The role of hindered Lewis bases on the catalyst performance of TiCl$_3$ for propylene polymerization

Marcos A. S. Costa, Fernanda M. B. Coutinho*

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, PO Box 68525, 21945-970 Rio de Janeiro, Brazil

SUMMARY

The effect of AlEt$_3$ modified by tributylamine (TBA), 1,4-diazabicyclo [2.2.2]octan (DO), 2,2,6,6-tetramethylpiperidine (TMPip), 2,6-dibutyl-4-methylphenol (BHT) and 2-*tert*-butyl-4-metoxyphenol (TBMP) on the propylene polymerization was studied using a catalyst based on TiCl$_3$ modified with di-n-butyl ether as internal base. The influence of these hindered Lewis bases on the isotacticity, catalyst activity, molecular weight ($\overline{M}$n) and molecular weight distribution (MWD) was investigated. It was verified that the Lewis bases modified the percentage of mm triad whereas no significant effect on I.I. was found.

INTRODUCTION

It is well known that catalyst systems for the stereospecific polymerization of an α-olefin should be modified in order to increase their polymerization activity and stereospecific performance, by reacting the organo aluminum compound with an electron donor (Lewis base). The addition of a Lewis base to Al-alkyl has a remarkable effect on the catalyst performance in propylene polymerization (1-7).

One of the roles of the electron donors is to complex or react with the aluminum alkyl cocatalyst. The nature of the modified cocatalyst depends on the stability of the donor-acceptor complex under the polymerization conditions (8).

The external donors markedly increase the stereospecificity and usually decrease the activity of Ziegler-Natta catalysts, but the detailed actions of the donors are still poorly known.

A large number of often contrasting opinions on the role of the Lewis bases is found in the literature: selective poisoning of atactic centers (9,10); transformation of atactic centers into isotactic ones (11); decrease of the alkylaluminium reducing power (12); increase in kp of isotactic centers (7).

The catalyst activity of the TiCl$_3$ for the polymerization of propylene is greatly improved when AlEt$_3$ is used instead of AlClEt$_2$ (13). Thus an obvious choice for the cocatalyst in this respect would be AlEt$_3$, but although this cocatalyst presents higher power to activate the catalytic centers, its stereoselectivity is invariably poorer.

The use of amines and phenols in nonsupported catalytic systems for propylene polymerization has been subject of many patents (14-16). On the other hand, a few basic

---

* Corresponding author

studies have been carried out on such systems. Thus, the objective of this work is to carry out a systematic investigation on the effect of those electron donors on propylene polymerization with δ-TiCl₃/AlEt₃ catalyst system.

EXPERIMENTAL PART

Materials

Propylene (from White Martins S.A., used after passage through 3Å molecular sieve), iso-octane (used after passage through a 3Å molecular sieve column), tributylamine (TBA), 1,4-diazabicyclo [2.2.2]octan (DO), 2,2,6,6-tetramethylpiperidine (TMPip), 2,6-dibutyl-4-methylphenol (BHT) and 2-*tert*-butyl-4-metoxyphenol (TBMP)(research grade, stored over 3Å molecular sieve), triethylaluminum (TEA)(from Alkyls do Brasil Ltda, used as solution in iso-octane)

Catalyst synthesis

The details of catalyst synthesis were already described in a previous paper (17).

