

The role of Lewis bases on the improvement of the stereospecificity and activity of $TiCl_3/AlClEt_2$ catalyst system

Fernanda M. B. Coutinho* and Luiz C. Santa Maria

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, P.O. Box 68525 Rio de Janeiro, RJ 21945, Brasil

Summary

The effect of di-n-butyl ether (DBE) in the synthesis of a highly active propylene polymerization catalyst was studied. Electron-donors having ester and phosphate groups (ethyl benzoate-EB, diisobutyl phthalate-DIBP and tri-n-butyl phosphate-TBP) were added as second internal bases (IB_2) to the catalysts prepared by the reduction of $TiCl_4$ with $AlClEt_2$ (DEAC) in the presence of DBE as a first internal base (IB_1). The crystalline forms were examined for all catalyst samples by X-ray method. Special attention has been paid to the δ - $TiCl_3$ samples showing the best catalytic properties. These catalysts were evaluated in propylene polymerization in the absence and presence of external bases (EB, DIBP and DBE). The effects of internal and external bases on the catalyst activity and stereospecificity are discussed.

Introduction

In recent years, catalysts for polypropylene synthesis based on $TiCl_3$ and having highly developed surface have been widely studied and introduced into industrial production. In the synthesis of these catalysts, the participation of electron donating compounds, specially ethers, during the process of the catalyst synthesis, the chemical and phase composition of the intermediate and final products, have not exhaustively been studied. Numerous publications, especially in the patent literature, have recently claimed a great number of additives (Lewis bases) as modifiers of Ziegler-Natta catalyst to enhance its activity and stereospecificity towards propylene polymerization(1).

Undoubtedly, most of the process of polyolefin synthesis are due to the fact that suitable Lewis bases have been used. The addition of bases to the system as internal and external electron-donors has several effects in terms of catalyst stereospecificity, polymerization kinetics and polymer molecular weight(2).

The increase in stereospecificity and decrease in the activity due to Lewis base addition is typical of $MgCl_2$ supported catalysts. With non-supported catalysts, except in few cases, both activity and isotacticity increase(3). In addition, it has often been proven that polymer isotacticity increase derives from the productivity decrease which is greater for the atactic polymer than for the isotactic one. On the ground of the above, the effects attributed to the addition of the Lewis base are:

- selective poisoning of atactic centres;
- transformation of atactic centres into isotactic ones; and
- increase in k_p of isotactic centres.

*To whom offprint requests should be sent

Several hypotheses have been formulated with regard to the nature of the active centres and their interaction with the base in order to clarify these phenomena. Some hypotheses may be summarized as follows:

- the base complexes with the aluminiumalkyl causing a decrease in the free alkyl concentration and, hence, decreasing its adsorption on the active centres(4);
- the poisoning effect of the base is due to reversible complexation with coordinatively unsaturated centres(5);
- the base reacts irreversibly with the Ti-R bond(6); and
- the adsorption of the base poisons the active centres.

At the same time, the base-alkyl complex transforms non-stereospecific centres into stereospecific ones(7). It is difficult to identify the most likely mechanism or even different mechanisms that may coexist as the data available in the literature were obtained under different conditions.

In the case of the non-supported catalyst, it is generally believed that the increase in the isotacticity is due to the selective action of the electron-donor on the different active catalyst centres. It has been shown that the electron-donor can be introduced in such a way that the increase in isotacticity is not accompanied by a loss of activity. This behaviour cannot be explained simply by the poisoning of active centres. Unambiguous interpretation of the results is, however, still difficult as the Lewis bases can complex or react with both the co-catalyst (aluminiumalkyl) and the catalyst (TiCl_3), affecting the activity and/or the stereospecificity of the catalyst system. Lewis bases have been found to activate or deactivate the polymerization depending on the nature of the catalyst system and on the type of the Lewis base(8).

