

## Interaction of $\alpha$ -TiCl<sub>3</sub> with organoaluminium compounds and its correlation with propylene polymerization

### IV. Effect of interaction parameters

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#### SUMMARY

The kinetics of the interaction between the catalyst components of a Ziegler-Natta stereospecific system formed by TiCl<sub>3</sub> and AlEt<sub>3</sub> in heptane was studied. The experimental results show that the rate of propylene polymerization is influenced by the rate of the interaction, activation energy, and the efficiency of interaction.

#### INTRODUCTION

The work of Arlman and Cossee (1-3), Boor (4) and Rodriguez et al. (5,6) show rather conclusively that chemical reaction between the catalyst components is a necessary condition for the formation of active centers. This was also observed in our earlier publication (7). On the other hand, Natta et al. (8) assume that the active centers are formed only by adsorption of the organometal on the solid surface. The present study was undertaken to examine the influence of the interaction reaction on the polymerization process. Catalytic components of a Ziegler-Natta stereospecific system formed by TiCl<sub>3</sub> and AlEt<sub>3</sub> in heptane were subjected to interaction for different times and after that the polymerization was initiated by the addition of monomer. The correlation between the interaction reaction and the polymerization was studied.

#### EXPERIMENTAL

$\alpha$ -TiCl<sub>3</sub>, AlEt<sub>3</sub>, AlEt<sub>2</sub>Cl, AlEtCl<sub>2</sub>, heptane, and pyridine were prepared and characterized as described earlier (9). The apparatus and procedure of following the alkylation exchange reactions have been described (9). Characterization of polypropylene, atactic, isotactic, and stereoblock was carried out by fractionation in heptane. Average molecular weight of the fractions was determined by viscosity.

#### RESULTS AND DISCUSSION

The amount of chlorine transferred from the solid to the liquid phase and the amount of gaseous products were determined during the interaction. The chlorine found in the liquid phase is defined as chlorine exchanged, Cl<sub>ex</sub>. The conversion

of exchanged chlorine is expressed in % of total Cl present in  $\text{TiCl}_3$ . Similarly, the amount of gaseous products is called hydrocarbon liberated, RH, and expressed in % of RH from decomposed 100% alkylated  $\text{TiCl}_3$ . The time dependence of the rate constant of polymerization and the time of reaction is presented in Fig. 1.

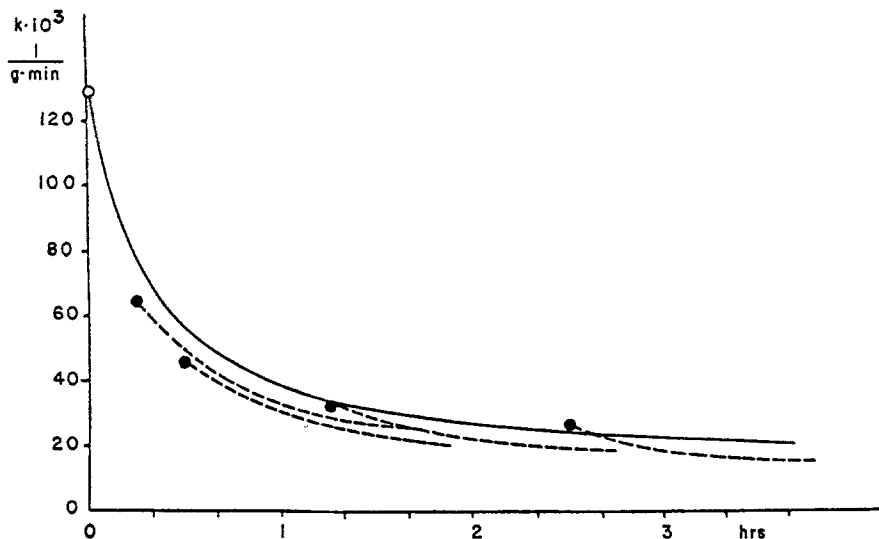


Figure 1 The time dependence of the rate constant of polymerization  $k$  on the time of previous interaction.

$S_{\text{TiCl}_3} = 35\text{--}60 \text{ m}^2/\text{g}$ ;  $\text{TiCl}_3 = 1 \text{ mmole/l}$ ;  $\text{Al/Ti} = 7.5$ ;

$M_0 = 2.38 \text{ mole/l}$ ;  $t = 50^\circ\text{C}$

---- during polymerization      ---- catalytic components reacted at  $50^\circ\text{C}$ , at point ● monomer was added.

