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Advances in Propene Polymerization Using $MgCl_2$-Supported Catalysts. Fundamental Aspects and the Role of Electron Donors

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SUMMARY: The fundamental factors determining the performance of state-of-the-art $MgCl_2$-supported catalysts for polypropylene are becoming increasingly evident. Polymer yield, isotacticity, molecular weight and molecular weight distribution are dependent on the regio- and stereoselectivity of the active species. Chain transfer with hydrogen after the occasional regioirregular (2,1-) insertion has a strong effect on molecular weight and is the main reason for the high hydrogen response shown by high-activity catalysts containing diether donors. Hydrogen response is also dependent on stereoselectivity. The probability of a stereo- or regioirregular insertion can be related to the lability of donor coordination in the vicinity of the active species. Results with different catalyst systems can be interpreted on the basis of a propagation model involving interconverting active species, such that polypropylene produced using $MgCl_2$-supported catalysts can be regarded as a stereoblock polymer comprising (highly) isotactic sequences, moderately isotactic (isotactoid) sequences and syndiotactoid sequences. Strongly coordinating donors will give stereoregular polymers in which highly isotactic sequences predominate.

Introduction

High-activity $MgCl_2$-supported catalysts, comprising $MgCl_2$, $TiCl_4$ and an “internal” electron donor, play a dominant role in polypropylene (PP) manufacture. They are used in combination with a trialkylaluminium cocatalyst and selectivity control is usually achieved by the use of an “external” electron donor present in polymerization. Successive “generations” of high-activity $MgCl_2$-supported catalyst systems$^{1-4)}$ for polypropylene are summarised below.

Catalyst	*Cocatalyst*	*External donor*
$MgCl_2/TiCl_4$/ethyl benzoate	AlR_3	aromatic ester
$MgCl_2/TiCl_4$/dialkyl phthalate	AlR_3	alkoxysilane
$MgCl_2/TiCl_4$/diether	AlR_3	-

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Currently, the most widely used catalyst system is that in which the internal donor is a phthalate ester such as diisobutyl phthalate (DIBP) and the external donor is an alkoxysilane. Under typical polymerization conditions (liquid monomer, 70 °C, 1-2 hours), PP yields of up to around 80 kg/g cat. can be achieved, more than double those obtained with the catalysts in which the internal donor is ethyl benzoate (EB). With the latest generation of $MgCl_2$-supported catalysts, in which the internal donor is a diether (typically a 2,2-disubstituted-1,3-dimethoxypropane), PP yields of up to around 160 kg/g cat. can be achieved. These catalysts are already being used in PP manufacture and it is expected that diether-based catalysts will have a significant impact on the industry.

An important function of the internal donor in $MgCl_2$-supported catalysts is to control the amount and distribution of $TiCl_4$ in the catalyst. Giannini5) has indicated that, on preferential lateral cleavage surfaces, the magnesium atoms are coordinated with 4 or 5 chlorine atoms, as opposed to 6 chlorine atoms in the bulk of the crystal. These lateral surfaces correspond to (110) and (100) faces of $MgCl_2$. It has been proposed that bridged dinuclear Ti_2Cl_8 species can coordinate to the (100) face of $MgCl_2$ and give rise to the formation of chiral, isospecific active species6,7), it being pointed out that Ti_2Cl_6 species formed by reduction on contact with $AlEt_3$ would resemble analogous species in $TiCl_3$ catalysts. Accordingly, it has been suggested8) that a possible function of the internal donor is preferential coordination on the more acidic (110) face of $MgCl_2$, such that this face is prevailingly occupied by donor and the (100) face is prevailingly occupied by Ti_2Cl_8 dimers.

Bidentate coordination of the internal donor to magnesium atoms on the (110) face of $MgCl_2$ appears to be an important feature in the case of diethers. It has been reported9) that the 1,3-diethers giving the greatest stereoregulating effect are those having the greatest preference for coordination on the (110) rather than the (100) face of $MgCl_2$. Catalysts in which the internal donor is a diether exhibit high isospecificity even in the absence of an external donor, due to the fact that the diether is not displaced from the catalyst surface on contact with the cocatalyst. In the case of catalysts in which the internal donor is ethyl benzoate or diisobutyl phthalate, a large proportion of the internal donor is lost as a result of alkylation and/or complexation reactions with $AlEt_3$, leading to poor stereoselectivity due to increased mobility of the titanium species on the catalyst surface.

