ELSEVIER

Journal of Molecular Catalysis A: Chemical 150 (1999) 53–69

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Effect of different donors on kinetics of Zn catalysts and molecular weight of the obtained polypropylene

María Luján Ferreira, Daniel E. Damiani *

PLAPIQUI-UNS-CONICET, 12 Octubre 1842-8000, Bahía Blanca, Argentina

Received 15 October 1998; received in revised form 15 December 1998; accepted 6 April 1999

Abstract

This paper studies $MgCl_2$/internal donor/$TiCl_4$//external donor/$AlEt_3$ catalytic systems where ethyl benzoate (E.B.) or 2,2,6,6 tetramethylpiperidine (TMPiP) are used as internal and external donors. E.B. as external donor does not change the molecular weight of the product with TMPiP as internal donor. The molecular weight of polypropylene decreases drastically and global productivity and stereoselectivity are very low with $MgCl_2$/internal Donor/$TiCl_4$//external donor/$AlEt_3$ when TMPiP is the external and internal donor. In this case the insoluble fraction in *n*-heptane is highly stereospecific and the molecular weight is similar to commercial products. We present a new explanation of these results, based on Ystenes proposal, comparing both precatalysts.

Keywords: $MgCl_2$ supported catalysts; Propylene polymerization; Ziegler Natta catalysts; Tetramethylpiperidine; Lewis bases; Internal and external

1. Introduction

The combination of $MgCl_2$/(an internal donor)/$TiCl_4$, the precatalyst, and $AlEt_3$/external modifier (external donor), the cocatalyst, is a typical Ziegler Natta catalyst for olefin polymerization.

Among several materials thoroughly analyzed, $MgCl_2$/ethyl benzoate (or a diester)/$TiCl_4$ is probably the best one studied. Most generally, the external modifiers are esters, amines and silanes. The literature concerning the use of amines as internal donors is not as abundant as in the case of esters. Chien et al. [1], Chien [2], Kashiwa and Yoshitake [3], Keszler et al. [4,5], Keszler and Simon [6], and Guyot et al. [7] studied the effect of the ester carefully. Dumas and Hsu [8], Samson et al. [9], Langer et al. [10], and Sacchi et al. [11] mentioned that the presence of sterically hindered amines as external donor has a favorable effect on the stereoselectivity. This motivated the present study of the performance of $MgCl_2$/ethyl benzoate (E.B.)/$TiCl_4$ and $MgCl_2$/a secondary amine/$TiCl_4$. The cocatalysts are $AlEt_3$, $AlEt_3$/E.B. and $AlEt_3$/secondary amine to evaluate the roll of the external and internal donors.

External modifiers in the old generation catalysts were amines in many cases [12,13]. There are few reports about their performance when they are used as internal donors. There are

* Corresponding author.

1381-1169/99/$ - see front matter
PII: S1381-1169(99)00208-3

studies about the roll of the amines only in catalysts based on $MgR_2/TiCl_4$ and with phosphate supports. In that case the productivity is very low, but the isotactic index (I.I.%) is as high as 90% [14]. The I.I. is the percentage of insoluble polypropylene in boiling *n*-heptane, and it is a measure of the isotactic content of the product at given conditions of temperature, propylene pressure and catalyst and cocatalyst concentration.

In the present work the internal donor was TMPiP or E.B. to obtain a comparative basis to investigate the effect of the internal donor and external donor in the product characteristics. The kinetics was correlated with precatalyst's characterization and molecular weight of polypropylene.

2. Experimental

2.1. The catalysts

We prepared two precatalysts keeping the Lewis base/$MgCl_2$ molar ratio at 0.3, the milling time of the Lewis base and the support and the impregnation temperature constant. They were: $MgCl_2$/E.B./$TiCl_4$ (7.8% Ti, 235 m^2/g) in the remaining part of the paper named system 1 and $MgCl_2$/TMPiP/$TiCl_4$ (11.5% Ti, 23 m^2/g), named system 2. The selected conditions in catalysts preparation, based on previous characterization of these catalysts [15], are common for these catalysts. Ti contents were evaluated by a spectrophotometric method [16]. We characterized the catalysts by XRD, FTIR, BET area measures and SEM at each step of preparation. These results were published [15,17].

Polymerization runs were carried out in a 600 cm^3 semibatch reactor, magnetically stirred at 500 rpm and at constant temperature. O_2 and H_2O in the feed were properly removed by means of a MnO/Al_2O_3 column placed immediately before the reaction vessel. The Al/Ti and external donor/Al molar ratio varied between 35–50 and 0.28–0.30, respectively. The molar ratio donor/Ti varied between 10 and 15. Propylene pressures ranged from 1.5 to 2 atmospheres while the reactor temperature fluctuated between 50 and 54°·C. The polymerizations were repeated 4–5 times to obtain reproducibility.

Once the reaction was terminated polymers were recovered with methanol and acetone, stirred during 12 h, decanted and dried until constant weight was achieved.

2.2. The polymers

The polymer as obtained is the global polymer (insoluble and soluble *n*-heptane fraction). The insoluble fraction is the polymer obtained after Soxhlet extraction. Global polymers were analyzed by GPC for both systems. Only insoluble fractions obtained with TMPiP as internal donor were analyzed by GPC.

Gel permeation chromatography was done in a Waters Chromatograph model 150-XCA-LC/GPC equipped with gels of polystyrene and polyethylene with molecular weight (M.W.) between 550 to 3.6E06 g and operating with 1,2,4 trichlorobenzene as solvent.

I.I. was measured by the conventional Soxhlet method, treating the polymer during 6 h with boiling *n*-heptane in dry N_2 atmosphere to avoid its degradation.

3. Results

In Table 1 we report the results in terms of productivity and the percentage of insoluble PP

Table 1
Productivity and selectivity

System	Cocatalyst	Productivity[a]	I.I.%
1	$AlEt_3$	236.1	50–60
2	$AlEt_3$	29.8	33–38
1	$AlEt_3$/E.B.	158.7	75
2	$AlEt_3$/E.B.	10.5	40
1	$AlEt_3$/TMPiP	121.2	89
2	$AlEt_3$/TMPiP	7.9	33–38

[a] Productivity: g PP/g catalyst h atm propylene.

in boiling *n*-heptane. In revised literature system 1 is one of the most stereoselective with E.B. as internal donor and TMPiP as external donor [18]. The external donor modifies the catalysts in such a form that the relative production of isotactic polypropylene increases. With our system 1 the best cocatalyst to obtain a high I.I. and productivity is $AlEt_3$/TMPiP when E.B. is the internal donor. Our results agree with Dumas and Hsu [8] and Samson et al. [9].

In the case of system 2, the productivity is very low, and the I.I. remains relatively constant. This implies that the external donor does not modify the catalyst's active sites to increase the isotactic productivity (evaluated as percentage of insoluble PP in boiling *n*-heptane), even when the productivity decreases. Later in the paper we show this. In both cases, the external donor changes the reaction media conditions, reacting with the cocatalyst and producing new cocatalysts.

3.1. Polymerization kinetics

The model in this case is a multisite model, usually applied to supported systems. It uses two main groups of sites: isospecific and non-isospecific. The latter are stable in time, but the others are not. Some authors propose a second order deactivation for the sites [19]. This law does not seem to adequately describe the overall decay phenomenon as it is only valid under some polymerization conditions and only for a portion of the kinetic curve. This law adequately describes the shape of the kinetic curve at 40 but not at temperatures below 23°C. Even at the higher temperatures the proposed expression is not valid for the polymerization at the initial stage. We tried to fit our data with these equations of second order deactivation, but it was not good. So we selected another correlation where the fast rate of propylene polymerization in the first minutes of reaction is due to the high productivity sites, which deactivate quickly. These could be characterized by a 'deactivation' constant k_d, using the following equation

$$R = R_{inf} + (R_0 - R_{inf})e^{-(k_d t)}$$

This equation is obtained from the general schema proposed by Kissin simplifying the general equation obtained assuming that initiation is fast and examines only the active center deactivation reaction [13] (p. 35).