Polymerization and polymer characterization

Propylene polymerization was carried out in a 1.0 dm³ glass reactor equipped with a mechanical stirrer. Determined amounts of AlEt₃, external donor and catalyst (TiCl₃) were added to the reactor containing 0.5 dm³ of iso-octane at 50°C. Then propylene was continuously fed to maintain a positive pressure of 100 mm Hg for 1 hr. At the stated time the monomer feeding was stopped, the polymer slurry degassed to remove unreacted propylene and the reaction mixture was cooled. The polypropylene was then filtered off, washed and dried at 80°C. Tributylamine (TBA), 1,4-diazabicyclo[2.2.2] octan (DO), 2,2,6,6-tetramethylpiperidine (TMPip), 2,6-dibutyl-4-methylphenol (BHT) and 2-*tert*-butyl-4-methoxy-phenol (TBMP) were employed as Lewis bases. For each polymer sample, the isotactic index (I.I.. weight % of polypropylene insoluble in boiling iso-octane) was determined by Soxhlet extraction with iso-octane for 6 hours. The soluble polymer content (SPC) in the reaction medium (iso-octane) was determined by evaporation of 10 ml iso-octane (polymerization diluent) solution and the results were expressed as a percentage of total polymer. The catalyst activity was expressed as the weight (g) of insoluble polypropylene (PP) produced at the end of each polymerization (gPP/gTi.h). The ¹³C NMR spectra were recorded at 120°C using a JEOL FX-100 spectrometer operating at 25 MHz. The solutions were made up in o-dichlorobenzene/benzene-d₆ (9/1, by vol.) up 10 wt. -%. The chemical shift was represented in ppm down field from internal hexamethyldisiloxane (HMDS). Gel-permeation chromatography (GPC) of polymers were performed on a Senshu Scientific Co., LTD (HT-GPC; SSC-7100) at 145°C and o-dichlorobenzene as solvent.

RESULTS AND DISCUSSION

Numerous patents describe the use of Lewis bases in order to improve the catalyst activity and stereospecificity of TiCl₃/AlEt₃ system. Generally, almost all conceivable Lewis bases have been claimed as effective, but it is well known that it is not so. The

catalyst used in this work was synthesized with di-n-butyl ether as internal electron donor [17].

Figure 1 shows that all Lewis bases provoked a decreasing in catalyst activity. This effect was remarkable for DO and TBMP. Thus, at mole ratio TBMP/AlEt$_3$ and DO/AlEt$_3$ = 0.5, the catalyst activity has decreased from 550 (absence of Lewis base) to 73 and 165 respectively. These bases present more than one active center for coordination and probably form a strong complex with those sites. On the other hand, the minor loss in activity for TMPip (Fig. 1c) indicates that it weakly complexes AlEt$_3$ and/or catalyst active centers.

Table 1 illustrates the effect of Lewis bases on the catalyst performance. It can be seen that a maximum value of I.I. (% of insoluble polymer, determined by means of extraction with boiling iso-octane during 6 hours) was achieved at a determined ratio of external donor/AlEt$_3$ for each one of the electron donors (TBA, DO, TBMP = 0.5; BHT = 1.5). In the case of TMPip no significant effect on I.I. was found. Although most Lewis bases were able to improve the I.I., the ^{13}C NMR analysis showed that only the nitrogen bases have improved the stereoregularity (% of mm triad) of polypropylene. It was verified that the phenols provoked a decreasing in % of mm triad without lowering the I.I. in comparison with the polymerization in absence of base. Probably these bases have modified the environment of the active centers and the produced isotactic polypropylene might contain syndiotactic and/or atactic sequences as stereoblocks. Similar behavior was verified for higher mole ratios TBA/AlEt$_3$ and TMPip/AlEt$_3$. From Tab.1 can also be seen that when lower concentration of DO was employed the I.I. decreased and the contrary was verified when higher concentration of this base was used. It seems that there is a minimum limit value of base concentration for the selective poisoning of the catalyst atactic centers to occur. The same behavior was found by Barbé and co-workers (18) for methyl-p-toluate with TiCl$_4$/MgCl$_2$-AlEt$_3$ catalytic system.

The soluble polymer content (SPC) in the reaction medium (iso-octane) decreased when TMPip was employed. Since the molecular weight of insoluble polymer was not so different in comparison with the polymer obtained in absence of base, it seems that the base has selectively poisoned some active centers responsible for the production of lower molecular weight polymers. A different behavior was observed at mole ratio DO/ AlEt$_3$ = 0.5, in this case the base provoked an increase on the molecular weight of the insoluble polymer and a decrease on the soluble polymer content.

