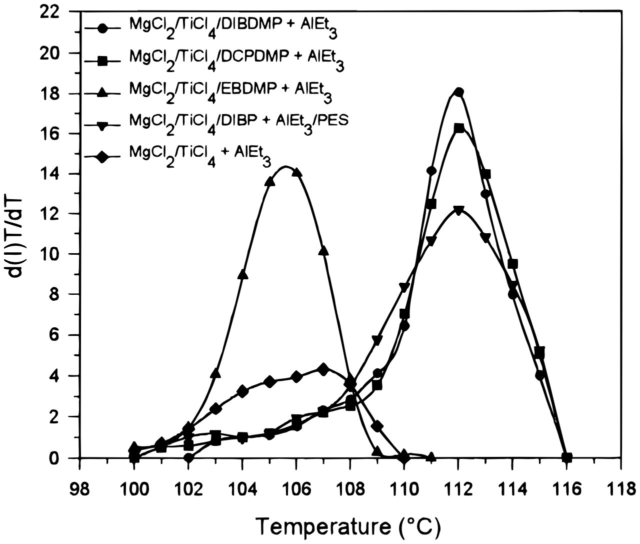

Figure 2. TREF elution profiles of PP's prepared with diether-based catalysts (comparison with "traditional" and "donor-free" $MgCl_2$-supported catalysts).

at 25 °C, while the less isotactic PP and the stereoblocks are collected as a single fraction (elution temperature (T_{el}) = 26−99 °C) and the subsequent fractions comprise isotactic polypropylene containing sterical errors mainly originating from a chiral site controlled mechanism of polymerization.

From the characterization of the fractions reported in Table 3, it turns out that the fractionation takes place mainly according to the isotacticity, although the MM also increases along with the T_{el}: in fact, at the same T_{el}, all the PP's fractionated show similar T_m's, whereas very different IV's are observed; on the other hand, by increasing the T_{el}, the T_m and the tacticity (mmmm %) increase. Therefore, as already observed by Kakugo,[10] the TREF elution profiles of the PP's can be considered essentially as their tacticity profiles.

From the elution profiles shown in Figure 2, it can be observed that the catalysts containing the highly stereoregulating diether donors (DIBDMP and DCPDMP) and the DIBP/PES donor pair produce PP's having a very similar tacticity distribution. The third diether-based catalyst (EBDMP) gives a less isotactic PP with an elution profile shifted to lower temperatures and similar to that shown by the isotactic fraction of the PP prepared with the donor-free catalyst.

In order to facilitate the presentation of the results, we arbitrarily subdivided the fractions of the polymer into four classes: (A) "atactic" (T_{el} < 25 °C); (B) stereoblocks (T_{el} = 26−99 °C; mmmm < 90%); (C) mainly isotactic (T_{el} = 100−108 °C; mmmm = 90−95%, with rrrr and rrrm still detectable even if present in extremely low amount); (D) = highly isotactic (T_{el} > 108 °C; mmmm > 95%). The distribution of the fractions, according to this classification, is reported in Table 4: we can observe that the D fraction is completely absent in the polymers obtained with the EBDMP-based and the "donor-free" catalysts, while their fraction B content is similar and about 2 times higher than that of the PP's produced with the highly stereoregulating donors. Moreover, the fraction C is present only in very low amount in the PP obtained with the "donor-free" catalyst.

With the aim of obtaining a better insight into the differences between a "high-performance" and a "low-performance" diether donor, we have studied the ste-

Table 4. Atactic, Stereoblock, Mainly Isotactic and Highly Isotactic PP Content

	DIBDMP-based cat. (wt %)	DCPDMP-based cat. (wt %)	EBDMP-based cat. (wt %)	DIBP/PES-based cat. (wt %)	"donor-free" cat. (wt %)
(A) "atactic" (T_{el} = 25 °C)	2.5	2.7	7.7	2.7	58.3
(B) stereoblocks (T_{el} = 26−99 °C)	18.0	20.0	39.4	21.1	31.1
(C) mainly iso-PP (T_{el} = 100−108 °C)	13.5	11.9	52.6	16.9	10.4
(D) highly iso-PP (T_{el} = > 108 °C)	66.0	65.4	0.3	59.3	0.2