In this equation, R stands for propylene consumption at a given time t. R_{inf} is the reaction velocity due to the stable sites (in the final stages of polymerization) measured at 'infinite' time. This relates to stable site's concentration. In case of unstable sites, they are characterized by a 'deactivation constant.' The factor $(R_0 - R_{inf})$ relates to the unstable site's concentration at the beginning of the reaction (see Fig. 1). Table 2 summarizes the values of k_d. These values were obtained with the activity measured by consumption of propylene at time equal final time of polymerization (R_{inf}) and the initial consumption of propylene obtained from experimental curves of total consumption. R is the

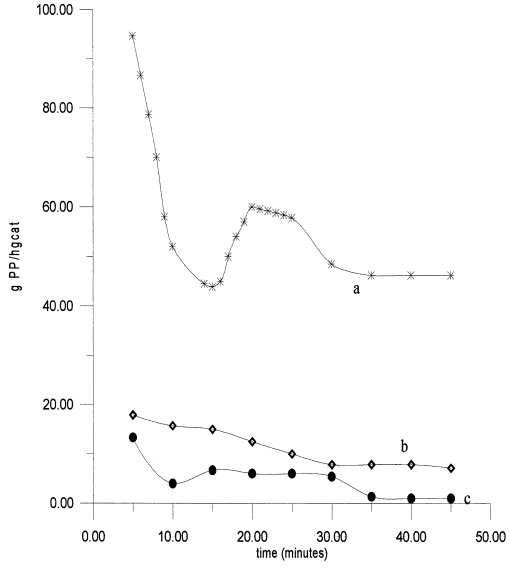


Fig. 1. Typical kinetic curves obtained with system 2: (a) $MgCl_2$/TMPiP/$TiCl_4$//$AlEt_3$; (b) $MgCl_2$/TMPiP/$TiCl_4$//$AlEt_3$/Ethyl benzoate; (c) $MgCl_2$/TMPiP/$TiCl_4$//$AlEt_3$/TMPiP.

Table 2
Deactivation constants

System	Cocatalyst	k_d (min^{-1})
1	$AlEt_3$	~ 0.090
2	$AlEt_3$	0.076
1	$AlEt_3$/E.B.	0.088
2	$AlEt_3$/E.B.	0.076
1	$AlEt_3$/TMPiP	0.062
2	$AlEt_3$/TMPiP	0.092

consumption of propylene at time t. Eq. (1) gives the value of k_d. We applied square least minimum fit to correlate the data.

$$\ln\left[(-R+R_{inf})/(R_0-R_{inf})\right] = k_d t$$

The most important fact in Table 2 is the difference in these constants when TMPiP is the external donor and we compare systems 1 and 2. There are some points to analyze. First, when external donor is not used or E.B. is used, the deactivation constants are both similar (near 0.090 in case of system 1 or 0.076 in case of system 2). Second, E.B. as external donor in both systems barely affects the values of k_d.

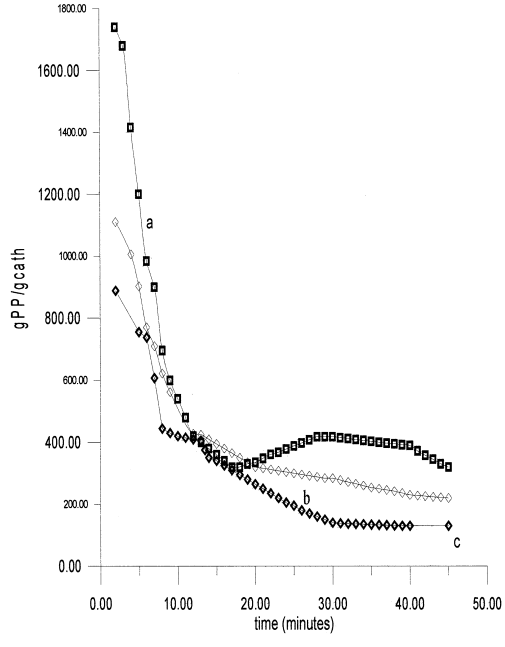


Fig. 2. Typical kinetic curves obtained with system 1: (a) $MgCl_2$/E.B./$TiCl_4$//$AlEt_3$; (b) $MgCl_2$/E.B./$TiCl_4$//$AlEt_3$/E.B.; (c) $MgCl_2$/E.B./$TiCl_4$//$AlEt_3$/TMPiP.

Table 3
Kinetics data of system 2, with a set of repeated runs

Cocatalyst	$\ln(R_0 - R)$[a]	k_d (min^{-1})	g PP	P[b]
$AlEt_3$	1.745	0.076	2.6	32–37
$AlEt_3$	1.174	0.076	1.31	27
$AlEt_3$/E.B.	1.925	0.081	2.86	10.2
$AlEt_3$/E.B.	1.436	0.072	0.82	10.7
$AlEt_3$/TMPiP	2.144	0.094	1.2	8.02
$AlEt_3$/TMPiP	1.663	0.090	1.07	7.74
$AlEt_3$/TMPiP	0.774	0.088	0.6	7.8

g PP: g of polypropylene produced.
[a] ln difference activity at elapsed time and activity at zero time.
[b] Productivity in g polypropylene/g catalyst h atm.

TMPiP does not replicate this effect. Fig. 1 shows the different shapes of the kinetics curves for system 2 using different cocatalysts. Fig. 2 shows the kinetic curves for system 1. Comparing these figures it can be seen that without an external donor, the activity decays, later increases (see Fig. 2a) and finally it is maintained for 15 min. In the case of system 1, the curves are similar for the evaluated systems with an external donor: pure decay (see Fig. 2b and c). The relative increase without an external donor is higher in system 2 than system 1 but the activity is not maintained (see Fig. 1a). When E.B. is used the initial activity is very low and the curve is of decay type. If the amine is used as an external donor, an increase in activity takes place, but it is lower than without an external donor. The activity is maintained for 25 min and later decreases (see Fig. 1c). Data reproducibility with system 2 is enough to elaborate conclusions (see Table 3).

Table 4
Productivity per area BET

Precatalysts	Cocatalyst	Productivity (g PP/m^2 catalyst h atm)
1	$AlEt_3$	1.02
2	$AlEt_3$	1.24
1	$AlEt_3$/E.B.	0.68
2	$AlEt_3$/E.B.	0.44
1	$AlEt_3$/TMPiP	0.55
2	$AlEt_3$/TMPiP	0.76

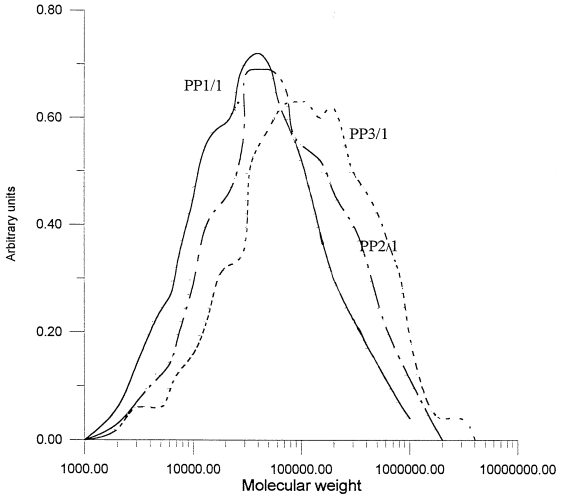


Fig. 3. Polymer obtained with system 1: ———— PP1/1, obtained with $AlEt_3$; – · – PP2/1, obtained with $AlEt_3$/E.B.; – – – PP3/1, obtained with $AlEt_3$/TMPiP.

Recent papers evaluate kinetics of similar systems with the following equation [9]:

$$R_p = \left(R_{p0}^{1-n} + (n-1)k_d t\right)^{1/(n-1)} \quad n \neq 1$$

Activity reported per gram of catalysts is lower for system 2. Based on the initial BET areas, the productivities for system 2 are greater than for system 1 either when tetramethylpiperidine is the external donor or when no external donor is present (see Table 4). This is not true for E.B. as external donor. This result means that system 2 probably has a longer distance between supported Ti active sites. Ti loadings are high, but similar to those obtained by Dumas and Hsu [8] and Samson et al. [9]. Probably the fraction of active sites from the total of supported Ti is lower for system 2. In Table 4 it is evident that E.B. is a stronger poison that TMPiP as external donor for system 2. The activity per m^2 for system 2 decreases from 1.24 to 0.44 g polymer/m^2. For system 1, TMPiP is the strongest poison in terms of productivity based on BET areas (from 1.02 to 0.55 g polymer/m^2).