In general, the polymer molecular weight increased as the base concentration increased suggesting that the base has provoked a decrease on the rate constant of chain transfer reaction.

The polydispersity was also affected by an increase of the base concentration. MWD values showed a progressive decrease as the base concentration increased in the range studied in this work. This behavior is indicative of the decrease of chain transfer reactions.

The bulk density of polypropylene decreased when Lewis bases were employed. A possible explanation for the decreasing on the bulk density is that the bases penetrated in the catalyst bulk producing as a consequence a more porous structure.

In order to obtain more information related to the effect of electron donors on the polymer structure, the polymer samples synthesized with BHT were fractionated with boiling iso-octane and were analyzed by ^{13}C NMR and GPC (Tab. 2). The molecular weight of the soluble fraction was lower than that of the insoluble one, indicating that in fact, the iso-octane soluble fraction presented shorter-chain material. In addition, it can be said that BHT affected both, isotactic and atactic active centers. Even if the molecular
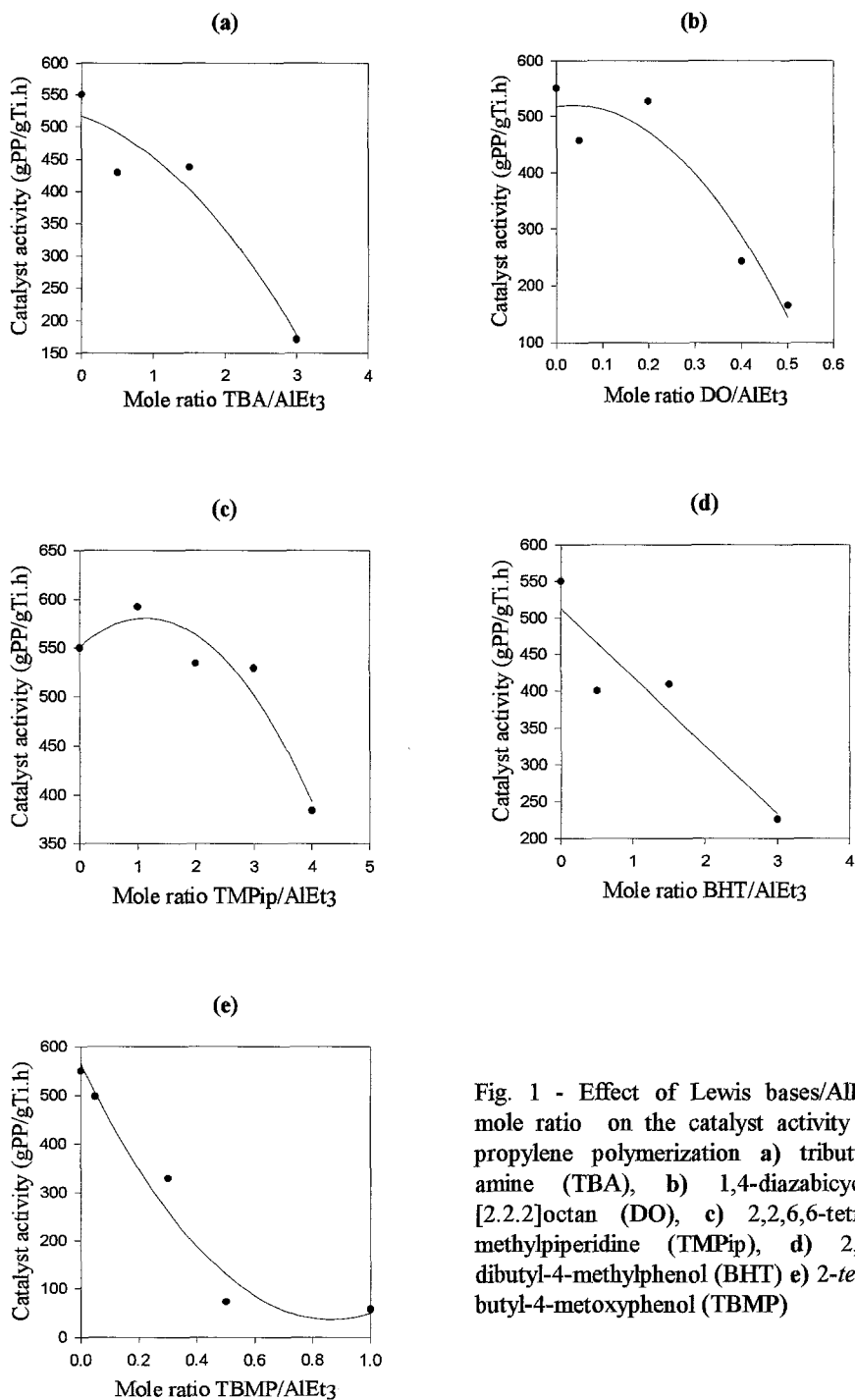
(a)