It is well known that there are at least four crystalline forms of TiCl_3 , namely α , β , γ and δ , among them, the α , γ and δ are violet forms and they have a cubic or hexagonal close packing of the Cl atoms. In particular, the α -form consist of a hexagonal close packing of Cl atoms where the Ti atoms occupy two thirds of the interstitial octahedral sites. The triple layers so constituted are arranged along the crystallographic c axis according to a regular, hexagonal succession. No certain structural evidence has yet been found for a disordered arrangement of Ti atoms in the α -form crystals, but other types of disorder must occur during mechanical activation. It should also be noted that the non-activated α -form yield a lower polymerization rate than catalytic systems based on the γ or δ -form of TiCl_3 . Unlike the α -form, γ - TiCl_3 crystallizes with a cubic close packing of Cl atoms. The β -form of TiCl_3 has a fibrous structure and is brown or dark brown, depending on its method of preparation. The reflection having an interplanar distance $d=5.78\text{\AA}$ is common to both α and γ - TiCl_3 , conversely, the lines with $d=2.51\text{\AA}$ (γ -form) and $d=2.71\text{\AA}$ (α -form) are highly specific. The β -form can be easily identified by the reflection of $d=5.14\text{\AA}$. Allegra(9) proposed a mixed cubic-hexagonal structure where stacking faults occur in the succession of the structural layers for the δ -form TiCl_3 .

In this work we attempt to explain the effect of the electron-donors employed as internal and external bases on the activity, stereospecificity and crystalline forms of the catalysts for the propylene polymerization.

Experimental Procedure

Propylene (from White Martins S.A., used after passage through 3\AA molecular sieve), TiCl_4 (research grade, distilled under N_2), di-n-butyl ether (research grade, dried over Na, fractionally distilled under N_2 and stored over 3\AA molecular sieve), iso-octane (used after passage through a 3\AA molecular sieve column), DIBP, EB and TBP (research grade, stored over 3\AA molecular sieve) and DEAC (from Alkyl do Brasil Ltda, used as a solution in iso-octane) were employed.

- Catalyst Synthesis

DBE solution in iso-octane (C_8) was added dropwise in a determined molar ratio DBE/ $TiCl_4$ to a $TiCl_4$ solution in C_8 cooled to $-64^\circ C$. After 30 minutes addition, a DEAC solution in C_8 was added dropwise in a molar ratio $TiCl_4/DEAC=4$. After 30 minutes addition, the temperature of the mixture was raised to $5^\circ C$ and maintained at this temperature for 2h30min. Before the thermal treatment at $70^\circ C$ for 4 hours, the electron-donor (TBP, DIBP or EB) in determined molar ratio $IB_2/TiCl_3$ was added. Finally $TiCl_3$ (violet) was thoroughly washed with C_8 (five portions of 100ml).

Propylene Polymerization

Propylene polymerization was carried out in a $0.5dm^3$ glass reactor equipped with a mechanical stirrer. Determined amounts of DEAC, catalyst and an external base were added into the reactor containing $0.3dm^3$ of C_8 at $50^\circ C$. Propylene was then continuously fed in order to maintain a positive pressure of 200mmHg for 1 hour. The reaction mixture was cooled and the polypropylene filtered off, washed with hexane and dried. For each polymer sample, the isotacticity index (I.I., weight% of polymer insoluble in boiling C_8) was determined by Soxhlet extraction with C_8 for 6 hours. The accuracy of the determinations was estimated at $\pm 1\%$.

Results and Discussion

Many studies in the non-supported Ziegler-Natta field have the objective of improving the catalyst stereospecificity, polymer morphology, productivity etc. At the same time, patents are usually written in a confused way and virtually all conceivable Lewis bases have been claimed as effective without a thorough quantitative study.

DBE is a suitable internal Lewis base for the $TiCl_3/DEAC$ system as it is well known in the literature. However, other Lewis bases (10,11) usually employed in the Ziegler-Natta catalyst are also able to improve the catalyst stereospecificity and activity. The objective of this study was to elucidate the role of these modifiers.