Table 5
Molecular weights of PP obtained with system 1

Polymer	Mw	Mn	Mv	*d*	Viscosity
PP1	89798	16220	75519	5.54	0.7414
PP2	151915	26293	124912	5.78	1.12
PP3	224012	36395	186703	6.16	1.52

Table 6
Molecular weights of PP insoluble obtained with system 2

Polymer	Mw	Mn	Mv	*d*	Viscosity
$PP1_{ins}$	352200	53800	290600	6.56	2.13
$PP2_{ins}$	339000	59200	282900	5.74	2.09

$PP1_{ins}$ and $PP2_{ins}$ are the insoluble fractions obtained with system 2 and $AlEt_3$ or $AlEt_3$/E.B.

3.2. Polymer analysis

With E.B. as internal donor, the polymerization product increases the molecular weight regardless of the external donor (see Fig. 3). With system 2, the use of E.B. as an external donor does not produce an effect in this direction while when TMPiP is used as external donor the molecular weight decreases drastically [17]. The very low molecular weights detected in the chromatograph give an error in the Mw and Mn calculation. The molecular weights presented in Tables 5 and 6 have a discrepancy of less than 5%.

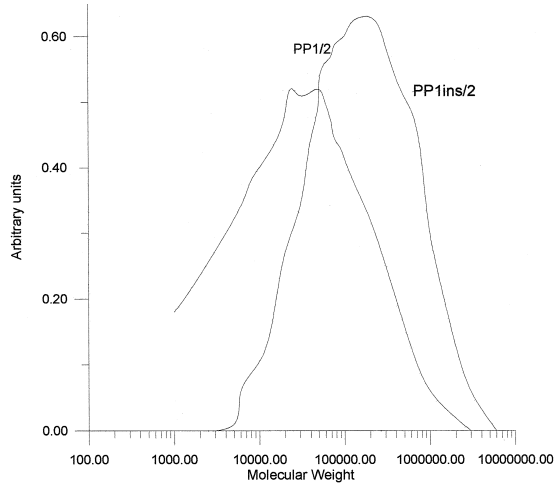


Fig. 4. (a) Polymer obtained with system 2//$AlEt_3$–PP1/2; (b) insoluble polymer obtained with system 2//$AlEt_3$–$PP1_{ins}$/2.

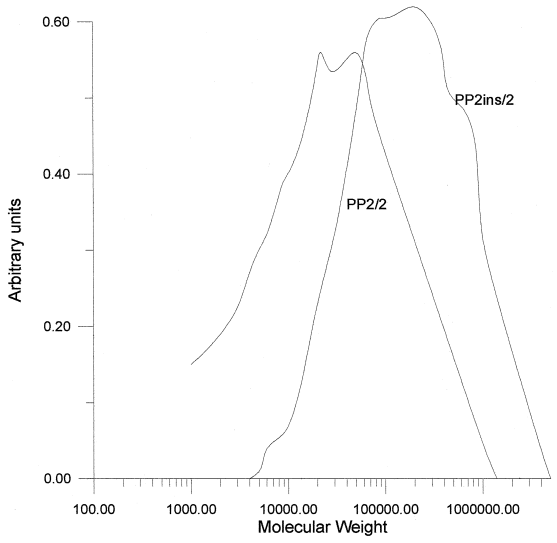


Fig. 5. (a) Polymer obtained with system 2//$AlEt_3$/E.B.–PP2/2; (b) insoluble polymer obtained with system 2//$AlEt_3$/E.B.–$PP2_{ins}$/2.

The GPC results are clearly different for systems 1 and 2. In Table 5 we summarized the results for global polymers of system 1. The global polymers have molecular weights from 90 to 225 000 (see Table 5 and Fig. 3). Thereafter, PP1 is the product obtained with $AlEt_3$, PP2 is obtained with $AlEt_3$/E.B. and PP3 is obtained with $AlEt_3$/TMPiP for each system (1 or 2). The molecular weight of PP1–2 shows two peaks: one between 20–30 000 and the other between 40–60 000 g/mol (see Fig. 4a). This system produces a fraction of high molecular weight ($PP1_{ins}$) (see Table 6 and Fig. 4b) with three peaks: two between 80 and 200 000 and one shoulder at 500 000. In these conditions of high concentration of $AlEt_3$ and low concentration of TMPiP from the surface it is probable that the amide concentration ($AlEt_2NR_2$) is low. When E.B. is used as an external donor the molecular weight of PP2 is unchanged but the molecular weight distribution of insoluble fraction $PP2_{ins}$ shows changes: the low molecular weight peak increase at 80 000 is more important but the shoulder of high molecular weight does not change (see Fig. 5a and b). In system 1 the E.B. increases the molecular weight and new fractions of high molecular weight appear (see Fig. 3 and compare it with Figs. 4 and 5). With system 1 the distribution is nearly monomodal to almost bimodal with an external

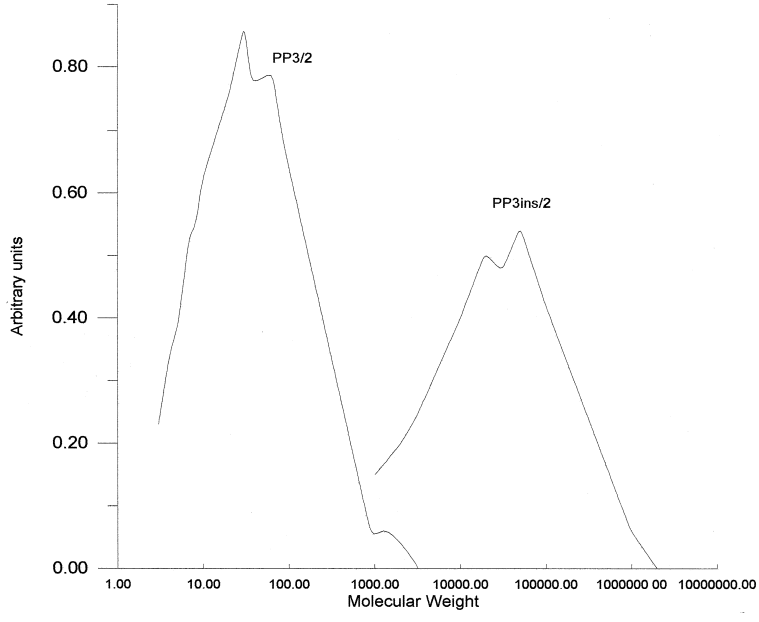


Fig. 6. (a) Polymer obtained with system 2//$AlEt_3$/TMPiP–PP3/2; (b) insoluble polymer obtained with system 2//$AlEt_3$/TMPiP–$PP3_{ins}$/2.

