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Propylene polymerization with δ-$TiCl_3/AlClEt_2$ and δ-$TiCl_3/AlEt_3$ catalyst systems

2. Effect of polymerization parameters

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Summary

Some parameters of propylene polymerization using δ-$TiCl_3/AlClEt_2$ and δ-$TiCl_3/AlEt_3$ catalyst systems were evaluated. The catalyst was prepared through the reduction of $TiCl_4$ complexed with di-n-butyl ether (DBE) (mole ratio DBE/$TiCl_4$=0.67) by $AlClEt_2$. Propylene polymerizations were carried out at different Al/Ti ratios, using $AlEt_3$ or $AlClEt_2$ as cocatalysts and different polymerization temperatures. The effects of these parameters on catalyst activity, stereospecificity and polymer molecular weight were investigated. The results indicate that these parameters strongly affect catalyst performance.

Introduction

The polymerization of α-olefins with heterogeneous Ziegler-Natta catalysts has provoked a remarkable industrial development in polymer field and there is a great interest in these catalyst systems. Although many new catalysts and processes have been announced, intensive research directed is still toward the understanding of the fundamentals of these processes. The fundamental questions include a mechanistic understanding of the influence of catalyst type, additives and polymerization conditions on catalytic properties (e.g., density, stereospecificity, activity), polymer morphology, polymer molecular weight distribution, etc (1). The understanding of polymerization mechanism owes much to the choice of triethylaluminium (TEA) as cocatalyst, since in this case a constant polymerization rate was achieved. Moreover, to avoid variations in catalyst stereocontrol the first important work was carried out with one particular sample of ball-milled α-$TiCl_3$, and more recently with disordered $TiCl_3$ obtained from the soluble system (δ-$TiCl_3$) (2-4).

With the use of diethylaluminium chloride (DEAC) as cocatalyst, polypropylene(PP) of improved steric purity can be obtained. High stereoregularity can be maintained at high polymerization rates by using modified catalysts of the

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*To whom offprint requests should be sent violet crystalline form of $TiCl_3$ (5). In the $TiCl_3$/alkylaluminium catalyst system the active site is the result of the interaction between the catalyst components, and catalyst activity depends on polymerization time. The question arises as to the cause of this change, which might be due to the formation, growth and later decrease of the number active centers.

Both components of Ziegler-Natta catalyst react with electron donors. Triethylaluminium exhibits such a strong tendency to fulfill the uncomplete shell of aluminium, that it exists as a bridged dimer. The surface of $TiCl_3$ acts as a strong adsorbent because Ti has uncomplete d orbitals suitable for chemisorption not only for α-olefins but also for electron donors (Lewis bases).

The present paper adds to this area of polymerization some understanding. The effects of polymerization temperature and $AlEt_3/TiCl_3$ and $AlClEt_2/TiCl_3$ mole ratios on the activity, stereospecificity and molecular weight were studied.

Experimental

Materials

Propylene (White Martins S.A., used after passage through 3Å molecular sieves), $TiCl_4$ (research grade, distilled under dry N_2), di-n-butyl ether (research grade, dried over Na, fractionally distilled under dry N_2 and stored over 3Å molecular sieves), iso-octane (used after passage through a 3Å molecular sieve column), $AlEt_3$ and $AlClEt_2$ (Alkyl do Brasil Ltda., used in iso-octane solution) were employed.

Catalyst synthesis

The catalyst (Cat. A) was prepared through the reduction of the $TiCl_4$.DBE complex (mole ratio DBE/$TiCl_4$=0.67) with $AlClEt_2$. Detailed catalyst synthesis was already described (6).

Propylene polymerization

Propylene polymerization was carried out in a $1dm^3$ glass reactor equipped with a mechanical stirrer. Determined amounts of cocatalyst solution in iso-octane (TEA or DEAC) and catalyst suspension were added to the reactor containing $0.5dm^3$ of iso-octane. Propylene was then continuously fed to maintain a positive pressure of 100mmHg for one 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 iso-octane) was determined through Soxhlet extraction with iso-octane for six hours.