Various studies[10-12] have indicated that the presence of an internal or external donor in the vicinity of active titanium species in $MgCl_2$-supported catalysts is an important factor in the formation of (highly) isospecific centres. Possible active species where high isospecificity is dependent on the coordination of a diether on a magnesium atom adjacent to the titanium centre have been illustrated by Barino and Scordamaglia[9]. Recently, studies by Busico et al.[13] have indicated that the stereosequence distribution in PP prepared with $MgCl_2$-supported catalysts can be described by a three-site model in which fluctuating isospecificity during the course of chain growth is related to (reversible) changes in the steric environment of the active centre, which in turn can be related to the presence or absence of a donor molecule.

In the present paper, effects of various types of electron donors on catalyst regio- and stereospecificity are discussed in relation to catalyst performance and polymer micro- and macrostructural control, with particular reference to how these effects can be interpreted in terms of donor coordination in the vicinity of the active species.

Effects of Regiospecificity

In addition to very high catalyst activity, an important feature contributing to the success of diether-containing catalysts is their sensitivity to hydrogen, so that relatively low concentrations of hydrogen are sufficient for effective molecular weight control. Polymers ranging from very low to high molecular weight can be produced. We have established[14] that the high hydrogen response of the catalyst system $MgCl_2/TiCl_4$/diether - $AlEt_3$ can be attributed to chain transfer with hydrogen after the occasional secondary (2,1-) monomer insertion. This leads to a polymer chain with a *n*-butyl terminal group, as opposed to an *i*-butyl group when chain transfer takes place after the usual primary insertion:

$\mathrm{Ti{-}CH_2{-}CH(CH_3){-}[CH_2{-}CH(CH_3)]_nPr} + \mathrm{H_2}$ ---> $\mathrm{Ti{-}H}$ + i-$\mathrm{Bu{-}CH(CH_3)[CH_2(CH_3)]_{n-1}Pr}$

$\mathrm{Ti{-}CH(CH_3){-}CH_2{-}[CH_2{-}CH(CH_3)]_nPr} + \mathrm{H_2}$ ---> $\mathrm{Ti{-}H}$ + n-$\mathrm{Bu{-}CH(CH_3)[CH_2(CH_3)]_{n-1}Pr}$

The higher incidence of chain transfer after secondary insertion with diether- as opposed to diisobutyl phthalate-based catalyst systems is apparent from the data in Table 1, obtained via ^{13}C

NMR analysis of xylene-insoluble (XI) fractions of polymers prepared at 67-70 °C in liquid monomer[14,15)]. It can be seen that the proportion of *n*-Bu terminated chains is dependent on the catalyst system and on the amount of hydrogen in polymerization. The proportion of *n*-Bu terminated chains increases with decreasing (but finite) hydrogen pressure, which can be ascribed to a relatively high equilibrium concentration of 2,1-inserted species at low hydrogen pressure. It is important to note that most of the polymers listed in Table 1 have fairly low molecular weights. This means that much of the PP produced worldwide using such catalysts, at lower hydrogen pressures, will predominantly comprise polymer chains having a *n*-butyl terminal group, underlining the practical importance of regiospecificity with regard to the hydrogen response of both phthalate- and diether-based catalysts.

Table 1. Effect of electron donors and hydrogen on polymer molecular weight, stereoregularity and chain-end composition.

Internal Donor	External Donor	Hydrogen pressure bar	[η] dL/g	*mmmm* in XI fraction %	*n*-Bu : *i*-Bu chain-ends in XI fraction
DIBP	CHMDMS	2.5	1.41	97.5	46 : 54
"	"	8	1.05	98.0	24 : 76
DIBP	DCPDMS	2.5	2.32	98.5	n.d.
"	"	8	1.35	99.0	34 : 66
diether	-	1	1.41	97.4	65 : 35
"	-	4	0.99	97.5	45 : 55

CHMDMS:cyclohexylmethyldimethoxysilane
DCPDMS: dicyclopentyldimethoxysilane
[η] : intrinsic viscosity of total polymer

Chain transfer after the occasional regioirregular (2,1-) insertion, such an insertion giving a species having low activity in chain propagation, also provides an explanation for the commonly observed activating effect of hydrogen in propene polymerization with $MgCl_2$-supported catalysts, an effect first reported by Guastalla and Giannini[16)].