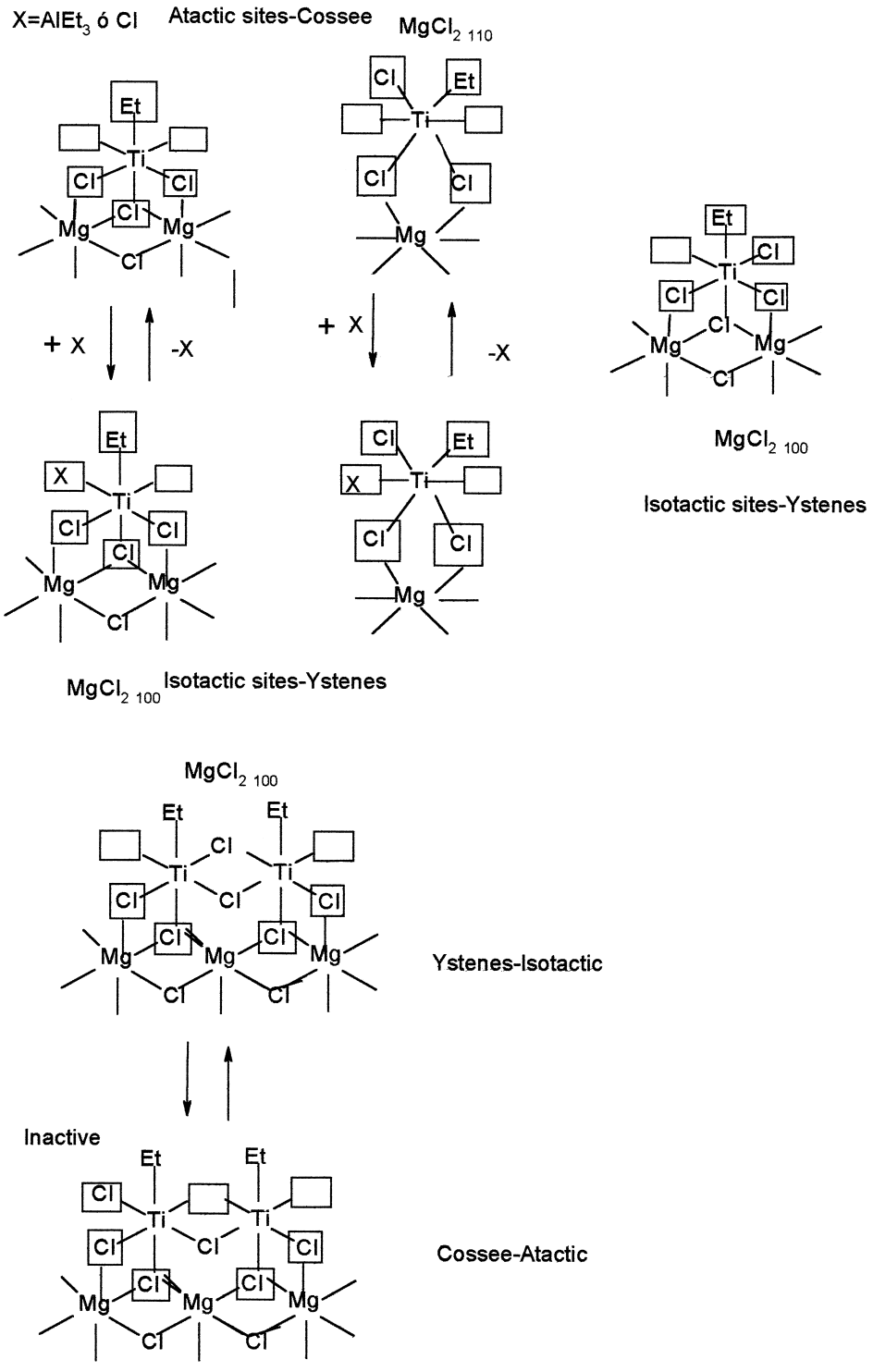


Fig. 7. Active sites without internal donor ($MgCl_2/TiCl_4//AlEt_3$).

donor added and with system 2 it is bimodal or multimodal, whatever the case.

With TMPiP as external donor in system 2 there are two peaks in the global polymer: one between 1 and 2000 and another between 4 and 6000 (see Fig. 6 and compare it with Fig. 3 PP3/1). The distribution is narrower. When the insoluble fraction is analyzed there are two peaks, too (see Fig. 6): one near 20 000 and the other near 50 000. The molecular weight distribution of this insoluble fraction is very similar to the global polymer obtained with $AlEt_3$ or with E.B. as external donor and system 2 (see Figs. 3 and 6).

This is a very interesting result to analyze, because it is unusual with $MgCl_2$ supported catalysts.

4. Discussion

When E.B. is used as internal donor, the external bases decrease the productivity and increase the I.I. [20]. This effect also depends

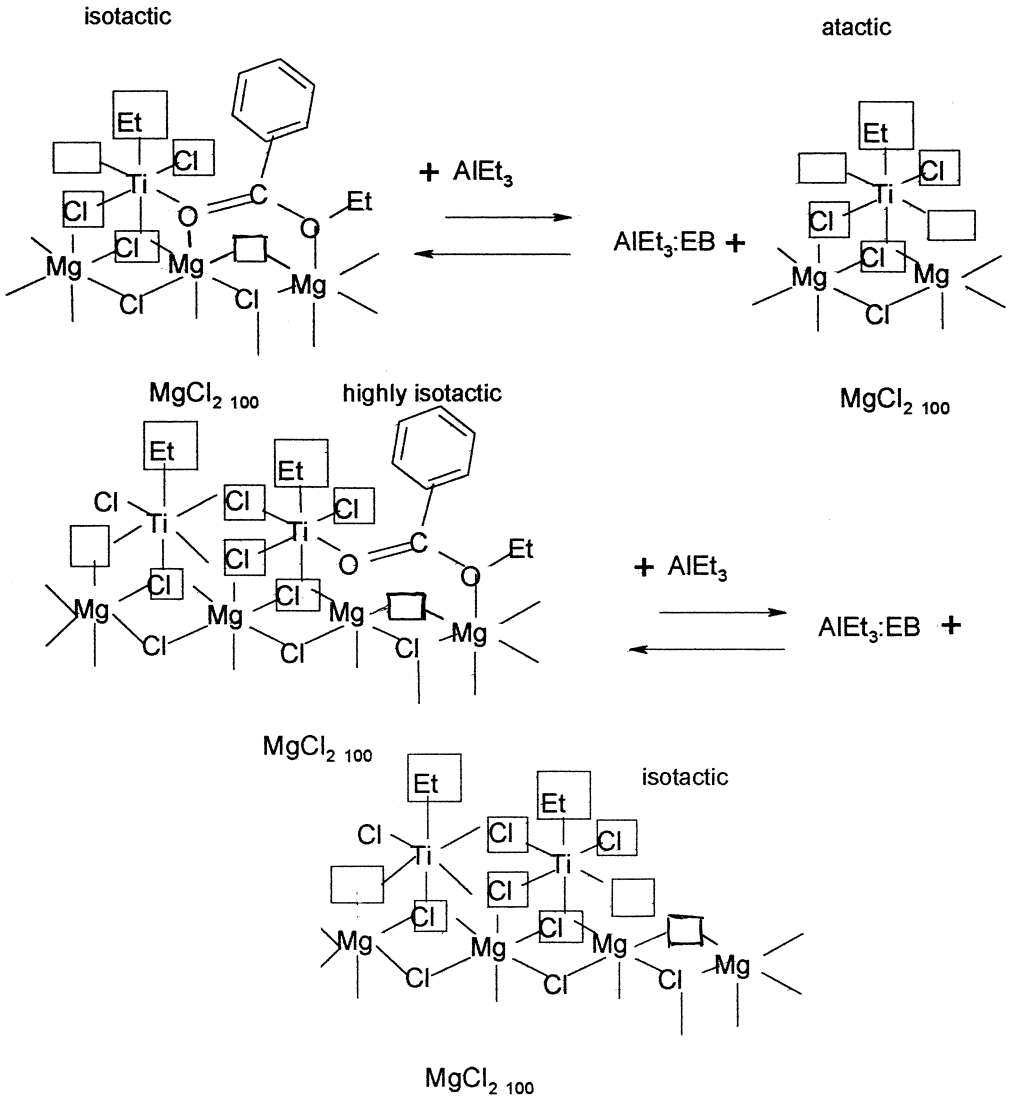


Fig. 8. Active sites with internal donor E.B.—System 1 ($MgCl_2$/E.B./$TiCl_4$//$AlEt_3$).

on what type of external donor is used. We can suppose that there is a poisoning of nonstereospecific active sites, the TMPiP being specially selective as Dumas and Hsu [8], Samson et al. [9] and Barbe et al. [19] say. On the other hand, when the amine is used as internal donor, regardless of the use of external donors, productivity decreases and the stereospecificity is low. A reasonable explanation is that in this case the poisoning is nonselective.

