

Kinetics study of Ziegler-Natta catalyst based on $TiCl_3$ modified by Lewis bases

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SUMMARY

The kinetic in propylene polymerization of catalysts containing di-n-butyl ether (DBE) - Cat.A or di-n-butyl ether and ethyl benzoate (EB) - Cat.B used as internal electron-donor compounds was investigated. Comparing catalyst compositions with performances, one could conclude that the different kinetics observed were due to the different Lewis bases employed during catalyst synthesis. It seems that the electron-donors have modified the catalyst sites. It has found that added ethyl benzoate modified the structure of the active sites and increased the polymerization rate constant.

INTRODUCTION

Since the discovery of Ziegler-Natta systems, the structure of active centres and the mechanism of their formation have been continuously discussed (1). According to Keii et al., the active centres are formed by an irreversible reaction between the monomer and the organometallic complex (2). Many possible mechanisms for the active site formation have been proposed (3,4). The alkylation and subsequent reactions proceed by different ways in different systems and they result in polymers with specific properties. A complete characterization of the different polymerization systems in regard to interactions of catalyst components is rather difficult. This problem becomes even more complicated when the system contains a third component, e.g. Lewis base, due to the ability of these bases to complex and/or react with both the cocatalyst (aluminum alkyl) and/or the catalyst (titanium trichloride) (5).

The rate decay observed in propylene polymerization has intrigued investigators in Ziegler-Natta chemistry for many years. The problem is especially vexing because the Ziegler-Natta polymerization of ethylene seems to be quite straightforward. The ethylene polymerization is first-order with respect to monomer concentration, but it

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exhibits a slight rate decline at the beginning of the reaction (6). When the rate data from propylene polymerization are examined on a first-order plot, an apparently continuous rate decline is observed for as long as the reaction is continued. Caunt (7) presented evidences that the rate decline could be attributed to the formation of ethylaluminum dichloride during the reaction. The author has shown that AlEtCl_2 decreases the rate of polymerization and many other authors have confirmed this conclusion (8). On the other hand, it is also possible that the rate decay is caused by chemical death of active sites. The rate is controlled by two rate constants, one for the polymerization and a second one for the site destruction. A second-order site decay kinetics has been proposed (9).

Most of the industrially important Ziegler-Natta catalyst are complex heterogeneous systems, often of ill-defined structure and probably containing more than one type of active site. Furthermore, problems of rate control by diffusion limited mass transfer, or by adsorption of monomer onto the catalyst surfaces, make kinetics studies difficult and often irreproducible. Although these problems clearly point to the need of simple models which can be studied quantitatively to provide insight into the complex real systems, it is clearly essential to have some knowledge about the nature of the active centres in polymerization initiated by transition metal catalysts before realistic models can be visualized.

During the last three years, we have been studying the Ziegler-Natta catalysts based on TiCl_3 modified by Lewis bases (5,10-12), to develop a new high active catalyst for propylene polymerization. Such catalyst, under proper operating conditions, make it possible to obtain highly stereoregular polymer with low content of catalyst residues due to the high catalyst activity. This paper deals with the kinetics behaviour of two catalysts based on TiCl_3 modified by DBE (Cat.A) and by DBE and EB (Cat.B). The propylene polymerizations using these catalysts were carried out under the same conditions (concentrations, temperature etc).

EXPERIMENTAL PART

All manipulations of the catalyst components were carried out under dry nitrogen using standard inert atmosphere techniques.

The sources of materials and their purification procedures were reported earlier (11).

Catalyst syntheses were described in a former paper (12).

Propylene polymerization was carried out in a 1000 mL glass reactor equipped with mechanical stirrer. Determined amount of AlClEt_2 solution in iso-octane was added to the reactor containing 500 mL of iso-octane under dry N_2 at 50°C . Then catalyst suspension (3 mmol of

Ti) was added to the reactor and propylene was continuously fed to maintain a positive pressure of 100 mmHg for a selected time at 50°C. The reaction mixture was cooled and the polypropylene filtered off, washed with hexane and dried. For each polymer sample, the isotacticity index (II, % weight of polymer insoluble in boiling iso-octane) was determined through Soxhlet extraction with iso-octane for 6 hours.