Regioirregular insertion has also been detected at the start of chain growth. Chain initiation via a secondary propene insertion into a Ti-H species, followed by successive primary insertions, leads to a 2,3-dimethylbutyl terminal unit, as opposed to *n*-propyl when the first insertion is primary. Significant proportions of 2,3-dimethylbutyl end groups have been found[17,18] in polymers prepared using metallocene catalysts and molecular modelling calculations[17] have indicated that primary and secondary propene insertion into the Zr-H bond in metallocene-catalyzed polymerization have similar probabilities. In xylene-soluble fractions of polymers prepared using $MgCl_2$-supported catalysts, we have observed that the proportion of chains having a 2,3-dimethyl terminal group is around 5 - 20 %. A typical ^{13}C NMR spectrum, taken from ref. 19, is shown in Fig 1.

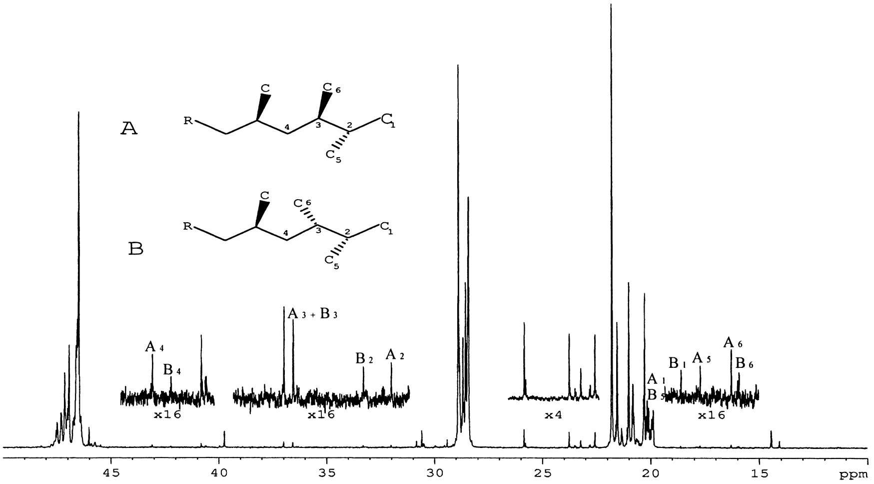

Fig. 1: ^{13}C NMR spectrum of the xylene-soluble fraction of a polymer prepared with the catalyst system $MgCl_2/TiCl_4$/DIBP - $AlEt_3$ - diether in the presence of hydrogen (for the peak assignments A_1, B_1, etc., the subscript numbers refer to the relevant carbon atoms indicated in structures A and B).

The above results indicate that, as is the case for metallocene catalysts, the probability of a secondary as opposed to a primary insertion into Ti-H species generated in chain transfer with hydrogen is much greater than the probability of secondary insertion into the growing polymer chain. Our earlier results[14] indicated approximately 1 secondary insertion for every 2000 primary insertions in propagation at isospecific centres with the catalyst system $MgCl_2/TiCl_4$/diether - $AlEt_3$. This very low incidence of regioirregular insertion is nevertheless sufficient to have a profound effect on the hydrogen response of the catalyst, as indicated above. The perception that a 2,1-insertion will drastically lower the chain propagation rate relative to the rate of chain transfer with hydrogen implies that this should also apply to the Ti-isopropyl reaction product of a 2,1-monomer insertion into a titanium-hydride bond. In other words, the probability of a further transfer reaction with hydrogen, generating propane, should be greater than the probability of chain growth and the formation of a 2,3-dimethylbutyl end group. This indeed appears to be the case. We have measured the formation of propane in propene polymerization using a diether-based catalyst and have estimated19) that this may be an order of magnitude greater than the extent of 2,3-dimethylbutyl chain end formation. Nevertheless, the amounts of propane formed were very small and only detectable at very high hydrogen concentrations, when about 0.1 % of the propene present was hydrogenated to propane.