$AlEt_3$ reacts with E.B. and/or TMPiP so the real cocatalyst is probably a mixture of $AlEt_3$,

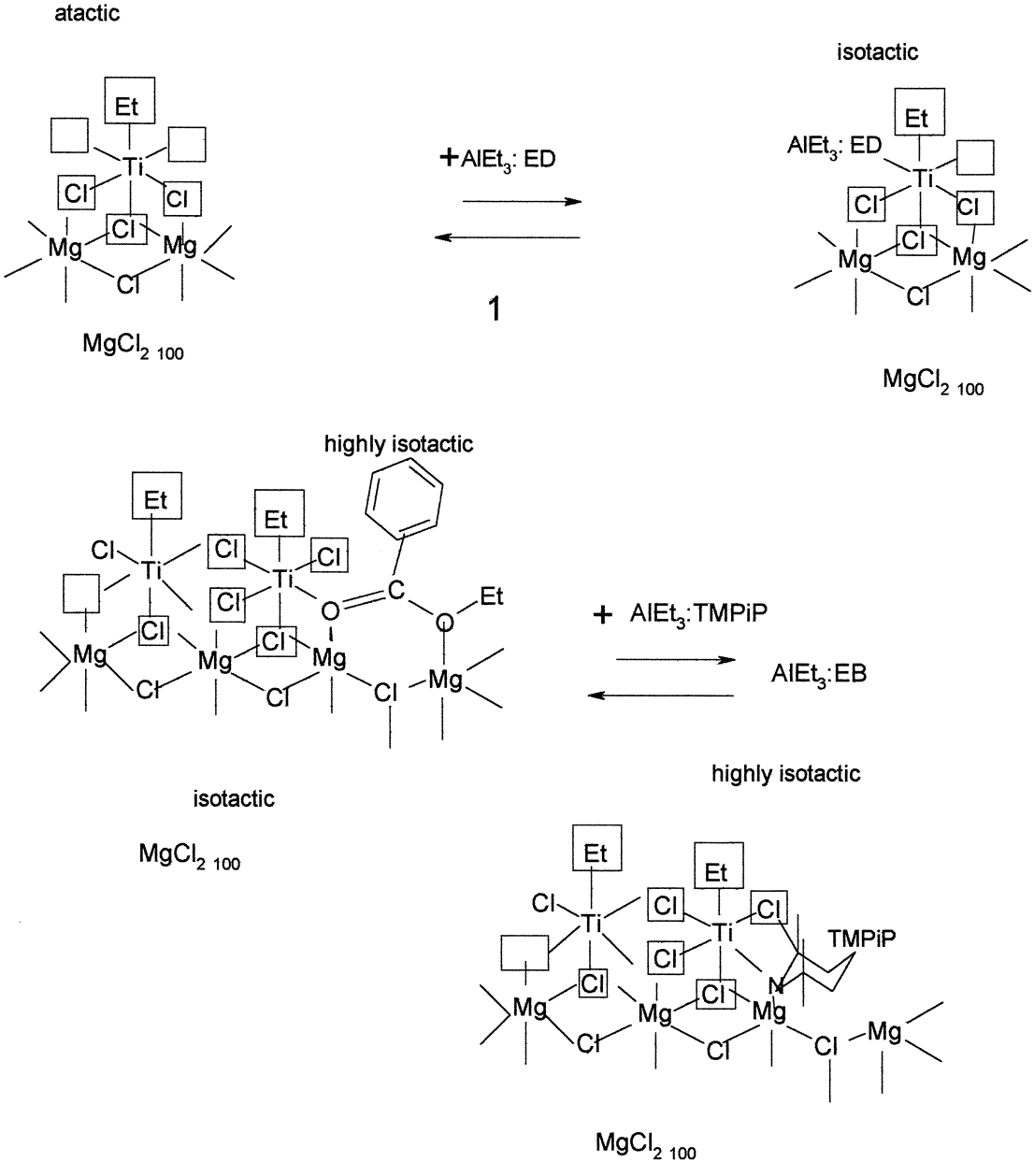


Fig. 9. Active sites in system 1 with external donor ($MgCl_2$/E.B./$TiCl_4$//$AlEt_3$/E.D.).

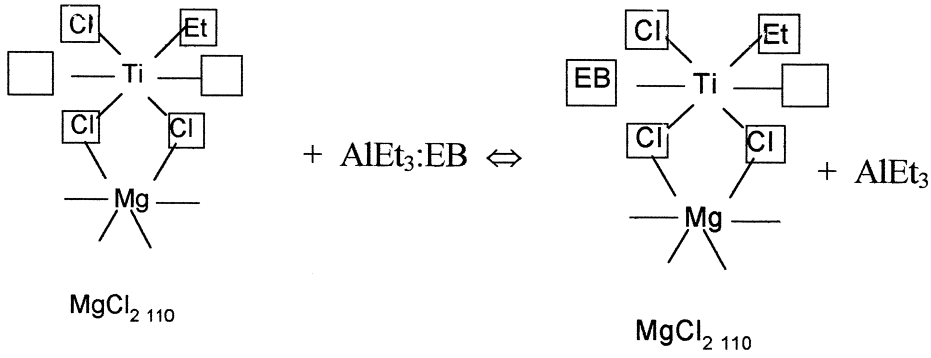
the dimer ($(AlEt_3)_2$) and different complexes (external or extracted internal donor:$mAlEt_3$). From the reaction between $AlEt_3$ and TMPiP probably there are several compounds as Guyot et al. report [7], especially monomeric amides. There are references about dimeric amides like $(Et_2AlNEt_2)_2$. Aluminium piperidides are very unstable by steric hindrance, so it is probable that monomeric amide is available in our reaction media, when the amine is available for $AlEt_3$.

$$AlEt_3 + H{-}NR_2 \rightarrow AlEt_2NR_2 + EtH \quad (1)$$

The different behavior of both precatalysts is assigned to their surface and chemical characteristics that result in different BET areas and percentage of Ti loading. In the case of system 1 several kinds of Ti sites are presumed to exist, as the literature claims [8,9]. Some of them should involve internal donors but others should not. These sites have different acidity, leading to a selective reaction of the external Lewis base with the more acidic sites as it is stated by several authors [1,2,21,22]. Recently, we considered two planes of $MgCl_2$: (100) and (110), with surface Mg penta and tetracoordinated for each one [16,23]. In Fig. 7 the presence of dimers can be seen, particularly on (100) planes of $MgCl_2$, without internal donor. An internal donor probably changes the distribution of Ti on the surface, blocking the most acidic sites on (110) planes, so the possibility of Ti active sites with two vacancies is not favored (see Fig. 8). The dimeric sites on (100) $MgCl_2$ are the most stereospecific ones, following several ideas of Chien et al. [1], Chien [2], Soga et al. [22] and Barbé et al. [24]. $AlEt_3$ may extract the internal donor. Using an external donor there would be less acidic sites that produce nonisotactic polypropylene, because the external donor blocks them (see Figs. 8 and 9), using the following schema for the atactic sites (Scheme 1). The atactic sites can be deactivated by coordination of two external donors. TMPiP as an external donor seems to be especially effective in this sense.

In the case of system 2, the surface could not have sites of different acidity. Chemically, it is probably more homogeneous (see Fig. 10). So the poisoning effect is not selective. This means that the poison effect in this case is indiscriminated, because the stereospecific and nonstereospecific sites have similar acidity. We think that the precursors of active sites in precatalyst 2 have a coordinated Lewis base in different ways: either $TiCl_4$ is interacting with the amine and the surface or there is an interaction $TiCl_4$–amine excluding the surface (see Fig. 10). The existence of the latter was found probable by Extended Huckel calculation [16,23].

When $AlEt_3$ is the cocatalyst in system 1, a large amount of ester is removed from the catalyst surface by forming a complex with the aluminium alkyl ($AlEt_3$:*n*E.B.). The I.I. is



Scheme 1.

