The influence of some synthesis parameters on Ziegler-Natta catalyst performance

Fernanda M. B. Coutinho*, Marcos A. S. Costa, and Luiz C. Santa Maria

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

ABSTRACT
        The role of di-n-butyl ether (DBE) in the synthesis of
highly active and stereospecific catalyst for propylene
polymerization has been investigated. The ether was used as
internal base (IB) or complexed with $TiCl_4$ and diethylaluminium
chloride (DEAC) in iso-octane solution (System A) or complexed
with triethylaluminium (TEA) in toluene solution (System B).
Many differences were observed in the catalyst performance.
The activity, the catalyst stereospecificity and the polymer
bulk density were evaluated.

INTRODUCTION
        Year by year the industrial use of the Ziegler–Natta
catalysts expands. Although many researchers have been engaged
in the study of this system, the catalyst behaviour is not
completely understood yet.
        Recently catalysts based on $TiCl_3$ modified with electron
donors for polypropylene (PP) synthesis have been studied and
introduced into industrial production (1–4). These electron
donor compounds play an important role at a certain stage in
the catalyst synthesis (1).
        Lewis bases such as esters, amines and ethers used for
coordination catalysts also have considerable importance in the
steric control of Ziegler–Natta catalysts (5,6). They are
supposed to exert their influence through adsorption on the
more accessible non stereospecific active centres of the
catalyst, blocking them (7). Thus, the use of electron donors
in the catalyst preparation can significantly improve its
performance.
        The "replica" relationship between the catalyst and the
polyolefin particle morphology has been studied (8). The
concept of total control of the polymer by using the proper
catalyst has gradually gained ground. Research has been
focussed more and more on finding a catalyst able to balance
out the limiting factors inherent to industrial production.
For example the bulk density is one the most important

*To whom offprint requests should be sent

characteristics for the processing of polyolefins, and is also one of the most difficult parameter to control.

In this work we attempt to explain the effect of some parameters in the catalyst synthesis for propylene polymerization.

EXPERIMENTAL PART

Materials

Propylene (White Martins S.A., used after passage through 3Å molecular sieve), $TiCl_4$ (research grade, distilled under dry N_2), di-n-butyl ether (DBE) and toluene (research grade, dried over Na, fractionally distilled under dry N_2 and stored over 3Å molecular sieve), iso-octane (used after passage through a 3Å molecular sieve column), triethylaluminium (TEA) and diethylaluminium chloride (DEAC) (Alkyl do Brasil Ltda., used as a solution in iso-octane or in toluene) were employed.

Catalyst synthesis

All manipulations of catalyst components were carried out under dry nitrogen using standard inert atmosphere techniques. The synthesis of catalysts prepared through $TiCl_4$ reduction with DEAC in the presence of DBE, in iso-octane solution (System A) was described in a preceding paper (3).

TEA complexed with DBE in toluene solution was added dropwise in a determined molar ratio $DBE/TiCl_4$ to a $TiCl_4$ solution in toluene cooled at $-68°C$ (System B). After 1h20min addition the temperature of the solution was raised to $-10°C$ and then maintained at this temperature for 3 hours. After the thermal treatment at $65°C$ for 5 hours, the catalyst was thoroughly whashed with iso-octane. The Ti contents of solid catalyst were determined by colorimetry and Al contents were determined by atomic absorption.

Propylene polymerization

Propylene polymerization was carried out in a 1000 mL glass reactor equiped with a mechanical stirrer. Determined amounts of cocatalyst solution in iso-octane (TEA or DEAC) and catalyst suspension were added to the reactor containing 500 mL of iso-octane. Propylene was then continously fed in order to maintain a positive pressure of 100 mmHg for one hour. The reaction mixture was cooled and polypropylene filtered off, washed with n-hexane and dried. For each sample, the isotacticity index (I.I., weight % of polymer insoluble in boiling iso-octane) was determined through Soxhlet extraction with iso-octane for six hours.

RESULTS AND DISCUSSION

As can be seen in Table 1, all catalysts presented low aluminium contents as a result of the action of DBE which is able to remove the aluminium compounds through the formation of soluble complexes. It can also be observed that the polymer bulk density was strongly influenced by the molar ratio DBE/TiCl$_4$. The bulk density decreased in the System A when molar ratio DBE/TiCl$_4$ increased. In the case of System B, the bulk density trends show a maximum at a determined value of molar ratio DBE/TiCl$_4$ (0.8). It seems that toluene plays an important role in the control of the particle morphology. It has been observed that the polymer particle obtained from System B presented a spherical form. On the other hand, the polymer particle prepared from System A (in iso-octane) showed irregular forms. A possible explanation for the decreasing in the bulk density is that DBE turned the catalyst particles more porous and consequently more fragile.