Table 5. TREF Results of the ^{13}C-Enriched PP's

	$MgCl_2/TiCl_4/DCPDMP + Al^{13}Et_3/ZnEt_2$					$MgCl_2/TiCl_4/EBDMP + Al^{13}Et_3/ZnEt_2$				
T_{el} (°C)	wt %	mm (%)	[e]	T_m (°C)	IV (dL/g)	wt %	mm (%)	[e]	T_m (°C)	IV (dL/g)
26−98	31.4	94.8	0.79	156	0.45	41.7	94.0	0.75	155	0.92
99	1.6					1.1				
100	2.2			160		1.5			159	
101	2.6					2.2				
102	3.2			161		2.6			161	
103	4.0				1.00	3.8				1.82
104	4.0	98.3	0.85	162		5.3	97.9	0.76	162	
105	4.5					8.5				
106	7.0				1.08	8.7				
107	9.5	98.5	0.87	164		9.1	98.1	0.78	163	
108	6.5					6.7				3.00
109	12.1	99.0	0.89	166		6.7	98.6	0.78	166	
110	9.2			167		2.1				
111	2.0					0.0				
112	0.2									
>112	0.0									
heptane ins.		97.9	0.86	161	1.10		96.2	0.76	159	1.60

reoregularity of the first monomeric unit insertion in PP's prepared using ^{13}C-enriched $AlEt_3$ as cocatalyst in the presence of $ZnEt_2$ as MM regulator with the DCPDMP- and the EBDMP-based catalysts.[13] As has been shown in previous work,[9] first-step stereoregularity is more influenced than propagation stereoregularity by the steric environment of the active center and so can give more information on the presence or absence of a donor in the active center neighborhood. The ^{13}C-NMR analysis of the heptane-insoluble fractions of the same selectively enriched samples has already been presented[15] and some inferences have been drawn on the internal/external donor action mechanism. This paper reports on the ^{13}C-NMR, DSC, and viscosimetric analysis of the most significant TREF fractions of the same polymers.

From the TREF results reported in Table 5 and in Figure 3, it can be noted that the two different diethers still give two different profiles: the low-performance diether still shows the lower temperature profile. The difference between these profiles and the corresponding profiles reported in Figure 2 could be due to the different MM regulator.

The microtacticity of the homologous fractions (from different PP's but at the same T_{el}) reported in Table 5 and shown in Figure 4 is again quite similar, showing that the PP's have been fractionated mainly according to their tacticity.

Considering the NMR data plotted in Figure 5, it can be noted that the molar fraction [e] of the erythro placement (representing the extent of the first insertion stereoregularity) is, for all the fractions, higher in the case of the PP obtained with the DCPDMP-based catalyst and it is, for both the polymers, higher than the [e] value (0.69) of the corresponding heptane-insoluble fraction obtained with a donor-free catalyst.[9] In addition, it can be noted that the [e] values of the fractions increase by raising the T_{el}.

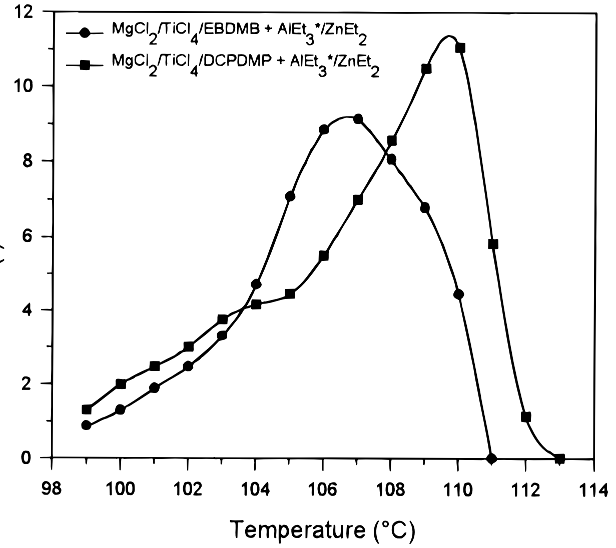

Figure 3. TREF elution profiles of ^{13}C-enriched PP's prepared with diether-based catalysts.