The catalyst components were subjected to interaction for different times and after that polymerization was initiated by the addition of monomer. Polymerization rate constant  $k$  was then compared with  $k$  for a system without prior interaction. The monomer was added after interaction times. It can be seen that the rate of polymerization, after the addition of monomer after specified interaction times, proceeds in the same manner as the polymerization without previous interaction.

Fig. 2 shows the time dependence of activation energies of interaction and polymerization. The activation energies of non-activated  $\text{TiCl}_3$  are very similar. After an initial period, the activation energy of polymerization coincides with the activation energy of interaction.

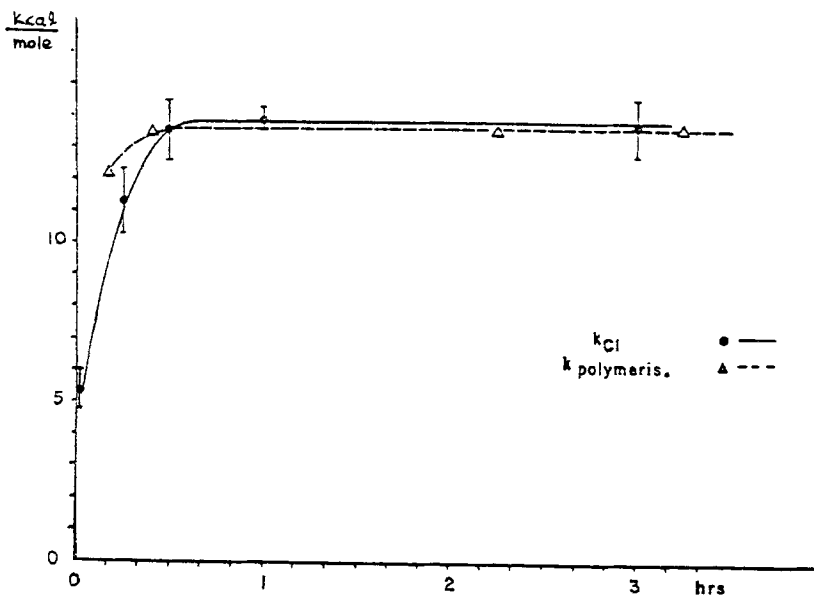


Fig. 2 The time dependence of the activation energies of interaction and polymerization.

$S_{\text{TiCl}_3} = 5 \text{ m}^2/\text{g}$ ; Polymerization :  $\text{TiCl}_3 = 5.3 \text{ mmole/l}$ ;  $\text{Al/Ti} = 3$ ;  $M_0 = 2.21 \text{ mole/l}$ ;  $t = 50-70^\circ\text{C}$   
 Interaction:  $\text{TiCl}_3 = 4.5 \text{ mmole/l}$ ;  $\text{Al/Ti} = 3$ ;  
 $t = 50-90^\circ\text{C}$

Table 1 Activation energies of interaction and polymerization

$S_{\text{TiCl}_3} \text{ m}^2/\text{g}$	5 (non-activated)	8 $K_{\text{cat}}/\text{mole}$	140 (activated)
interaction	$13.5 \pm 1.5$	$6.2 \pm 1.0$	$3.1 \pm 1.0$
polymerization	$13.5 \pm 0.5$	$10.5 \pm 0.5$	$7.1 \pm 1.0$

The activation energies of activated and non-activated  $\text{TiCl}_3$  are shown in Table 1. The results show that a decrease of activation energy of polymerization coincides with a decrease of activation energy of interaction. The difference in activation energies of activated and non-activated  $\text{TiCl}_3$  confirms the result of previous study that by activation, defect sites could be formed with a different reactivity to

active center formation.

The mode of activation has also a very strong effect on the efficiency of the interaction. By milling  $\alpha$ -TiCl<sub>3</sub> in the absence of heptane, completely different interaction and polymerization parameters were obtained (Fig. 3).