RESULTS AND DISCUSSION

Based on a wide body of experimental data, a variety of roles has been ascribed to the electron-donors. Thus, they have been deemed to:

- selectively poison non-stereospecific sites;
- increase the number, activity, or stability of the stereospecific sites;
- modify the properties of the stereospecific sites (stereospecificity, chain transfer constant etc).

From a mechanistic point of view the electron-donors have been assumed to play their roles either by being directly coordinated to the sites, modifying them, or indirectly by influencing the equilibrium between the dimeric form and the monomeric form of the cocatalyst (e.g. Al_2Et_6 and AlEt_3).

Our results show that the presence of different electron-donors used (DBE and EB) caused quantitative and qualitatively different effects on kinetic behaviour, increase of catalyst activity and increase of stereospecificity. These differences seem to imply a different active centre on the solid catalyst. The DBE employed as a first internal base (Cat.A) and EB employed as a second one (Cat.B) produced the same crystalline form ($\delta\text{-TiCl}_3$). The introduction of ethyl benzoate after the TiCl_4 reduction in the presence of di-n-butyl ether (first internal base) resulted in changes of the catalyst sites.

Figure 1 shows that the introduction of EB as a second internal base provoked a strong change of catalyst. Cat.B exhibited a similar behaviour observed on the $\text{TiCl}_4/\text{MgCl}_2$ supported catalyst, indicating a similarity between the active sites of these catalyst systems. It is also possible that Cat.A causes the same type of build-up period as Cat.B after two minutes of polymerization. Probably this was not observed due to the imprecision of the gravimetric method employed. Both systems showed decay and stationary periods. The decay is attributed to deactivation of active centres. Comparing the systems (Cat.A and Cat.B), the addition of EB stabilizes the active sites because the decay period of Cat.B was not as pronounced as to Cat.A.

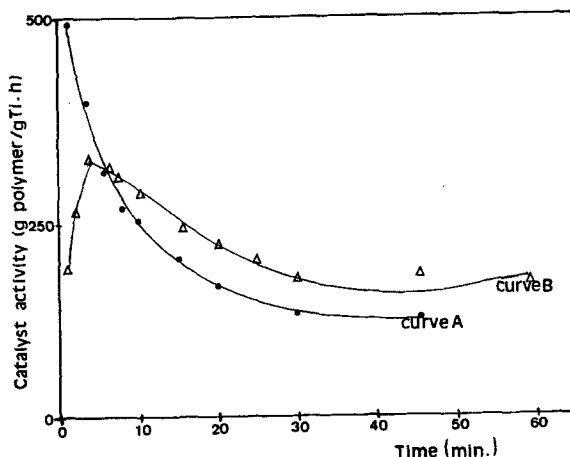


Figure 1 - Time dependence of the rate of propylene polymerization (Cat.A - curve A and Cat.B - curve B)

Tables 1 and 2 also show that the stereospecificity of Cat.A and Cat.B enhanced during the polymerization. Probably the decay periods observed in Figure 1 were due to the deactivation of the catalyst sites which produce the atactic and low molecular weight isotactic polymers. This behaviour is normally attributed to the high rate constant of these active sites.

Table 1 - Influence of reaction time on the catalyst performance of Cat.A

Polymerization time (min.)	Catalyst productivity ^a	Isotacticity index (%) ^b
2	16	91
4	22	92
6	32	94
8	34	94
10	42	96
15	50	96
20	56	95
30	62	96
45	96	97

a - g Polypropylene/g Ti

b - Isotacticity index determined by extraction with iso-octane

Table 2 - Influence of reaction time on the catalyst performance of Cat.B

Polymerization time (min.)	Catalyst productivity ^a	Isotacticity index (%) ^b
2	7	88
4	17	90
6	21	91
8	40	91
10	46	93
15	60	96
20	72	96
25	82	96
30	83	97
45	138	98
60	175	98

a - g Polypropylene/g Ti

b - Isotacticity index determined by extraction with iso-octane

CONCLUSION

Catalyst performances were strongly influenced by the presence of EB employed as a second internal base in Cat.B synthesis. It was found that the addition that the addition of this Lewis base did not change the crystalline form of the catalyst (δ -TiCl₃) obtained by TiCl₄ reduction in the presence of DBE as first internal base; EB addition changed the kinetics. Maybe this change has been a result of the stabilization of the catalyst sites by EB.

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