(b)

(c)

(d)

(e)

Fig. 1 - Effect of Lewis bases/AlEt$_3$ mole ratio on the catalyst activity in propylene polymerization **a)** tributyl-amine (TBA), **b)** 1,4-diazabicyclo [2.2.2]octan (DO), **c)** 2,2,6,6-tetra-methylpiperidine (TMPip), **d)** 2,6-dibutyl-4-methylphenol (BHT) **e)** 2-*tert*-butyl-4-metoxyphenol (TBMP)

weight of the whole polymer did not vary with the increase of the BHT/AlEt$_3$ ratio, $\overline{M}$n and MWD values of the insoluble and soluble fractions suggest that the stability of the donor-acceptor complex has been modified according to the employed BHT/AlEt$_3$ mole ratio. Although in the insoluble fraction $\overline{M}$n values tend to enhance and MWD values tend to decrease with the BHT/AlEt$_3$ mole ratio, the results of the soluble fraction can induce to new conclusions. Perhaps insoluble polymer presenting a higher degree of steric defects is being formed when the BHT/AlEt$_3$ ratio shift from 1.5 to 3.0.

Table 1 - Effect of Lewis bases on propylene polymerization with δ-TiCl$_3$/AlEt$_3$ catalyst system

Lewis base (LB)	LB/AlEt$_3$ mole ratio	I.I. [a] (%)	% mm triad [b]	Bulk density (g/cm^3)	$\overline{M}$n [c] x 10^{-4}	$\overline{M}$w/$\overline{M}$n [c]	SPC [d] (%)
-	-	97	90.1	0.41	4.14	11.01	14
TBA	0.5	99	91.2	0.25	3.35	8.74	16
TBA	1.5	95	85.3	0.25	3.69	8.60	15
TBA	3.0	97	85.0	0.32	7.55	5.48	10
DO	0.05	95	88.8	0.36	5.38	7.35	15
DO	0.2	95	89.1	0.35	3.72	7.52	13
DO	0.4	95	n.d	0.37	n.d.	n.d.	12
DO	0.5	98	92.3	0.36	18.1	4.44	6
TMPip	1.0	97	91.7	0.30	n.d.	n.d.	6
TMPip	2.0	96	92.7	0.30	5.10	7.78	7
TMPip	3.0	96	88.2	0.35	n.d.	n.d.	7
TMPip	4.0	97	83.8	0.36	4.99	9.80	6
BHT	0.5	96	85.1	0.37	n.d.	n.d.	17
BHT	1.5	98	86.5	0.22	3.52	7.45	27
BHT	3.0	96	81.2	0.43	4.00	8.98	17
TBMF	0.05	97	86.7	0.28	n.d.	n.d.	14
TBMF	0.3	97	87.1	0.37	6.21	5.52	16
TBMF	0.5	98	88.8	0.25	2.70	5.54	12

TBA - tributylamine; DO - 1,4-diazabicyclo[2.2.2.] octan; TMPip - tetramethylpiperidine; BHT - 2,6-dibutyl-4-methylphenol; TBMP- 2-*tert*-butyl-4-methoxyphenol
a) I.I.: Isotactic index (wt.-%), determined by means of extraction with boiling iso-octane;
b) Determined by ^{13}C NMR;
c) Determined by GPC;
d) SPC: Soluble polymer content in diluent of polymerization (See experimental part)
n.d.: not determined