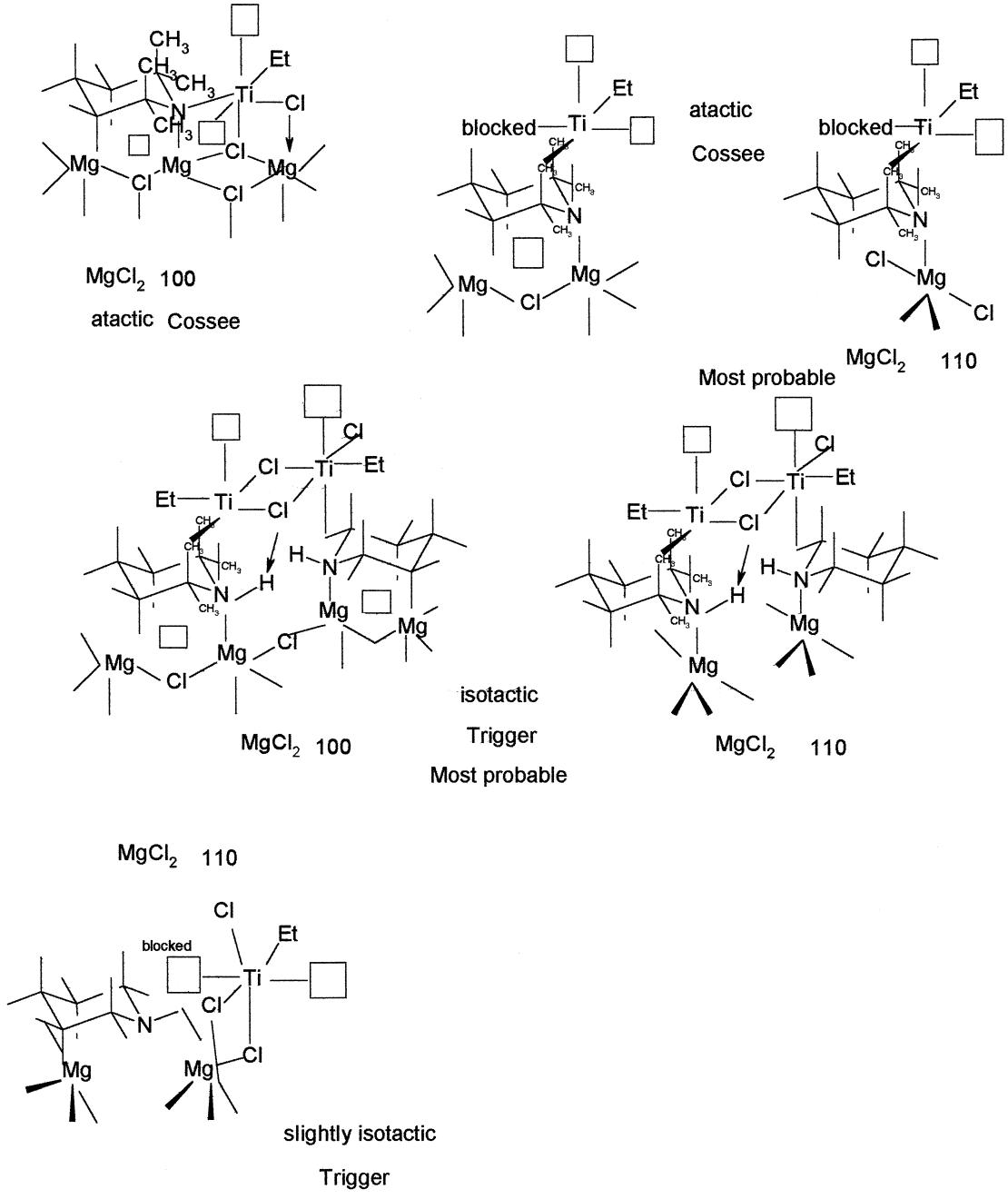


Fig. 10. Active sites with internal donor TMPiP—System 2 ($MgCl_2$/TMPiP/$TiCl_4$//$AlEt_3$).

higher than the one usually obtained with MgCl2/$TiCl_4$//$AlEt_3$ (50–60% vs. 20%) but lower than that obtained by adding an external donor (entries 1, 3 and 5, see Table 1). The activity is higher than this case because the relation External donor/Aluminium alkyl is low and probably there is no free ester [10]. With system 2 the internal donor is removed and so

in this case the kinetics show an increase (see Fig. 1a).

An explanation for the different behavior of these two systems must take into consideration the precatalyst's characterization (when the active sites' precursors are formed), the reaction kinetics and the product characterization.

We believe that the systems have different active site structures and this leads to different main polymerization mechanisms (compare Figs. 1 and 2). The 'trigger' mechanism proposed by Ystenes [25] is a useful idea to apply to the results of system 1.

In this model: (1) The monomer site is never a free site. There is no flopping of the polymer chain. The active center is hexacoordinated. None of the ligands can change their positions. (2) The active complex is never penta-coordinated. (3) The monomer site is always occupied by a monomer and it is needed for the triggering. The monomer will be preferred over other Lewis bases. (4) The formation of the active site must involve a monomer. (5) The free site reacts with a base or a monomer. When it reacts with a base, a sleeping or a deactivated site is formed. They may be reactivated by alkylation.

This mechanism proposes that in the stereoselective catalysts, the active site is hexacoordinated in the initial state and heptacoordinated in the transition state. In this model there is a selection of the monomer to polymerize because a second monomer 'triggers' the insertion of a previously coordinated monomer (two vacancies occupied). Therefore, the Lewis bases in that case, facilitate the triggering by increasing the steric restrictions to the monomer movement. This mechanism can explain the results with system 1 (see Fig. 2). When the active site is not initially hexacoordinated, the restriction does not act and Lewis bases poison the sites. It is probable that, if the mechanism is a modified Cosee [26], the propagation constant is low, the polymer is atactic and the external donors produce a decreasing of molecular weight following Ystenes [25]. Even more syndiotactic polymerization could occur with triggering, but with a pentacoordinated site. Highly isospecific sites produce the fraction of high molecular weight with trigger mechanism in both systems.

Similar results in terms of the variation of the molecular weight for system 1 were obtained by Kashiwa [21]. In their case, using E.B. as an external donor in $MgCl_2/TiCl_4//AlEt_3$ the molecular weight of insoluble fraction and overall polymer increases. This author concludes that there are two sorts of isotactic sites, those capable of associating with ester and those not able to associate with ester. Those active sites associating with ester are characterized by the formation of the relatively high molecular weight isotactic polymer. Soga et al. [22] pointed out that using phenyltriethoxysilane (PTES) as an external donor with a system like 1 the molecular weight of the atactic polymer decreases with an increase in the PTES concentration. Therefore, the idea of two mechanisms works: one for isospecific polymerization and another for an atactic one. The highly isospecific and isospecific sites are too sterically hindered to react with PTES but this donor can produce highly isospecific sites blocking the neighbors of slightly isospecific sites. The addition of PTES improves the I.I. largely without changing the kinetics. This author concludes that the presence of a diester is not necessary for the formation of highly stereospecific sites. The most important function of the phthalate ester is its effect on the distribution of Ti on the catalyst, leading to a first order deactivation, as we also found. This would be an indirect evidence of our explanation. Atactic sites polymerizing by Cossee mechanism are strongly affected by Lewis bases. The isotactic and highly isotactic sites, polymerizing with triggering, are unchanged and the molecular weight is improved when a small amount of PTES is added (like TMPiP in system 1). Chadwick et al. [14] found that the fraction of atactic polymer formed increased with decreasing ester content in the catalyst for $MgCl_2$/phtalate ester/$TiCl_4$. Polypropylene yield and isotactic regularity increase when polymerization is carried out in the

presence of amine. He concludes that the external donor is actively involved in the generation of isospecific sites, particularly in catalysts with low or no internal donor contents. Kakugo et al. [27] have used elution fractionation to demonstrate that the external donor not only decreases atactic formation but also increases the degree of steric control at isospecific sites. Chadwick et al. [14] consider the existence of three basic types of active sites. They point out an aspecific site having two coordination vacancies, an isospecific site containing a single coordination vacancy and a highly isospecific site formed by complexation of the external base with one of the coordination vacancies of the aspecific site. This interaction explains both the increases in catalytic activity that he observes in the presence of tetramethylpiperidine and the overall increase in steric purity of the isotactic fraction. Aspecific sites have much a lower activity than isospecific sites. In system 1 there is a distribution of sites such as Figs. 7–9 show. Fig. 9 presents the most important effects of an external donor in system 1: poisoning of atactic sites, modification and exchange in isotactic ones.

It must be considered that although an external donor is added with system 1 there are several adsorption–desorption equilibria with these systems, where $AlEt_3$ is involved. Therefore, some of the sites can convert to atactic or poorly isotactic, even syndiotactic, as can be seen in Fig. 7. We do consider the situation of the cocatalyst adsorption on vacancies. It must be mentioned as an additional way to modify the sites, especially when an internal/external donor is absent and the molar ration Al/Ti are high.