For polymerization in the absence of hydrogen, the most significant chain termination reaction is transfer with monomer. We have established19) that chain transfer with monomer is independent of hydrogen concentration but strongly dependent on catalyst stereospecificity, a decrease in (site) stereospecificity leading to an increase in chain transfer. In contrast to chain transfer with hydrogen, transfer with monomer takes place predominantly after primary insertion, giving a vinylidene-terminated chain:

$$\text{Ti-CH}_2\text{CH(CH}_3\text{)-Pol} + \text{CH}_2\text{=CHCH}_3 \rightarrow \text{Ti-CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_2\text{=C(CH}_3\text{)-Pol}$$

Effects of Stereospecificity

The results in Table 1 illustrate that the stereoregularity of the isotactic (xylene-insoluble) polymer fraction, as indicated by the *mmmm* pentad content, is dependent on the electron donor(s) present in the catalyst system. A more comprehensive picture of the effects of catalyst composition on polymer isotacticity can be obtained by temperature rising elution fractionation (TREF). This technique has been finding increasing use in the characterization of polymers prepared using $MgCl_2$-supported catalysts20-22), including previous studies carried out in Ferrara12,14,23).

The proportions of weakly tactic polymer (eluting at 25 °C), moderately isotactic polymer (26-95 °C) and highly isotactic polymer (96-125 °C) in PP samples prepared using different catalyst systems are given in Table 2. It can be seen that the internal/external donor combinations ethyl benzoate / ethyl p-ethoxybenzoate and diisobutyl phthalate / 3,3,3-trifluoropropyl(methyl)-

dimethoxysilane give significant proportions of polymer eluting in the range 26-95 °C. Such fractions can be attributed to polymer chains containing relatively high proportions of defective isotactic ("isotactoid") sequences, as will be discussed in more detail below.

Table 2. Effect of catalyst composition on PP tacticity distribution.

Internal Donor	External Donor	Wt.-% eluted in TREF temperature range 25 °C	26-95 °C	96-125 °C	T_{peak} °C
EB	PEEB	5.1	19.2	75.7	113
DIBP	TFPMDMS	3.8	21.4	74.8	110
DIBP	CHMDMS	3.2	7.2	89.6	111-112
DIBP	DCPDMS	2.4	4.6	93.0	117
Diether	-	2.4	5.9	91.7	113

T_{peak} : Peak elution temperature in TREF
PEEB : ethyl p-ethoxybenzoate
TFPMDMS : 3,3,3-trifluoropropyl(methyl)dimethoxysilane
CHMDMS : cyclohexyl(methyl)dimethoxysilane
DCPDMS : dicyclopentyldimethoxysilane

The TREF elution profiles for the (highly) isotactic fractions are shown in Fig. 2. Significant differences in elution temperature range are apparent, with the polymer prepared with the internal/external donor combination DIBP/DCPDMS eluting at the highest temperature, as may be expected taking into account the previous results (Table 1).

Selected TREF fractions were analyzed by GPC and ^{13}C NMR, giving the results in Table 3. It is apparent from the data in Tables 2 and 3 and from Fig. 2 that, while the donor combinations EB/PEEB and DIBP/TFPMDMS both give products containing around 20 % of a moderately isotactic fraction (*mmmm* ca. 80 %), the EB/PEEB combination gives a significantly more stereoregular isotactic fraction, on a par with that obtained using the diether-based catalyst. The latter catalyst gives a much narrower tacticity distribution, however, with a relatively small fraction eluting at temperatures less than 96 °C. In line with the narrow tacticity distribution of PP prepared using diether-based catalysts is the fact that these systems also give relatively narrow molecular weight distribution[24).