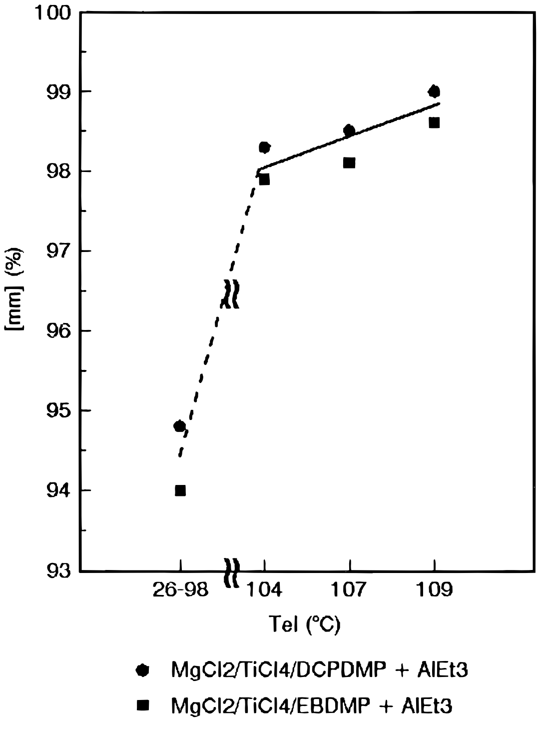

Figure 4. Propagation stereoregularity vs elution temperature.

In Table 6, all the characteristics of the catalysts and of the corresponding polymers are summarized in order to facilitate both the comparison among the catalysts and the rationalization of the experimental data discussed.

Many models of catalytic centers present on the surface of $MgCl_2$ have been proposed by different authors. According to Corradini,[12a,b] highly stereospecific active centers derive from chiral Ti_2Cl_6 dimers located on (100) edges of $MgCl_2$ layers; two different

Table 6. Summary of the Catalyst and Polymer Characteristics

	DIBDMP	DCPDMP	DIBP/PES	EBDMP	"donor free"
a-PP productivity	very low	very low	very low	medium	high
Iso-PP productivity	very high	high	high	medium	very low
stereoblock/highly isotactic ratio	low	low	low	medium	very high
hydrogen response	medium	medium	medium	medium	high
MMD	narrow	narrow	medium	narrow	broad
T_m	high	high	high	low	low
TREF profile centered at	higher *T*	higher *T*	higher *T*	lower *T*	lower *T*
tacticity distribution	broad	broad	broad	broad	broad
[e] heptane-insol fract	nd	high	nd	medium	low

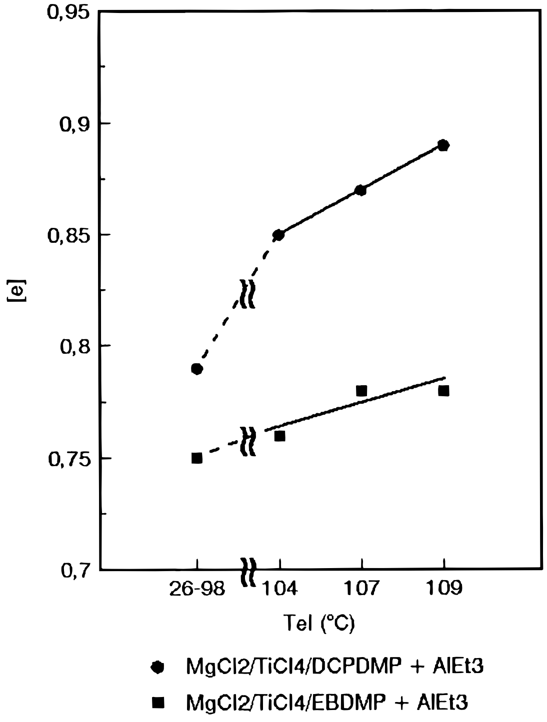

Figure 5. First-step stereoregularity vs elution temperature.

types of aspecific centers should derive from mononuclear $TiCl_3$ present on the (110) and (100) faces. The main function of the donor should be to avoid the location of $TiCl_4$ on the (110) face, through a competitive coordination.