Following the ideas of Busico et al. [28] and Busico [29], the sites can interconvert each other by several adsorption–desorption equilibria. They pointed out that the active sites on heterogeneous Ziegler Natta catalysts (including the highly isospecific) may reversibly change their environment in times which are shorter than the average growth times of the polymer chains. They concluded about the switches between an enantiomorphic site controlled isospecific and chain-end controlled syndiospecific chain propagation. We propose that this switching produces a change in the polymerization mechanism from isotactic Ystenes to syndiotactic Ystenes. If the resulting site is a monomeric one and has two vacancies, the polymerization mechanism will be Cossee, giving atactic polymer. So the different fractions could include sequences of different length of the three compositions, as Busico [29] pointed out. Following the ideas of Ystenes, we think that the dimeric most stereospecific sites can switch to syndiotactic by loosing one ligand and remaining like a two vacancies site (see Fig. 8). The group of Paukkeri and Lehtinen [30] pointed out that the isotactic fraction includes some syndiotactic and heterotactic sequences. They proposed a three sites model, two enantiomorphic and one Bernouillian sites. We can explain these results with Ystenes syndiotactic polymerization if the dimeric isotactic sites loose the internal or external donor during the reaction. However, in these sites the affinity by the external donor rises so quickly it is re-coordinated. In the case of atactic sites, the length of the isotactic and syndiotactic chains is short but differences in this length changes the solubility of the different fractions in different solvents and therefore the existence of several fractions is explained [30].

The effect of the external donors on system 2 may be explained with the chemical characteristics of TMPiP [18]. It is known that there is an exchange external donor–internal donor when the catalyst is made active. In this sense, the TMPiP displaces E.B. from $MgCl_2$ surface when it is used as external donor and E.B. is the internal donor. So there is an especially strong linking between $MgCl_2$ and TMPiP. E.B. acting as external donor could not remove TMPiP from the surface in system 2. Probably $AlEt_3$ alone removes a fraction of the amine so the activity increases (see Fig. 1). E.B. cannot act like a modifier of the active sites, but like a poison, decreasing productivity only (compare Fig. 1a and b, see Fig. 11). When TMPiP acts

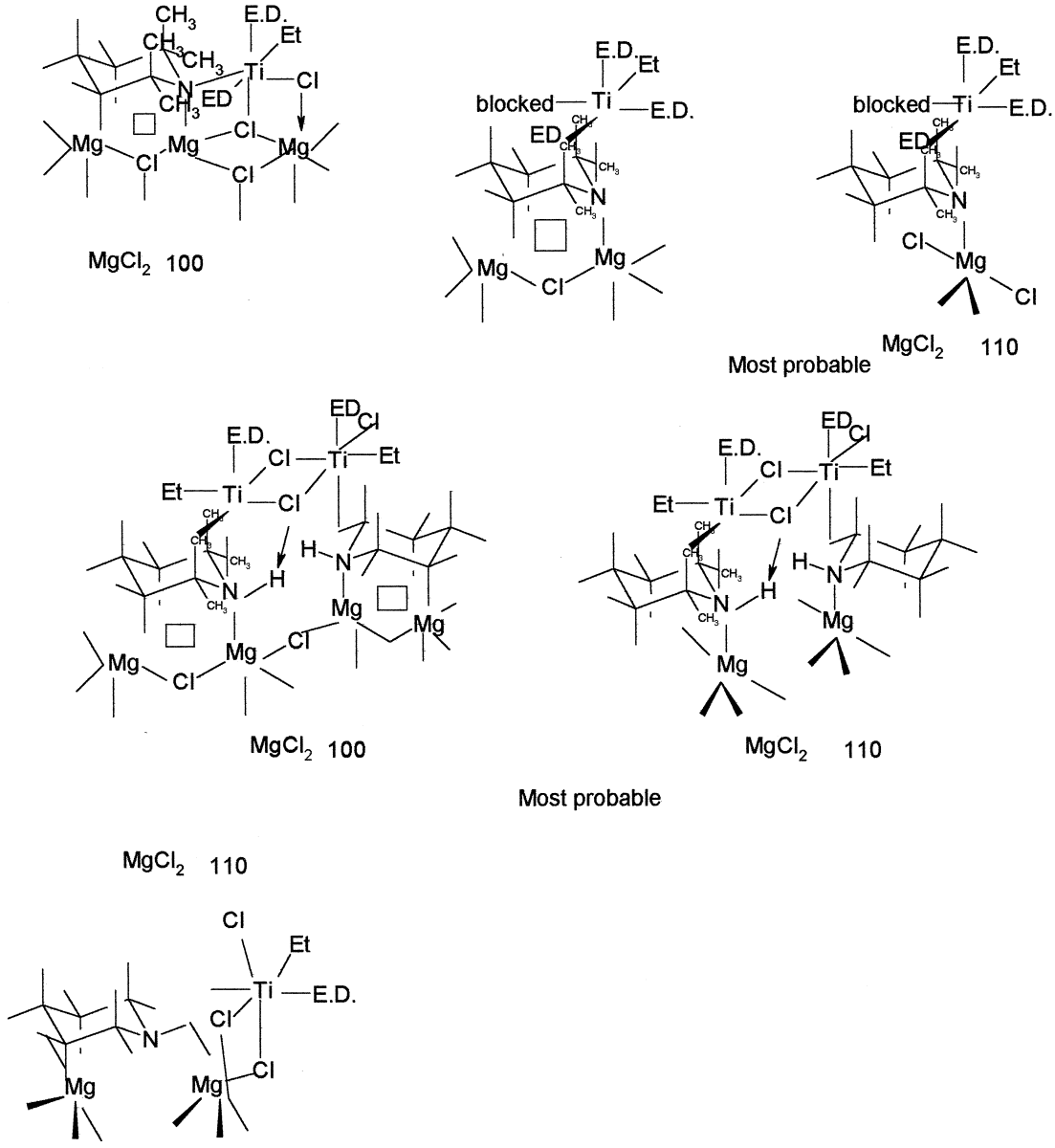


Fig. 11. Inactive sites in system 2 with external donor (specially when TMPiP is E.D.) ($MgCl_2$/TMPiP/$TiCl_4$//$AlEt_3$/E.D.). Some of the ED in these sites can be removed by external $AlEt_3$.

as external donor the effect in the molecular weight of the polymer with system 2 may be attributed to the increased concentration of transfer chain agents (see Fig. 9). TMPiP is active in this function, having an active H, in case of free amine.

$$Ti{-}P + H{-}NR_2 \rightarrow H{-}P + Ti{-}NR_2 \quad (2)$$

Probably the free amine concentration is low because the interaction with alkyl produces monomeric $AlEt_3$–amide, so the most important reaction could be

$$Ti{-}P + AlEt_2{-}NR_2 \rightarrow AlEtNR_2{-}P + Ti{-}Et \quad (3)$$

The productivity of system 2 with $AlEt_3$/TMPiP is slightly lower than with ester, therefore this is probably the most important transfer reaction. Consequently, the $Ti–NR_2$ bond is probably inactive or difficult to reactivate.

If E.B. is the internal donor, this effect of the amine as a transfer chain agent is not present. The Ystenes proposal explains this. E.B., when it is present as internal donor, is able to generate hexacoordinated initial active sites where the external Lewis bases trigger the monomer insertion, replacing the internal base or increasing the steric hindrance near the site (see Figs. 8 and 9). In the presence of a monomer, the sites are occupied only by the olefin and they do not react with the external donor. Both E.B. and TMPiP trigger the monomer insertion and in this case the amine is better because it is more difficult to extract from the surface, after the exchange with the ester. Probably the reaction proposed for system 2 is occurring but the activity is only slightly diminished in system 1, because the interaction with a Lewis base like a poison is not as probable as in system 2.