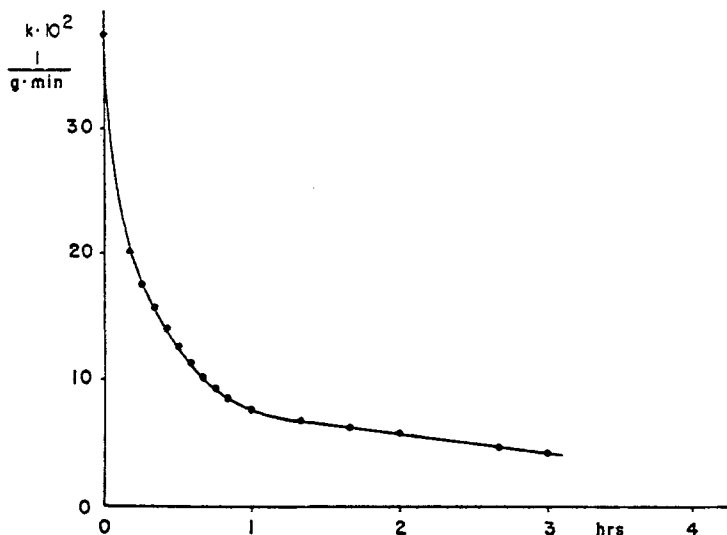


Fig. 3 The time dependence of the rate constant of polymerization.

$S_{TiCl_3} = 10-12 \text{ m}^2/\text{g}$ ;  $TiCl_3 = 0.59 \text{ mmole/l}$ ;  
 $Al/Ti = 5.7$ ;  $M_0 = 2.1 \text{ mole/l}$ ;  $t = 50^\circ\text{C}$

Correlation between the interaction and polymerization activities for differently treated  $\alpha$ -TiCl<sub>3</sub> is shown in Table 2.

Table 2 Effect of  $\alpha$ -TiCl<sub>3</sub> activation on interaction and polymerization rate (temp. 50°C, time 180 min.)

	$\alpha$ -TiCl <sub>3</sub> (m)	$\alpha$ -TiCl <sub>3</sub> (s)	$\alpha$ -TiCl <sub>3</sub> (n)
$s \text{ (m}^2/\text{g)}$	80	10-12	5
$k_{cl} \cdot 180 \text{ (\%)}$	19	8.6	1.1
$k_{cl} \cdot 10^2 \text{ (\%/min.)}$	1.7	2.6	0.15
$k \cdot 10^2 \text{ (1/g.min.)}$	2.4	3.7	0.75
$k_{cl}/\bar{k}$	0.71	0.70	0.20

$\alpha$ -TiCl<sub>3</sub>(m) - activated by milling in heptane  
 $\alpha$ -TiCl<sub>3</sub>(s) - activated by dry milling  
 $\alpha$ -TiCl<sub>3</sub>(n) - non-activated

The results show that the ratio  $k_{cl}/\bar{k}$  is almost the same for activated TiCl<sub>3</sub>. This would support the existence of a close correlation between interaction and polymerization. The efficiency of interaction was higher for non-activated TiCl<sub>3</sub>. A quantitative comparison between the interaction and polymerization reaction is shown in Table 3.

Table 3 Comparison of the rate of interaction and the rate of initiation for  $\alpha$ -TiCl<sub>3</sub> (temp 50°C and time 180 min.)

$s_{TiCl_3}$ m <sup>2</sup> /g	3 (non-activated)	80 (activated)	120
rate of initiation . 10 <sup>5</sup> ( $\bar{K}$ )	4.6	21	15
rate of exchange reaction . 10 <sup>5</sup> ( $K_{cl}$ )	2.6	51	66
<u>rate of exchange reaction</u> rate of initiation	0.56	2.4	4.4

From the results it is clear that in regard to the order of magnitudes, the rate of initiation is in agreement with the rate of the exchange reaction. In addition, the difference between the non-activated and activated TiCl<sub>3</sub> indicate that the efficiency of the exchange reaction decreases with activation. It is possible that only a part of potentially active centers formed by the interaction of the catalytic components gives active polymerization centers, or in addition to the formation of polymerization centers the interaction also occurs on faces unsuitable to provide active sites.

#### CONCLUSIONS

The rate of interaction between the catalyst components of the system formed by TiCl<sub>3</sub> and AlEt<sub>3</sub> influences the rate of polymerization. The decrease in activation energy of polymerization coincides with a decrease in activation energy of interaction. The mode of activation has also a very strong effect on the efficiency of the interaction reaction. The efficiency of the exchange reaction decreases with the activation of TiCl<sub>3</sub>.

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