

Interaction of α -TiCl₃ with organoaluminium compounds and its correlation with propylene polymerization

III. Formation of active centers

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SUMMARY

The characterization of polymer system by means of interaction reaction between the catalyst components of a Ziegler-Natta stereospecific system formed by TiCl₃ and AlEt₃ in heptane was carried out. The experimental results show that the formation and decay of the active centers are interdependent. The interaction of the catalyst components, which causes a destruction of the solid phase, influences the rate of polymerization.

INTRODUCTION

A basic condition for the polymerization activity of the catalyst is an interaction of the catalyst components, i.e. alkylation of the solid phase. A possible mechanism for the formation of active centers from the catalytic components has been discussed (1-3). An investigation of the alkylation with various types of catalyst including ternary systems involving electron donors was reported in our previous publications (4,5). The alkylation and subsequent reactions proceed with different ways in different systems and they result in a characteristic course of the polymerization as well as in characteristic physical properties of the polymer. A complete characterization of the different polymerization systems by means of interaction reactions of catalyst components is rather difficult (6). The present study concerns the formation and decay of active centers of the catalyst components and their influence on polymer properties.

EXPERIMENTAL

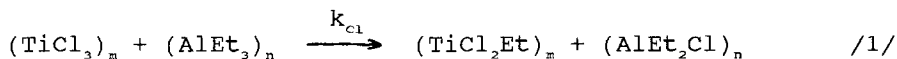
α -TiCl₃, AlEt₃, AlEt₂Cl, AlEtCl₂, heptane, and pyridine were prepared and characterized as described earlier (4,7). The apparatus and procedure for following the alkylation exchange reactions have been described (4,7). Characterization of polypropylene, atactic, isotactic, and stereoblock, was carried out by fractionation in heptane. Average molecular weight of the fractions was determined by viscosity.

RESULTS AND DISCUSSION

During the interaction of the catalyst components, the

amount of chlorine transferred from the solid to the liquid phase and the amount of gaseous products were determined. The portion of chlorine found in the liquid phase is defined as chlorine exchanged, Cl_{ex} . The conversion of exchanged chlorine is expressed in % of total Cl present in $TiCl_3$. Similarly, the amount of gaseous products, corresponding to the alkyl of the respective organometal, is called hydrocarbon liberated, RH, and expressed in % of RH from decomposed 100% alkylated $TiCl_3$.

The exchange reaction can be expressed as follows (1,8):



Where k_{cl} is the instantaneous rate constant of chlorine exchange. Similarly, the rate of hydrocarbon formation may be characterized by the constant k_{RH} . According to Rodriguez et al. (1,8) the hydrocarbons are formed by two different reactions:

$$RH = RH_{total} = RH_c + RH_d \quad /2/$$

Experimentally it is difficult to distinguish between RH_c and RH_d and therefore k_{RH} can be used only for a qualitative evaluation.

The rate of exchange reaction can be described by the following equation:

$$k_{cl} = (k_{oc1} - k_{cl}) \cdot e^{-k_{sc1} t} + k_{cl} \quad /3/$$

Where the rate constants are defined as follows:

k_{oc1} - at time 0 %/min.

k_{cl} - at time t %/min.

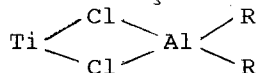
k_{cl} - at time t, when equilibrium is reached %/min.

k_{sc1} - diminution of exchange reaction with time¹/min.

The physical meaning of the equation /3/ may be visualized as follows:

1) At the beginning, a fast alkylation of the $TiCl_3$ crystal surface takes place on the basal (0001) as well as on the lateral faces, and on defect sites.

2) Basal faces of $TiCl_3$ are covered by the product,



and become inactive for further chemical reaction. After washing away these products, one may open the surface for further reaction (6,9).

3) The lateral faces undergo a continuous destruction which enables further reaction on the open surface or defect sites. Contrary to the results of Rodriguez et al. (1,8) it was shown

earlier (4) that chlorine atoms present on α - TiCl_3 surface faces are also involved in the exchange.