In the additional models of isospecific centers proposed by other authors, the base is able to convert aspecific centers into isospecific ones by creating a suitable steric environment: the base can be bridged between a Ti and a Mg atom[11] or bonded to a Mg atom adjacent to the active Ti.[16] The steric environment of the active site can be conditioned, depending on the different situations, by the oxygen atom or the methyl group of the ethereal moiety or by the bulky groups present on the central carbon atom of the 1,3-diether. The second hypothesis (modification of the active Ti species from a steric and possibly an electronic point of view through the interaction of the donor with an unsaturated Mg atom adjacent to the active center) seems to be more in agreement with spectroscopic studies on the solid catalytic component containing electron donors. In fact, many IR studies exclude a direct coordination of the base with Ti atoms,[7b] and, on the other hand, the weakening of Ti−Cl bonds observed in Raman spectra[17] when the donor is present suggests a coordination of the base to Mg atoms adjacent to Ti species able to modify their electronic behaviors.

The formation of stereoblocks has been explained by assuming a reversible dissociation of the isospecific dinuclear Ti adducts[12e] or with the reversible migration of a chlorine ligand from the active Ti to the neighboring Ti atom in the same dinuclear adduct.[11] The donor can reduce the formation of stereoblocks by saturating the coordination vacancy of the Mg atoms adjacent to the isospecific dinuclear adduct or by saturating the vacancy of the inactive Ti of the Ti_2Cl_6 dimer, thus avoiding respectively the reversible dissociation of the dimer or the reversible migration of the chlorine ligand. Moreover, we suggest that stereoblocks (fraction B) and/or the mainly isotactic chains (fraction C) could also derive from the active centers sterically conditioned by the donor if the stability constant of the related complex is not sufficiently high.

In light of this complex but plausible picture, we can try to justify at least some of the results of our experimentation.

First of all, the presence of a multiplicity of active centers differing in stereospecificity and likely in regiospecificity and consequently in the propagation rate constant can account for the broad tacticity and MM distributions. The comparison between the two good diether-based catalysts (DIBDMP and DCPDMP) and the phthalate/silane-based catalyst shows that they have very similar behavior (see Table 6). This supports the hypothesis that the action mechanism of a donor is the same when it is present from the beginning as an internal donor (1,3-propane diether donors) and when it replaces the internal donor during polymerization (phthalate/silane system).[15] In all three cases, the increase in isotactic productivity with respect to the donor-free catalyst and the high percent of highly isotactic D fraction can be explained by the above-mentioned mechanism models, that is, by the increased number of dimeric Ti species[12c,d] and/or by the formation of new isospecific Ti species,[9−11,16] while the decreased atactic fractions can be explained by the selective complexation of the tetracoordinated Mg atoms. The differences in the isotactic productivity observed in the three systems may be due to the different ability that the internal donors (diethers or phthalate) have to produce the highest number of isospecific centers and to the different propagation rate shown by the different isospecific centers. The presence of an external donor can also be considered the reason for the lower activity observed in the phthalate/silane-based catalyst. Indeed, an external donor inevitably causes a more or less marked deactivation of the catalyst, depending on its structure and concentration. In fact, when the same two diether donors are used as external donors in the presence of a catalyst containing phthalate as an internal donor, the yields can be as low as half the corresponding yields observed when they are used as internal donors.[7a,15]

The difference between the low (EBDMP) and the high (DIBDMP and DCPDMP) performance diether donors is more subtle. Indeed, in comparison with the donor-free catalyst, EBDMP also gives a noticeable increase of isotacticity index (92%) and of isotactic productivity. The hydrogen response is also quite similar to that observed with DIBDMP and DCPDMP. However, while with DIBDMP and DCPDMP donors the polymers prevailingly consist of the highly isotactic D fraction (Table 4), with EBDMP most polymer (53%) is constituted by the mainly isotactic C fraction, and the D fraction is nearly absent. Moreover, this C fraction shows an elution curve similar to that of the small (10%) C fraction of the polymer obtained with the donor-free catalyst. The melting temperature of the polymer obtained with EBDMP is also similar to that obtained with the donor-free catalyst.