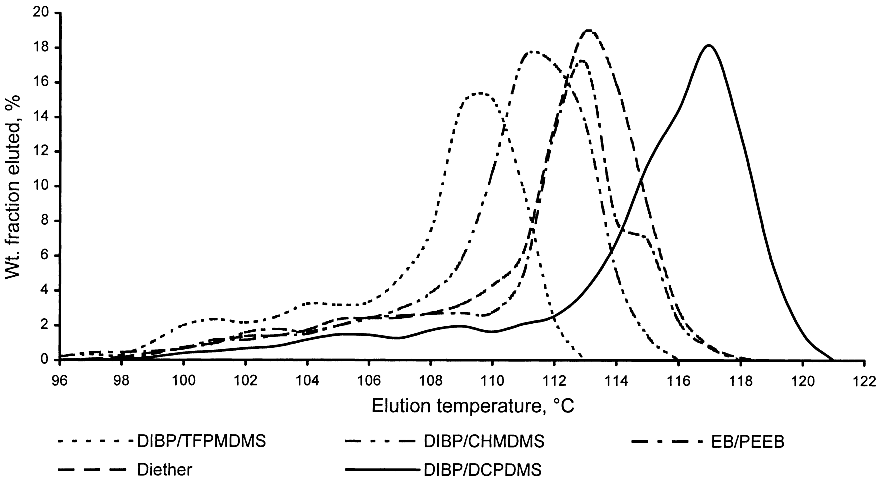

Fig. 2: Comparison of TREF elution profiles.

Table 3. Molecular weight and stereoregularity of selected TREF fractions.

Internal Donor	External Donor	TREF fraction °C	wt.-%	M_n x 10^{-3}	M_w x 10^{-3}	M_z x 10^{-3}	*mmmm* %
EB	PEEB	26-95	19.2	25	84	211	79.9
"	"	111-114	43.2	283	722	1538	97.1
"	"	115-117	9.9	415	998	2018	98.3
DIBP	TFPMDMS	26-95	21.4	21	73	210	84.1
"	"	110	15.1	141	332	746	97.0
DIBP	CHMDMS	26-95	7.2	16	67	206	77.6
"	"	113-114	18.9	163	494	1173	97.3
DIBP	DCPDMS	26-95	4.6	7	28	98	80.3
"	"	113-114	10.9	80	162	288	97.4
"	"	116	14.5	144	345	743	98.2
"	"	118-119	18.6	266	718	1793	99.7
Diether	-	26-95	5.9	10	42	143	83.6
"	"	113-114	35.0	92	234	465	98.0

Discussion

We will now attempt to rationalize the different effects of the various internal and external donors, in the light of current insight regarding the symmetry and steric requirements of the active species. Recent studies carried out by Busico et al.25) have demonstrated the presence of C_1-symmetric active species in $MgCl_2$-supported catalysts. This resulted from the observation that the *mrmrmm* heptad, which would arise from two consecutive stereoerrors during isotactic propagation, was absent in high-resolution ^{13}C NMR spectra of the polymer, even in highly stereoirregular fractions. This indicates that the two coordination sites on the titanium atom, one of which is occupied by the growing chain and the other is available for monomer coordination, are non-equivalent. This was confirmed by the finding25,26) that increased polymer isotacticity is obtained at low monomer concentration, showing that isotactic propagation is analogous to that predicted27) and observed28) with certain C_1-symmetric metallocenes, in the sense that propene insertion at a highly enantioselective site tends to be followed by chain "back-skip" rather than a less regio- and stereoselective insertion when the chain is in the coordination position previously occupied by the monomer.

$MgCl_2$-supported catalysts also contain syndiospecific species, where syndiotactic propagation originates from chain-end control. The fact that syndiotactic sequences have been identified in predominantly isotactic PP fractions29) indicates that isospecific and syndiospecific sites are able to interconvert rapidly during the time of chain growth, which for a single polymer chain is typically less than a second. In the past, it has been common to use a two-site model to describe chain propagation, assuming the pentad distribution to obey enantiomorphic site statistics30). This model (enantiomorphic site + chain-end control site) gives an adequate fit for stereosequence distribution determined via ^{13}C NMR at the pentad level, but not for high-resolution NMR data obtained at the heptad level. A better fit was found with the combination C_1-symmetric site + chain-end control site, but the best model was found to be the *three* site model enantiomorphic site + C_1 site + chain-end control site13). According to this model, polypropylene produced with $MgCl_2$-supported catalysts comprises three different types of stereosequences: highly isotactic, moderately isotactic (isotactoid) and syndiotactic. Furthermore, these same (stereoblock) sequences are present in (xylene-)soluble and insoluble fractions, but in different proportions.