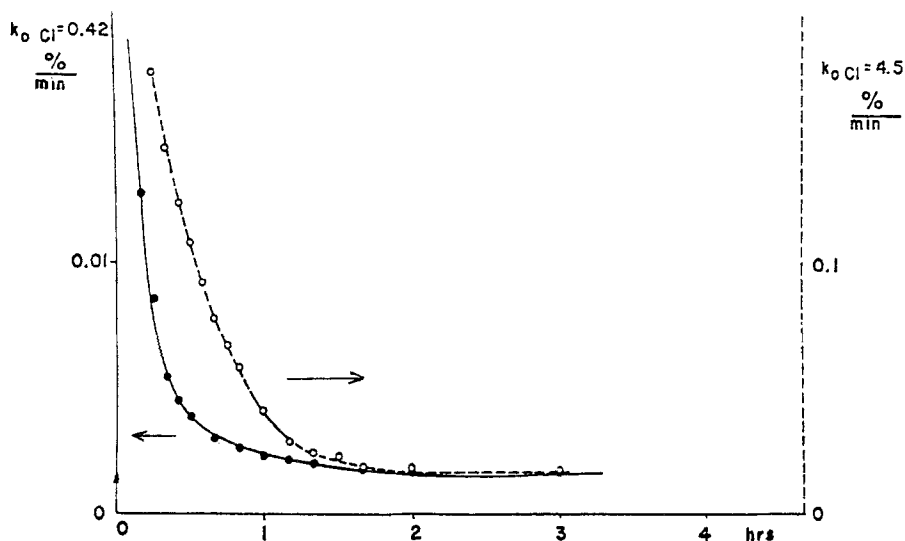


Fig. 1 The time dependence of the rate of chlorine liberation. $\text{TiCl}_3 = 4.54$ mmole/l; $\text{Al/Ti} = 3$
 ----- TiCl_3 ; $s = 5$ m^2/g ; ----- TiCl_3 ; $s = 80$ m^2/g .

From the Fig. 1 it is clear that the exchange did not stop but that only an equilibrium value (k''_{Cl}) has been reached for activated and non-activated TiCl_3 . Considering the subsequent inactivity of basal faces it is more probable that the interaction would continue at a constant rate on the lateral faces or at defect sites. Beside the basal faces, non-activated TiCl_3 has mainly the lateral faces. If the active centers were formed by interaction on lateral faces at a constant rate and if all active centers stayed, the polymerization rate should increase continuously. This, however, was not observed. In that case it is more probable that after certain time, an equilibrium is established between the formation and destruction of active centers. In the case of activated α - TiCl_3 , the situation is little more complicated. Beside the basal and lateral faces, defect sites could be formed by preliminary milling. At these defect sites the exchange reaction may not proceed at constant rate and one should rather consider a decrease in the rate of exchange, because of the defects present on basal faces, which are later passivated by reaction products.

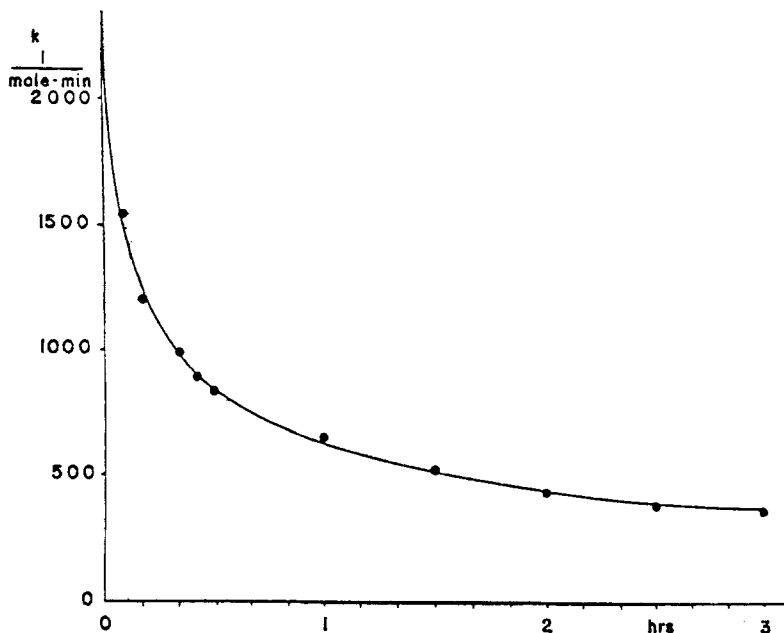


Fig. 2 The time dependence of the rate of polymerization.
 TiCl_3 ; $s = 80 \text{ m}^2/\text{g}$; $\text{TiCl}_3 = 0.76 \text{ mmole/l}$;
 $\text{Al/Ti} = 6.7$; temperature = 50°C ; $[\text{M}]_0 = 2.21 \text{ mole/l}$