TABLE 1

The synthesis parameters and the catalyst characteristics

Experiment	Parameters of Synthesis		Chemical Composition		Catalytic Properties	
	Type of Solvent	Molar Ratio DBE/TiCl$_4$	Titanium Content (mmolTi/ g cat.)	Aluminium Content (%)	Bulk Density (g/cm^3)	Soluble Content (%)
A[c]	Toluene[f]	0.3	5.86	0.2	0.26	35
B[c]		0.5	6.36	0.4	0.32	24
C[c]		0.6	5.86	0.1	0.36	15
D[c]		0.8	6.11	0.1	0.41	15
E[c]		1.0	6.28	–	0.36	15
F[c]		1.5	6.21	0.1	0.26	15
G[d]	Iso-octane[g]	0.5	6.37	–	0.36	–[e]
H[d]		0.67	6.06	0.3	0.25	–[e]
I[d]		0.7	5.79	–	0.25	–[e]
J[d]		0.9	5.77	–	0.25	–[e]
K[d]		1.1	4.69	–	0.17	–[e]

a) The titanium content was determined by colorimetry method.
b) The aluminium content was determined by atomic absorption.
c) Catalyst prepared by the TiCl$_4$ reduction with TEA at -10°C (System B).
d) Catalyst prepared by the TiCl$_4$ reduction with DEAC at 5°C (System A).
e) The soluble contents of catalyst prepared by the TiCl$_4$ reduction with DEAC were very low (<5%).
f) Triethylaluminium (TEA) was employed as cocatalyst in propylene polymerization.
g) Diethylaluminium chloride (DEAC) was employed as cocatalyst in propylene polymerization.

Table 1 shows that soluble polymer contents produced with System B were higher than those from System A. TEA being a stronger reductant agent than DEAC has provoked more chain transfer producing then higher soluble polymer contents (lower molecular weight).

In Figure 1 is plotted the relation between the activity and molar ratio $DBE/TiCl_4$. A marked increase in the activity was observed when the catalysts were prepared in toluene solution. It is possible that in toluene, a better solvent, the action of the internal base has exposed a greater number of active centers. The decrease of the activity observed in both systems is probably due to the poisoning of active sites by the excess of base (9).
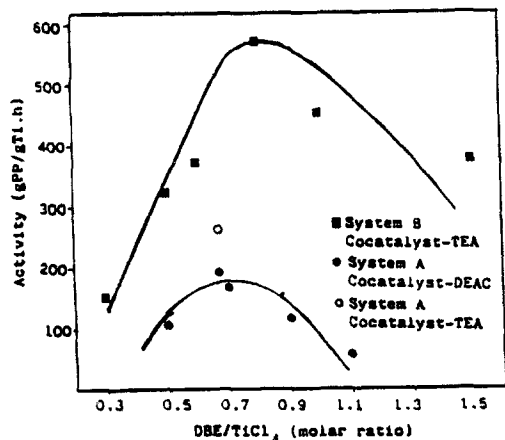

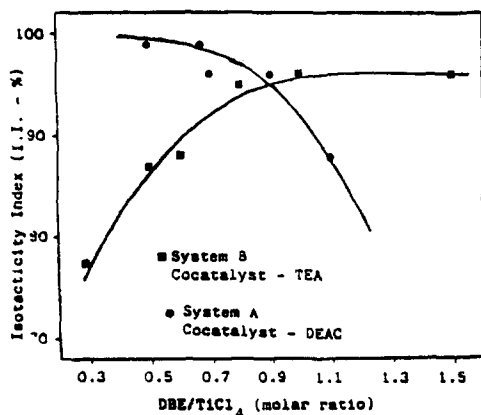Figure 1 – Influence of the molar ratio $DBE/TiCl_4$ on the catalyst activity

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

As can be noted in Figure 2 a completely different trend in the isotacticity· index, with Systems A and B was achieved. The stereospecificity of catalysts prepared with iso-octane (System A) diminished when the molar ratio $DBE/TiCl_4$ increased while the opposite was attained with the System B. This behaviour can be explained by the DBE action in the catalyst formation. This base can transform atactic sites into isotactic ones by producing more imperfections in the catalyst crystals and consequently turning it more stereospecific (10,11).

It is well known that ethers with short chains, such as di-n-buthyl ether, are more soluble in aromatic solvents than

in aliphatic ones. Thus toluene employed in System B forms
a more homogeneous system during catalyst synthesis,
consequently more homogeneous catalyst particles are formed.

ACKNOWLEDGEMENTS

REFERENCES

1. R. Kh. Denilov, I.A. Voloshin and Yu. M. Nikiforov, Plast.
   Massy, 6, 55 (1983).
2. F. M. B. Coutinho and L. C. Santa Maria, Eur. Polym. J.,
   27(7), 987 (1991).
3. F. M. B. Coutinho and L. C. Santa Maria, Polym. Bull., 26,
   535 (1991).
4. F. M. B. Coutinho, T. H. S. Costa, L. C. Santa Maria and
   Romeu Pereira, submitted to Eur. Polym. J. for publication.
5. US 4210738 to Solvay and Cie, 1980.
6. JP 25365 to Mitsubshi Chemical Industries, 1983.
7. J. Boor, Polym. Sci. B, 3, 7 (1965).
8. J. C. Bailly, R. Hagege, Polymer, 32, 181 (1991).
9. N. Kashiwa, MMI Press. Symp. Ser., 4, 379 (1983).
10. K. Soga, J. R. Park and T. Shiono, Makromol. Chem., Rapid
    Commun., 11, 117 (1990).
11. R. P. Nielsen, MMI Press Symp. Ser., 4, 47 (1983).