In the first step of this work, we determined the best molar ratio DBE/ $TiCl_4$ for the catalyst synthesis with the aim of finding a soluble system and a stereospecific and active catalyst. The catalysts were prepared with the molar ratios DBE/ $TiCl_4$: 0.5; 0.6; 0.7; 0.9; 1.1. Figures 1 and 2 show that the best ratio was 0.7. Below it, the base is not enough to solubilize the system completely after the $TiCl_4$ reduction. With these molar ratios, a violet catalyst was not obtained, but a reddish-brown one. Above it, the system became soluble and a violet $TiCl_3$ was obtained after the thermal treatment, although some active centres were poisoned (Figure 1). It is possible to see in Figure 2 that above the molar ratio DBE/ $TiCl_4=0.7$ the isotacticity index decreased. Probably the base exposed more non-stereospecific centres than stereospecific ones.

The other catalysts were prepared with three different electron-donors: EB, DIBP and TBP used as IB_2 and DBE used as IB_1 on the fixed molar ratio (DBE/ $TiCl_4=0.7$). In Table 1, the catalysts are designated numerically according to their constituents and their Ti contents. These contents were found by a colorimetric method. It can be seen that the contents decreased when a IB_2 was used in the catalyst synthesis. The excess of DBE used in the catalyst synthesis solubilizes $TiCl_3$ formed by the reduction of $TiCl_4$. After the thermal treatment, the violet catalyst precipitates as $TiCl_3 \cdot xAlCl_3$, so it is possible that the IB_2 has remained coordinated with Al and Ti as a solid complex, decreasing the removal of the Al and then decreasing the relative Ti contents.

TABLE 1
Titanium Contents of the Catalysts

Catalyst Number	Type of IB_2	$IB_2/TiCl_3$ (molar ratio)	Titanium Content of the catalyst (mmol Ti/g catalyst)
1	-	0.00	4.85
2	-	0.00	4.51
3	-	0.00	6.22
4	DIBP	0.02	5.54
5	DIBP	0.04	6.10
6	DIBP	0.06	5.12
7	EB	0.02	5.09
8	EB	0.04	5.63
9	EB	0.06	5.22
10	TBP	0.02	5.09
11	TBP	0.04	5.36
12	TBP	0.06	4.22

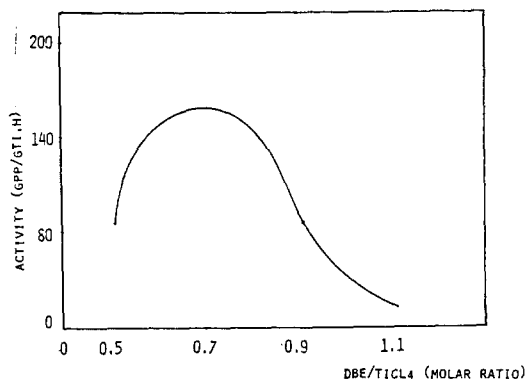


Figure 1 - Influence of the molar ratio $DBE/TiCl_4$ on the catalyst activity

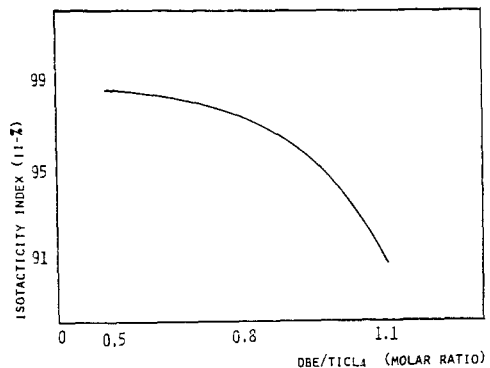


Figure 2 - Influence of the molar ratio $DBE/TiCl_4$ on the polymer isotacticity index

The data for the catalyst prepared with a IB_2 show that, at the molar ratio $IB_2/TiCl_3=0.04$, the Ti content had a maximum value (Table 1). All these catalysts, except those prepared with TBP, showed the highest activities as can be seen in Figures 3 and 4. It seems that TBP poisoned some catalyst centres.