Taking into account the fact that a (temporary) loss of steric hindrance from one side of an active species with local C_2-symmetry, giving a C_1-symmetric species, may result in a transition from highly isospecific to moderately isospecific propagation and that loss of steric hindrance on both sides may lead to syndiospecific propagation in which chain-end control becomes dominant, the model illustrated in Fig. 3 was proposed13). The steric hindrance required for site control via orientation of the growing chain31) when the chain is in the position S1 or S2 arises from the presence of the ligands L1 and L2 respectively. Highly isotactic propagation can occur when both ligands are present (species *a*), or if one ligand is present (species *b*) but is large enough to inhibit monomer approach at the more hindered site. An important implication of this model is that even in highly isotactic chains the stereodefects are not randomly distributed along the chain but are present as clusters in "isotactoid" segments of the chain.

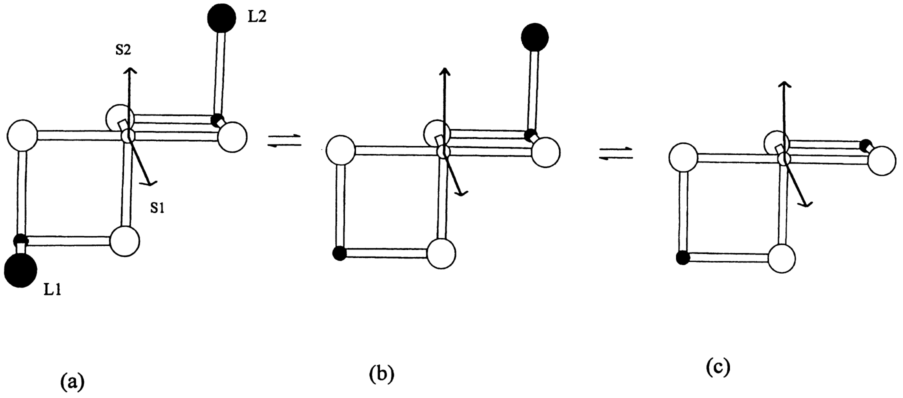

Fig. 3: Model of possible active species for highly isotactic (a), isotactoid (b) and syndiotactic (c) propagation13).

If it is considered that the steric hindrance in the vicinity of the active species can result from the presence of a donor molecule, and that the coordination of such a donor is reversible, the above model provides us with an explanation for the fact that strongly-coordinating donors will give stereoregular polymers in which the highly isotactic sequences predominate.

Returning to the results outlined in the previous sections, and considering first the effects of the different silane donors in the catalyst system $MgCl_2/TiCl_4$/DIBP - $AlEt_3$ - alkoxysilane, we can see that (cyclopentyl)$_2$Si(OMe)$_2$ gives highly isotactic PP. The high elution temperature range in TREF and the high isotactic pentad content and high molecular weight of the high-temperature TREF fractions indicate the presence of active species for which isotactic (as opposed to isotactoid) propagation is dominant. In contrast, $CF_3CH_2CH_2$(Me)Si(OMe)$_2$ gives a polymer in which a high molecular-weight, highly isotactic fraction is essentially absent. The relatively low isotactic stereoregularity of the polymer indicates a high proportion of isotactoid sequences. It is likely that the latter donor is more easily displaced from the catalyst surface, giving a relatively labile coordination. This may lead to the formation of species of type *b* and even *c*. The lower specificity of these species will lead to decreased isotacticity and the increased probability of misinsertion will lead to a greater incidence of chain transfer and lower molecular weight.