Results and discussion

Effect of the temperature on propylene polymerization

The first set of experiments was carried out to observe the influence of temperature on catalyst activity, stereospecificity, and molecular weight. Four different temperatures (40, 50, 60 and 70°C) were used. The results are shown in Table 1. Temperature had a strong influence on the catalyst activity and stereospecificity. The stereospecificity of δ-$TiCl_3/AlEt_3$ and δ-$TiCl_3/AlClEt_2$ catalyst systems diminished with the rise in temperature. Probably it was due to the loss of stereocontrol on monomer insertion at the transition metal-carbon bonds (active centers) when the vibration level of the catalytic complex increased by the increase of temperature. Higher temperatures can also break the π-complex formed (donor-acceptor complex) between the catalyst system (active site) and the monomer. Table 1 shows that the activity of δ-$TiCl_3/AlClEt_2$ increased when the temperature increased. This could be due to two factors: a higher number of active centers was formed and the propagation rate increased at higher temperature. Table 1 also shows that the use of $AlEt_3$ provoked a decrease in the activity with the rise of the polymerization temperature. This decrease probably is due to a reduction of Ti^{+3} to Ti^{+2} at higher temperatures, and it is well known that Ti^{+2} is not active for propylene polymerization The data show that the optimum temperature for our catalyst is 60°C with $AlClEt_2$ and 50°C with $AlEt_3$.

Table 1 - Influence of the polymerization temperature on the catalyst activity and stereospecificity and molecular weight on propylene polymerization using Cat.A and mole ratio Al/Ti=2

Temperature (°C)	Type of co-catalyst	Activity (gPP/gTi.h)	I.I. (%)	Molecular weight ($\bar{M}_v$) $\bar{M}_v.10^{-5}$
40	$AlClEt_2$	98	98.8	8.42
50		137	97.8	8.81
60		151	96.8	3.30
70		211	81.8	2.83
40	$AlEt_3$	263	97.8	3.30
50		282	96.3	5.13
60		243	95.8	2.83
70		230	95.1	4.96

PP - polypropylene I.I. - Isotacticity index

Effect of Al/Ti mole ratio on propylene polymerization

Table 2 shows that the catalyst activity of the δ-$TiCl_3$/$AlEt_3$ system was higher than that of δ-$TiCl_3$/$AlClEt_2$. This result is due to the higher reactivity of $AlEt_3$ which forms more active sites than $AlClEt_2$. On the other hand, the stereospecificity of the δ-$TiCl_3$/$AlEt_3$ system was lower than that of the δ-$TiCl_3$/$AlClEt_2$ system. It was also observed that the

Table 2 - Influence of the mole ratio Al/Ti on the catalyst activity and stereospecificity and polymer molecular weight on propylene polymerization using Cat.A at 50°C

Mole ratio Al/Ti	Type of co-catalyst	Activity (gPP/gTi.h)	Isotacticity index (weight %)	Molecular weight ($\bar{M}_v$) $\bar{M}_v.10^{-5}$
1	$AlClEt_2$	99	98.1	3.95
2		137	97.8	6.55
3		198	98.3	9.59
4		222	98.3	10.38
5		224	98.3	10.18
10		114	93.1	-
15		104	89.5	-
0.5	$AlEt_3$	208	95.8	-
1		371	96.7	5.67
2		340	96.5	5.31
3		323	96.5	6.01
4		274	96.7	5.31
5		281	96.1	4.96

PP - polypropylene

δ-$TiCl_3$/$AlEt_3$ system forms a higher fraction of soluble products (low molecular weight polymer) than δ-$TiCl_3$/$AlClEt_2$ (approximately 2% and 1% respectively). This is probably due to chain transfer. The isotacticity index (I.I.) of the polymers obtained with the δ-$TiCl_3$/$AlEt_3$ system were not influenced by the Al/Ti ratio while the catalyst activity was strongly influenced by it. The catalyst activity increased as the $AlClEt_2$/Ti mole was increased to 4.0 and above this value the activity decreased. It seems that above that value the over-reduction of Ti becomes more important and thus the catalyst activity decreases. Nevertheless, in the range of values studied, when $AlEt_3$ was used as cocatalyst, an increase in the Al/Ti ratio provoked a decrease in the catalyst activity. A possible explanation could be that as $AlEt_3$ is a stronger reducing agent than $AlClEt_2$, the over-reduction of Ti occurs at lower ratios and produces Ti^{+2} which is inactive for propylene polymerization (7-9).

It was observed that the suspension of the δ-$TiCl_3$/$AlEt_3$ catalyst system became darker when the mole ratio Al/Ti increased; this indicates a reduction process (the Ti^{+2} compounds, $TiCl_2$ for example, are black). The results obtained in this work have shown that $AlClEt_2$ is more selective than $AlEt_3$ because with the system δ-$TiCl_3$/$AlClEt_2$ the highest values of stereospecificity were attained. It can be concluded that the best mole ratio Al/Ti was 4.0 when $AlClEt_2$ was employed as cocatalyst and 1.0 when $AlEt_3$ was used. Although the isotactic content has been lower for the δ-$TiCl_3$/$AlEt_3$ catalyst system than for the δ-$TiCl_3$/$AlClEt_2$, it is possible to improve it, e.g., when external-donors (third components) are employed (10).

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