The addition of EB and DIBP was able to increase the catalyst activity even more (Figure 3). It is possible that these bases coordinate with impurities (Ti^{+2} , for example) removing them from the catalyst in the moment of its formation, promoting the increase of the activity up to molar ratio $IB_2/TiCl_3=0.04$. Above this value, probably poisoning occurs of some active centres and hence, the decrease of the catalyst activity. On the other hand, the addition of TBP at all employed ratios as IB_2 caused a decrease in the catalyst activity (Figure 3). Figure 4 shows that the use of DBE, DIBP and EB as external bases promotes an increase in the activity for most of the catalyst prepared. It can be suggested that these bases penetrate into the catalyst, exposing more active centres and thus enhance its activity.

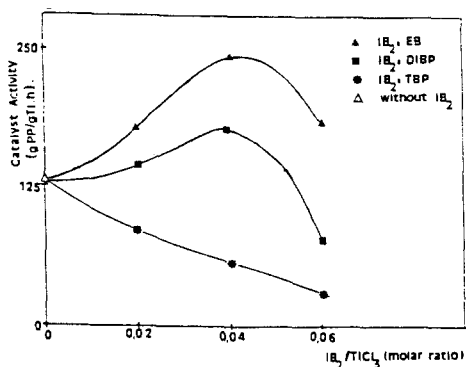


Figure 3 - Influence of the amount and type of IB₂ on the catalyst activity for the propylene polymerization in the absence of external base

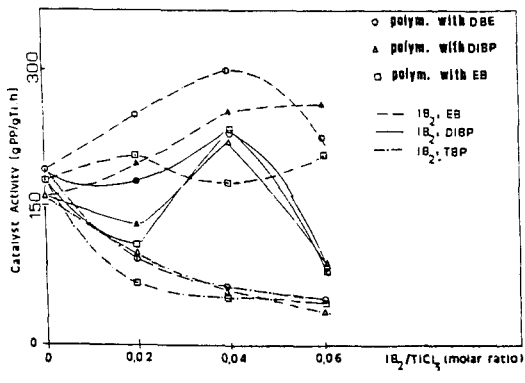


Figure 4 - Influence of the type of external base on the catalyst activity for propylene polymerization

The variation of the catalyst stereospecificity produced by the introduction of IB₂ (see Figures 5 and 6) was insignificant when DIBP and EB were used. The interaction between these esters and Ti is strong and some is retained on the catalyst surface forming a complex with DEAC during the polymerization. The catalysts prepared with TBP as IB₂ showed a different behaviour. The stereospecificities and activities of these catalysts were not as high as the catalysts prepared with EB and DIBP as IB₂. Probably TBP forms a stronger complex with DEAC during the polymerization liberating more non-specific sites to the monomer.

Figures 5 and 6 show that EB and DIBP increased the catalyst stereospecificity. The coordination of DIBP and EB with DEAC seems to be not as strong as in the case of TBP. So the catalyst stereospecificity is not strongly dependent upon the presence of an external base, except in the case of the catalyst prepared with TBP as second internal base. TBP probably acted as a poison, forming a strong complex with the co-catalyst (DEAC) and then causing a decrease of the catalyst stereospecificity and activity.

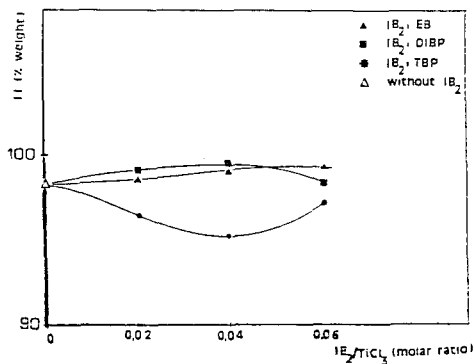


Figure 5 - Influence of the amount and type of IB_2 on the catalyst stereospecificity for propylene polymerization in the absence of external base

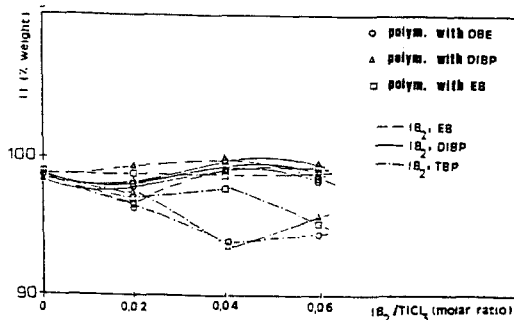


Figure 6 - Influence of the type of external base on the catalyst stereospecificity for the propylene polymerization