The polymerization was performed under similar conditions as the interaction. The generally accepted kinetic equation

$$dP/dt = \bar{k} [\text{M}] = k_p \cdot c \cdot [\text{M}] = P = k_p [\text{M}] \int_0^t c \cdot dt \quad /4/$$

P = polymer formed (mole of monomer/mole _{TiCl_3})

t = time (min.)

k = propagation constant (l/mole min)

c = number of active sites

$[\text{M}]$ = monomer concentration (mole/l)

\bar{k} = rate constant (l/mole min)

shows that the change in the rate constant \bar{k} is due to the change in the number of active centers. For the sake of simplicity, k_p is assumed to be independent of possible variations in the formation of active centers. The time dependence of the rate constant k is shown in Fig. 2. The rate of polymerization decreased with the increase in reaction time. For non-activated TiCl_3 , the rate constant is very small. The variation in time dependence of non-activated $\alpha\text{-TiCl}_3$ may be due to an enlargement of the catalytic surface at the start of the polymerization with a corresponding increase in the concentration of active centers.

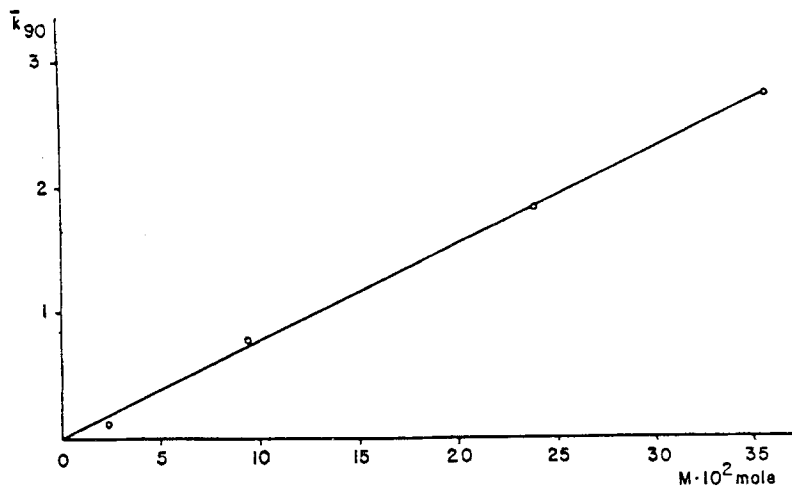


Fig. 3 The time dependence of the rate of polymerization on monomer concentration.

TiCl₃; s = 120 m²/g; TiCl₃ = 0.80 mmole/l;
Al/Ti = 6.7; temperature = 50°C; time = 90 min.

The effect of monomer concentration on the rate of polymerization is shown in Fig. 3. The straight line obtained proves that the decrease in polymerization activity is not a consequence of decreasing rate of diffusion of monomer to the active site. The course of the molecular weight-time dependence follows closely the course of the chlorine exchange-time dependence. The molecular weight undergoes substantial changes during the initial period of the interaction, whereas the molecular weight and the rate of chlorine liberation are almost independent of time during the later stages of polymerization and interaction.

CONCLUSIONS

The reaction between the catalyst components of the system formed by TiCl₃ and AlEt₃ in heptane can be followed by the determination of chlorine liberated from the solid phase and hydrocarbons formed by the destruction of solid phase and/or resulting from subsequent reactions. Studies with activated and non-activated TiCl₃ showed that the amount of chlorine liberated exceeds the amount of chlorine present on the surface. It has been observed that the rate of polymerization is closely related to the interaction of catalyst components.

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