Table 2 - Isotactic index (I.I.), % mm triad, $\overline{M}n$ and MWD of polymer obtained in presence of different amounts of BHT (2,6-dibutyl-4-methylphenol)

$\dfrac{BHT}{AlEt_3}$ Mole ratio	I.I. (%) (a)	Whole polymer			Insoluble fraction			Soluble fraction		
		% mm triad (b)	$\overline{M}n$ x 10^{-4} (c)	MWD (c)	% mm triad (b)	$\overline{M}n$ x 10^{-4} (c)	MWD (c)	% mm triad (b)	$\overline{M}n$ x 10^{-3} (c)	MWD (c)
0.0	97	90.1	4.14	11.01	95.9	4.48	9.74	62.0	3.63	7.52
1.5	98	86.5	3.52	7.45	95.4	3.98	7.08	64.0	6.16	9.71
3.0	96	81.2	4.00	8.98	81.8	7.33	5.43	54.5	2.14	38.6

(a) I.I.: Isotactic index (wt.-%), determined by means of extraction with boiling iso-octane;
(b) Determined by ^{13}C NMR;
(c) Determined by GPC.

ACKNOWLEDGEMENTS

REFERENCES

1. F.M.B. Coutinho and L.C. Santa Maria, *Polym. Bull.*, **26**, 535 (1991)

2. F.M.B. Coutinho and L.C. Santa Maria, *Makromol. Chem.* **193**, 1739 (1992)

3. F.M.B. Coutinho and L.C. Santa Maria, *Eur. Polym. J.*, **27**, 987 (1991)

4. L.C. Santa Maria, F.M.B. Coutinho and C. Alencar, *Makromol. Chem.*, **194**, 1397 (1993)

5. M.C. Sacchi, I. Tritto and P. Locatelli, *Eur. Polym. J.*, **24**, 137 (1988)

6. A.W. Langer, T.J. Burkhardt and J.J. Steger. In *Transition Metal Catalyzed Polymerizations: Alkenes and Dienes, Part A* (Edited by R.P. Quirck), p. 421, Harwood, New York (1983)

7. E. I. Vizen; L.A. Rishina & F.S. Dyachkovsky - *Eur. Polym. J.*, **18**, 773 (1982)

8. K. Tashiro, M. Yokoyama, T. Sugano and K. Kato, *Contemp. Top. Polym. Sci.*, **4**, 647 (1984)

9. B.L. Goodall - In *Transition Metal Catalyzed Polymerizations, Alkenes and Dienes, Part A*, (Edited by R.P. Quirck), p. 355, Harwood, New York, (1983)

10. P. Galli, L. Luciani, G. Cecchin, *Angew. Makromol. Chem.*, **94**, 63 (1981)

11. K.Soga, J.R. Park, T. Shiono, N. Kashiwa, *Makromol. Chem., Rapid Commun.*, **11**, 117 (1990)

12. I.I. Zakharov, V.A. Zakharov, G.D. Bukatov, *Proc. IUPAC 28th Macromolecular Symposium*, Amherst, Mass. USA 1982, p. 243

13. F.M.B. Coutinho, C. Alencar and L.C. Santa Maria, *Polym. Bull.*, **27**, 645 (1992)

14. Shell Internationale Research, European Patent 0021 478 (1981)

15. Shell Oil Company, US Patent 4 478 989 (1984)

16. Montecatini Edison, German Patent 1 302 896 (1972)

17. F.M.B. Coutinho, M.A.S. Costa and L.C. Santa Maria, *Polym. Bull.*, **28**, 55 (1992)

18. P.C. Barbé; L. Noristi & M.A. Schexnayder. *International Symposium "Recent Advances in Polyolefin"*, Chicago, USA, 1985.