The problem of establishing the relationship between the chemical composition and the crystalline form of the catalyst based on $TiCl_3$, in spite of many investigations in this field, has received inadequate study. Many differences among the crystalline modifications of $TiCl_3$ are observed: a β -modification is brown with a fiber-shaped structure; α , γ and δ modifications are violet with a lamellar structure. The catalyst system based on the β -modification of $TiCl_3$ and organoaluminium compounds exhibits low stereospecificity and activity in the propylene polymerization. The violet modifications based on $TiCl_3$, specially the δ -modification, produce highly active and highly stereospecific catalyst systems for propylene polymerization. During the catalyst synthesis, the $TiCl_3$ undergoes a number of physical transformations. A necessary condition for obtaining a high-quality product is through the control of the structural changes of the catalyst. The most informative method for studying such catalysts is X-ray structural analysis. In this paper, we examine the influence of the type of Lewis base on the crystalline structure of the catalysts based on $TiCl_3$. Figures 7 and 8 show the X-ray diffraction patterns obtained using a JOEL mod. JDX8P (Cu-radiation). Figure 7 shows the X-ray patterns of catalysts obtained without internal base. The first one relates to the

catalyst obtained by the reduction of $TiCl_4$ with DEAC without DBE. This brown $TiCl_3$ presented the β -form. The second one is the X-ray pattern of the same catalyst, but submitted to one hour thermal treatment at $170^\circ C$. This violet $TiCl_3$ was confirmed as a γ -form. These two catalysts presented lower titanium contents. As the Lewis acid strength of $TiCl_3$, $AlCl_3$ and $AlEtCl_2$ differ, the products of the interaction with the different bases depend on the type of the synthesized $TiCl_3$ and on the type of Lewis base and its concentration. The titanium contents of these catalysts have increased from 4.9 to 6.2 mmol Ti/g catalyst due to the action of these modifiers, see Table 1.

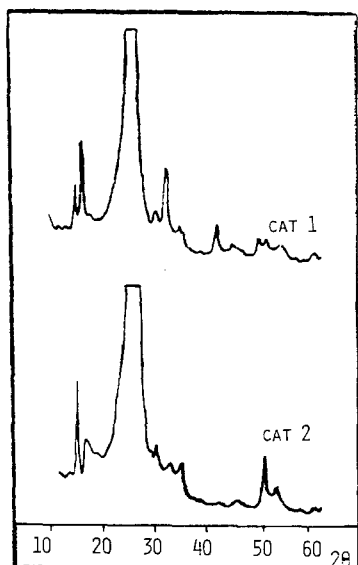


Figure 7 - The X-ray diffraction patterns of the catalysts prepared without IB_1 and IB_2

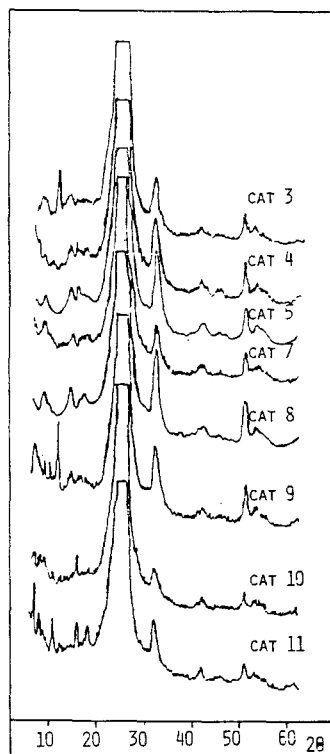


Figure 8 - The X-ray diffraction patterns of the catalysts prepared with IB_1 and IB_2