On the basis of these data, one could deduce that the action mechanism of this low-performance donor is similar to that of the high-performance donors only from some aspects. In principle, EBDMP could strongly inhibit the formation of aspecific centers and sensibly contribute to the formation of the Ti_2Cl_6 stereospecific centers, which are present only in small amount in the donor-free catalyst, without however affecting the environment of the active centers. In other words, the low-performance donor would only increase the number of isospecific centers but it would not be present in the vicinity of the active centers and would not have any direct effect on their steric control. However, this hypothesis is in conflict with the stereochemical data, according to which the first-step stereoregularity, even if rather low, is undoubtedly higher than that observed with the donor-free catalyst.[9] This suggests that also this diether, as well as the better performance ones, is present in the vicinity of at least some of the active centers and establishes the right steric environment through one of the above proposed mechanisms. This hypothesis could also explain the lower rate of the chain transfer with hydrogen, similar to that observed with DIBDMP and DCPDMP, because the base should decrease the electrophilicity of the adjacent active Ti as suggested by Raman spectroscopy.[18]

At this point, if the action mechanism of the low- and high-performance diethers is basically the same, we must still explain the absence of the highly stereospecific D fraction and the low [e] values observed with EBDMP, that is, the apparent lack of highly stereospecific centers. Indeed, Table 5 and Figure 5 show that the [e] values of all the fractions relative to EBDMP are noticeably lower than the [e] values of the corresponding fractions relative to DCPDMP. The differences are particularly significant for the fractions eluted at higher temperatures (107 and 109 °C). Two different factors could account for the absence of the highly isotactic D fraction:

(a) EBDMP, unlike the more stereoregulating diethers, shows values of the oxygen−oxygen distance for the most probable configurations spread out over a wide range[7b] and for this reason could be unsuitable for a strong chelation.[19] Thus we can suppose that the stability constant of the complexes of this donor with the coordinatively unsaturated species present in the catalyst is not sufficiently high. As a consequence, the complexes could dissociate and reassociate during polymerization, so causing the occurrence of steric errors in the chains which are growing on the active sites sterically conditioned by the base.

(b) EBDMP bears linear and less bulky hydrocarbon substituents with respect to the more stereoregulating diethers and thus it could be unable, when coordinated on the Mg adjacent to the active titanium atoms, to make the active centers highly stereospecific. Indeed, molecular modeling calculations have shown[16] that titanium centers which do not have the correct chirality for isotactic polymerization because of a chlorine vacancy can be converted into stereospecific centers when the hydrocarbon substituents of the central carbon of the 1,3-diether approach the position of the chlorine vacancy. In order to make this happen, the hydrocarbon substituents must be bulky enough.

It seems likely that the low [e] values are prevailingly due to the lower steric bulkiness of the substituents rather than to the lower stability of the complex between the donor and the Mg adjacent to the active titanium. Indeed, due to statistical reasons, this last factor should only slightly affect the stereoregularity of the first monomer insertion. The fact that a less bulky donor makes the active center, in the environment of which it is located, less highly isotactic than a bulkier one was already evidenced in a previous work on the phthalate/silane system, in which it was shown that first-step stereoregularity strongly depends on the size of the hydrocarbon substituents of the alkoxy silane donor. A variation of [e] value from 0.82 to 0.92 was observed by passing from $Me(EtO)_3Si$ to the bulkier $Ph(EtO)_3Si$.[9c]

Conclusions

The results of the structural characterization of TREF fractions of polypropylenes obtained with catalyst systems containing electron donors endowed with different stereoregulating capabilities allow us to draw the following conclusions:

(i) The nearly total coincidence in the behavior of catalytic systems containing a good-performance 1,3-propane diether donor and a "traditional" phthalate/silane donor pair suggests that the same action mechanism accounts for the increase of isotactic productivity observed both when the diether internal donor remains fixed on the catalyst during polymerization and when the phthalate internal donor is replaced by the silane.

(ii) The observed difference in the behavior between a low- and a high-performance diether donor can be accounted for by the fact that the former, bearing linear, not sufficiently bulky hydrocarbon substituents, on one hand, gives complexes with the Mg adjacent to the active titaniums with a lower stability constant, and, on the other hand, even when present in the environment of active titaniums, is unable to make the active centers highly stereospecific.

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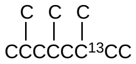
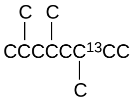
(13) When polymerization starts on the enriched Ti−$^{13}CH_2CH_3$, the two possible arrangements of the chain end groups are distinguished by ^{13}C-NMR:[14]

erythro:

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

threo:

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

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 propylene unit, the molar fraction [e] of the erythro placement represents the extent of the first-step stereoregularity.

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