The above interpretation is in agreement with a previous suggestion32) that the high stereospecificity obtained using silanes having one or more bulky hydrocarbyl groups is due to the silane stabilizing "fluctuating" isospecific sites, the bulky hydrocarbyl groups protecting the silane from removal from the catalyst surface via complexation with aluminium alkyl. We have observed that the use of Al^iBu_3 rather than $AlEt_3$ as cocatalyst in propene polymerization using the catalyst system $MgCl_2/TiCl_4$/DIBP – AlR_3 – alkoxysilane can give a broadening in molecular weight distribution, as a result of the presence of a fraction having high isotactic stereoregularity and high molecular weight. Accordingly, it can be reasoned that a weaker complexation between the silane donor and Al^iBu_3, as opposed to $AlEt_3$, will lead to a less labile catalyst-donor interaction at sites where the presence of the donor is required for selectivity control.

The molecular structure of the alkoxysilane external donor also affects the PP molecular weight distribution, which tends to be broader for catalyst systems giving relatively low hydrogen response (i.e. requiring relatively high hydrogen concentrations for molecular weight control). A low hydrogen response is indicative of the presence of highly regio- and stereoselective active species, these species giving the highest molecular weight polymer fraction. However, the presence of other species having much higher hydrogen response will result in the formation of a significant fraction of lower molecular weight polymer, broadening the molecular weight distribution.

Relatively narrow molecular weight distribution and high hydrogen response is obtained with diether-containing systems, but these systems give significantly higher isotactic stereoregularity the effects of chain transfer after the occasional regioirregular (2,1-) insertion. A predominance of *n*-Bu terminated chains resulting from transfer with hydrogen after 2,1-insertion is noted in oligomeric and xylene-soluble fractions[24,33)] as well as in (highly) isotactic polymer fractions[14)]. These results point to a similar type of behaviour of the various active species present in the diether-based catalysts, leading to a more uniform polymer composition than is obtained with ester-based catalysts.

In contrast, a relatively broad molecular weight distribution is obtained with the catalyst system $MgCl_2/TiCl_4$/ethyl benzoate - $AlEt_3$ – aromatic ester. The presence of a significant low molecular weight fraction having moderate isotacticity is apparent from the TREF results, indicating the presence of propagating species interconverting rapidly between isotactic and isotactoid propagation. This may reasonably be interpreted as being the result of labile coordination of the monoester donor in the vicinity of the active centre. However, this system also gives a significant proportion of high molecular weight, stereoregular polymer and the hydrogen response is relatively low. It is suggested that this system also contains a significant proportion of species for which high selectivity is not dependent on the presence of an electron donor in the immediate vicinity of the active site. These species may result from dinuclear Ti_2Cl_8 coordination on the (100) face of $MgCl_2$, as suggested by Corradini et al.[6,7)]. An alternative type of species not requiring the presence of an electron donor for high stereospecificity is a 5-fold Ti species on the (110) face of $MgCl_2$, proposed by Boero et al.[34)]. On the other hand, the fact that a high molecular weight tail appears to be essentially absent in PP prepared[24)] with the catalyst system $MgCl_2/TiCl_4$/diether - AlR_3 indicates that such species, not involving the close proximity of a donor, may not be present in diether-containing systems. It is possible that the use of a bidentate internal donor such as a 1,3-diether leads to the preferential formation of the (110) face of $MgCl_2$ in these systems, and that active Ti species are present on the same face. The present results provide further support for close interaction between the donor and Ti, such as has been postulated[9)] for active species on the (110) surface of $MgCl_2$ where the presence of a donor is required for high isospecificity.

Conclusions

The electron donors present in $MgCl_2$-supported catalyst systems for polypropylene play a vital role in determining not only isotacticity but also polymer yield, molecular weight and molecular weight distribution. These factors are interrelated and to a large extent are dependent on the regio- and stereoselectivity of the active species, which can change during chain growth depending on the nature of donor coordination in the environment of the active species. Diether donors give relatively narrow tacticity and molecular weight distribution and it is probable that the donor is present in the vicinity of the active species. The latter also applies to phthalate ester / alkoxysilane donor combinations, where strongly coordinating silanes tend to give high molecular weight, highly isotactic polymers, while more labile donors give lower stereoregularity and molecular weight. A broad tacticity distribution is obtained using benzoate esters as internal and external donors. The presence of a significant fraction of defect-rich polymer is indicative of labile donor coordination, but the polymer also contains a highly isotactic, high molecular weight fraction. It is proposed that this system also contains active species which do not require the close proximity of a donor for high isospecificity.

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