The study of the phase transitions during the synthesis of the catalysts in the presence of ether and other Lewis bases (EB, DIBP and TBP) led to elucidation of the effect of these bases in the formation of various $TiCl_3$ modifications and enabled us to determine the relation between the catalytic properties and the effect of these Lewis bases on the crystalline modifications. It can be seen in Figure 8 that the catalysts prepared with IB_1 and IB_2 presented a higher disorder and have the X-ray diffraction pattern of δ - $TiCl_3$. At $2\theta=15.28^\circ$ and $2\theta=51.64^\circ$, these

reflections appear as an attenuated and broad peak differently of the γ -TiCl₃ form where they are intense and narrow. It can still be seen that considerable structural modifications with respect to γ and α -TiCl₃ occurred, for example, in the angular range 28-38° where all the peaks disappeared $2\theta=30.91^\circ$ and $2\theta=32.97^\circ$ (characteristic of the α -TiCl₃) and $2\theta=35.77^\circ$ (characteristic of γ -TiCl₃). Thus we could conclude that the crystal form of our catalyst is a δ -one. The rather sharp peaks of the diffraction pattern of δ -TiCl₃ are related to the close packing of the Cl atoms within the structure layers, which is unaffected by the disorder produced by the dry-milling and in our case, it is due to the TiCl₃ precipitation from the soluble system. The most intense peaks at $2\theta=17.20^\circ$ ($d=5.15\text{\AA}$) and $2\theta=33.8^\circ$ ($d=2.65\text{\AA}$) are the characteristic ones of the γ -form. The peak position is intermediate between the sharp peaks at $2\theta=32.97^\circ$ of the hexagonal α -TiCl₃ and $2\theta=35.77^\circ$ of the cubic γ -TiCl₃. Based on these results, Allegra (12) proposed a mixed cubic-hexagonal structure for the δ -TiCl₃. The presence of Lewis bases in the synthesis is essential the δ -TiCl₃ formation. Nevertheless, a large increase in the ratio IB₁/TiCl₄ in the synthesis leads to complete dissolution of the catalyst after the reduction process, that is not desired. However, an excess of the base is necessary to promote the extraction of Al compounds from the TiCl₃ lattice and consequently to improve the catalyst porosity. The development of the porous structure, the precipitation of TiCl₃ from Lewis base complexes and the dissolution of AlCl₃-base complex adsorbed on TiCl₃ surface occur during the thermal treatment. At this stage, the δ -TiCl₃ with enhanced activity is formed.

Acknowledgements

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho de Ensino para Graduados e Pesquisa (CEPG/UFRJ) and Polibrasil S.A. for financial support.

References

1. N.S. Bukharkina, V.P. Konovalov, L.L. Yezhenkova, I.A. Voloshin, A.A. Baulin, O.M. Zvyagin, M.V. Mal'gina, N.V. Ivanova and R.Kh. Denilov, *Polymer Science USSR*, **30**, 621 (1988).
2. P.C. Barbé, L. Noristi and M.A. Schexnayder, *International Symposium "Recent Advances in Polymer"*, Chicago, 1985.
3. P. Pino and R. Mulhaupt, *Angew. Chem.*, **19**, 857 (1980).
4. T. Keii, *Makromol. Chem.*, **183**, 2285 (1982).
5. A. Caunt, J.A. Licchelli, I.W. Parsons, R.N. Harward and R.Y. Al-Hillo, *Polymer*, **24**, 121 (1983).
6. B.L. Goodall, *MMI Int. Symp. "Transition Metal Catalyzed Polymerization: Unsolved Problems"*, Midland, 1981.
7. R. Spitz, J.L. Lacombe and A. Guyot, *J. Polym. Sci., Chem. Ed.*, **22**, 2625 (1984).
8. F.M.B. Coutinho and L.C. Santa Maria, *Eur. Polym. J.*, accepted for publication.
9. G. Natta, P. Corradini and G. Allegra, *J. Polym. Sci.*, **51**, 399 (1961).
10. US Patent 4060493 to Mitsubishi Chemical Industries, 1977.
11. JP Patent 25365 to Mitsubishi Chemical Industries, 1983.
12. G. Allegra, *Nuovo Cimento*, **23**, 1962 (1962).