Using TMPiP as an internal donor is not effective. Probably in this case, the most probable initial active site is pentacoordinated, with two vacancies. Some of the sites are hexacoordinated by dimerization, but their concentration is low. In this case as Ti sites associated with amine are far away from the surface they are similar in both planes (see Fig. 10). In this case, there is no shielding for monomeric species and one should expect a reduction in the molecular weight upon adding Lewis Bases. With E.B. the effect is not so important because it does not replace TMPiP from active sites or their neighbors. In the first case (system 1) with E.B. as internal donor, the amine does not act like in system 2 because the Lewis base shields the active site and triggers the insertion. Lewis bases in system 1 increase the molecular weight. On the contrary, Lewis bases in system 2 decrease the molecular weight, instead. Both Lewis bases in both systems decrease productivity, but this effect is stronger in system 2. The productivity of system 2 with Lewis bases is 25 to 35% of the productivity without it, while system 1 decreases productivity only from 50 to 65% on similar basis. The Lewis bases effect in system 1 is selective and in system 2 it is nonselective. The difference in productivity is shown in Fig. 1, where the kinetic curves are presented. All the facts discussed here are applied to the explanation of the curves (decreased productivity with external donor, decay type of the curve especially with donor, low activity of system 2). Looking at Fig. 1a, the increased activity is explained taking into consideration the high concentration of $AlEt_3$ that is able to displace amine from the surface. So several blocked sites are free of amine and they polymerize, modified by the different coactivators. The sites where Ti is directly bonded to N from TMPiP and not bonded to $MgCl_2$ surface are unchanged (see Fig. 10). Only the sites with amine near Ti bonded to the surface are considered (see single species on (100) and (110) in Fig. 10). These sites can polymerize, resembling species without an internal donor (see Fig. 10). Some of them can be reduced easily. The results confirm the idea that TMPiP has an activating effect at low concentrations and a poisonous effect at high concentration [8,9]. Dumas and Hsu say that TMPiP does much more than poison active sites. Perhaps it reacts with active centers to increase the polymerization activity. In our case we observed in system 2 the instantaneous polymerization rate stopped, decreased and later increased, when the internal donor is removed from the surface by $AlEt_3$ (see Fig. 1). This effect can be seen with system 2 and $AlEt_3$/TMPiP as cocatalyst, but the activation effect is low because the blocking effect of the amine is strong. The kinetic curve shows a decay type in case of $AlEt_3$ (after the activation period). They are almost stable after the first 30 min in the case of using E.B. as external donor, where the activation period does not occur. With TMPiP there is a very low polymerization activity but the curve has a shape similar to that obtained with $AlEt_3$ (see Fig. 1). The activation period is

longer but the activity is very much lower. Dumas and Hsu [8] and Samsom et al. [9] say that the decrease in activity associated with the use of additives may be a result of side reactions so the effective concentration of aluminium alkyl is minor. This fact supports the idea presented above about the effect of the amine in two different ranges of concentration.

With our system 2, global and insoluble polymer remains almost unchanged when E.B. is added. The molecular weights of the insoluble fractions ($PP1_{ins}$ and $PP2_{ins}$) are near the commercial values. Following the ideas presented above, there are in this system several kinds of isotactic and atactic sites. Both kinds of sites are either slightly affected or not affected at all by E.B. however tetramethylpiperidine modifies them (see Fig. 11). Therefore, the sites that polymerize with triggering are interacting with the amine at high concentrations. The atactic sites are severely affected by amine. These sites probably are pentacoordinated initially (atactic sites) (see Fig. 10). The hexacoordinated sites are the isotactic ones. In conclusion, in system 2 there are several kinds of active sites: two producing low molecular weight polymer and two (three) sites producing isotactic polymer of high molecular weight (see Figs. 1, 10 and 11). In the case of the highly isotactic sites, their concentration is low and probably some of them interact with TMPiP, producing isotactic shorter chains. When the isotactic chains are short, the polymer can be soluble in *n*-heptane. So, the I.I% is unchanged.

We think that the Ystenes and Cossee models give us enough tools to explain our results, together with the ideas of Busico et al. [28], Busico [29], Cossee [26] and others [1,2,14,21]. We think that ours is a coherent explanation but, of course, it is not absolute because it needs more polymer characterization to be proved. However, we use several authors results to achieve a deeper comprehension of our systems and it seems to us that their results and ours can be explained by these two sites group-two polymerization mechanisms. Moreover, the Ystenes mechanism has been proposed as an alternative to explain the metallocene/MAO system behavior in several α-olefins copolymerizations [31].

This study clearly shows that the functions of internal and external donors are different. The chemical, steric and electronic characteristics of selected donors are very important. Even more, the performance of a catalyst depends on the complementary and individual effects of both bases. In that sense, we agree with the ideas of Sacchi et al. [11,18], Soga et al. [32,34] and Chien et al. [33].

Acknowledgements

The authors would like to thank CONICET for financial support and C. Frova (PLAPIQUI) for GPC polymer's analysis.

References

[1] J.C.W. Chien, J.C. Wu, C.I. Kuo, J. Polym. Sci. Chem. Ed. 20 (1982) 2019.
[2] J.C.W. Chien, Catal. Rev. Sci. Eng. 26 (3/4) (1984) 613.
[3] N. Kashiwa, J. Yoshitake, Makromol. Chem. Rapid Commun. 3 (1982) 211–214.
[4] B. Keszler, A. Grobler, E. Tabacs, A. Simon, Polymer 22 (1981) 818.
[5] B. Keszler, G. Bodor, A. Simon, Polymer 21 (1980) 1037.
[6] B. Keszler, A. Simon, Polymer 23 (1982) 916.
[7] A. Guyot, R. Spitz, L. Duranel, J.L. Lacombe, in: Kodansha (Ed.), Catalytic Olefin Polymerization, 1989, p. 147.
[8] C. Dumas, H. Hsu, J. Appl. Polym. Sci. 37 (1989) 1605–1625.
[9] J.J.C. Samson, P.J. Bosman, G. Wieckert, K.R. Westerterp, J. Polym. Sci. Part A: Polym. Chem. Ed. 37, 219.
[10] A. Langer, T.J. Burkhardt, J.J. Steger, in: C. Price, E. Vandenberg (Eds.), Coordination Polymerization, 1983, p. 225.
[11] M.C. Sacchi, I. Tritto, C. Shan, L. Noristi, Kodansha (Ed.), Catalytic Olefin Polymerization, 1990, p. 185.
[12] J. Boor, Ziegler Natta Catalysts and Polymerizations, Academic Press, 1979.
[13] Y.V. Kissin, Isospecific Polymerization of Olefins, Chap. 1, Springer-Verlag, 1985.
[14] J.C. Chadwick, A. Miedens, B.J. Ruisch, O. Sudmeyer, Makromol. Chem. 193 (1992) 1463.
[15] M.L. Ferreira, D.E. Damiani, J. Polym. Sci., Part A: Polym. Chem. 32 (1994) 1137.

[16] M.L. Ferreira, A. Juan, N. Castellani, D.E. Damianis, J. Mol. Catal. 87 (1994) 137–150.
[17] M.L. Ferreira, D.E. Damiani, Lat. Am. Appl. Res. 26 (1996) 55–60.
[18] M.C. Sacchi, I. Tritto, C. Shan, R. Mendichi, L. Noristi, Macromolecules 24 (1991) 6823.
[19] P.C. Barbé, G. Cecchin, L. Noristi, Adv. Polym. Sci. 81 (1987) 3–77.
[20] E. Albizatti, V. Busico, P. Corradini, L. de Martino, A. Proto, V. Savino, Makromol. Chem. 186 (1985) 1279–1288.
[21] N. Kashiwa, Preprints ACS 26 (N2) (1985) 370.
[22] K. Soga, T. Sano, K. Yamamoto, T. Shiono, Chem. Lett. 4 (1988) 25.
[23] M.L. Ferreira, A. Juan, D.E. Damiani, J. Mol. Catal. A: Chem. 122 (1997) 25–37.
[24] P.C. Barbé, G. Baruzzi, L. Noristi, Makromol. Chem. 192 (1991) 1115–1127.
[25] M. Ystenes, J. Catal. 129 (1991) 383.
[26] P. Cossee, J. Catal. 3 (1964) 80.
[27] M. Kakugo, T. Miyatake, Y. Naito, K. Mizunuma, Macromolecules 21 (1988) 314.
[28] V. Busico, P. Corradini, R. De Biasio, A.L. Segre, L. Landriani, Macromolecules 27 (1994) 4521.
[29] V. Busico, Conference at the VI Simposio LatinoAmericano y IV Congreso IberoAmericano de Polímeros, October 25–28, 1998.
[30] R. Paukkeri, A. Lehtinen, Polymer 35 (N8) (1994) 1673.
[31] G. Fink, N. Herfert, Makromol. Chem. 193 (1992) 3265.
[32] K. Soga, J.R. Park, T. Shiono, N. Kashiwa, Makromol. Chem. Rapid Commun. (1990) 117.
[33] J.C.W. Chien, C.I.J. Kuo, Polym. Sci. Polym. Chem. Ed. 23 (1985) 761.
[34] K. Soga, E. Kaji, T. Uozumi, J. Polym. Sci., Part A: Polym. Chem. 36 (1998) 129.