Polymer Bulletin 22, 103–110 (1989)

Polymer Bulletin

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Interaction of α-$TiCl_3$ with organoaluminium compounds and its correlation with propylene polymerization

I. Kinetics of interaction

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SUMMARY

The interaction between the catalytic components of a Ziegler-Natta sterospecific system formed by $TiCl_3$ and $AlEt_3$ in heptane was studied. The extent of interaction was monitored by following the rate of chlorine exchange between the solid and liquid phase and by the development of gaseous hydrocarbons. The experimental results show that interaction between the catalytic components is a necessary but not the only condition for the formation of active centers of sterospecific polymerization.

INTRODUCTION

Since the discovery of Ziegler-Natta systems the structure of active centers and mechanism of their formation from the catalytic components has been continuously discussed in the literature (1-4). According to Keii et.al. the real active centers of polymerization are formed by an irreversible reaction between monomer and the equilibrium surface complex of titanium trichloride with an organoaluminium component (5). In the present work, an attempt was made to correlate the interaction occcuring between the catalytic components and the polymerization process.

EXPERIMENTAL

Chemicals and their purification

N-heptane was first rectifed in a column, then treated with sulfuric acid, washed with distilled water and dried with anhydrous Na_2So_4. The product was subsquently re-distilled with sodium metal and stripped with purifed nitrogen before use.

Titanium trichloride was prepared by the reduction of titanium teterachloride with hydrogen on tungsten sprial and ground under inert atmosphere in an Attritor-type ball mill (6). Triethylaluminium, diethylaluminium chloride and ethylaluminium dichloride were purifed by vacuum rectification and stored in n-heptane solution. Propylene used after rectification had the following composition: 99.88% C_3H_6; 0.11% C_3H_8.

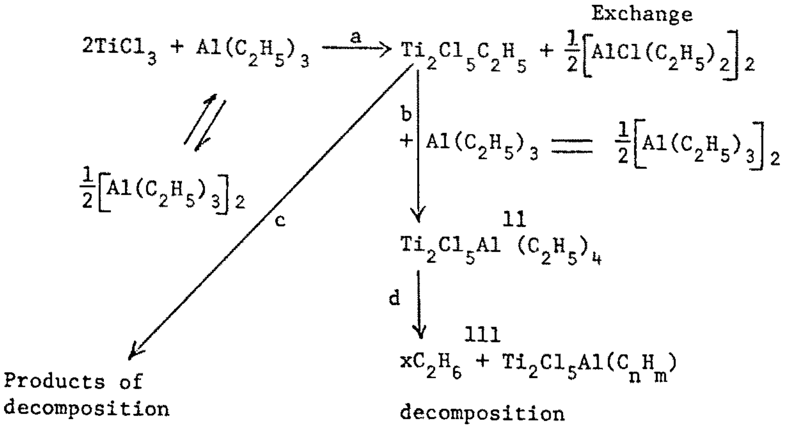
Apparatus and Procedure

The interaction of the catalytic components was carried out in a stirred 300 ml glass reactor joined to a high-vacuum line through a ground joint (7). While the interaction was underway, samples of the gaz phase were taken out and analysed by gas chromotography. Methane, ethane and ethyl were seperated using a 1m column packed with alumino-silicate while the hydrocarbons were analysed on a 9m column packed with 20% di-(2-ethylhexyl)phthalate on Chromosorb W. A flame ionisation detector was used in both cases. For hydrogen, an Alusil-packed column was employed in combination with a thermal conductivity detector.

Further analysis was carried out to find out the composition of the solid phase remaining after the interaction. For this, the liquid phase was removed by centrifuging the slurry and the remaining solids were dried in a vacuum oven. Titanium, chlorine, carbon and hydrogen contents were deterimned by elemental analysis.

RESULTS AND DISCUSSION

The kinetic study of interaction reactions is based on following degree of conversion of the exchange and decomposition reactions (1,2). The portion of chlorine found in the liquid phase, called cl_{ex}, is expressed in % of total Cl originally present in $TiCl_3$; the degree of conversion of decomposition reaction is related to the theortical quantity of hydrocarbon (RH, ethane in the case of $AlEt_3$) formed by the exchange of all Cl in $Ticl_3$ and by the decomposition of alkylated titanium.



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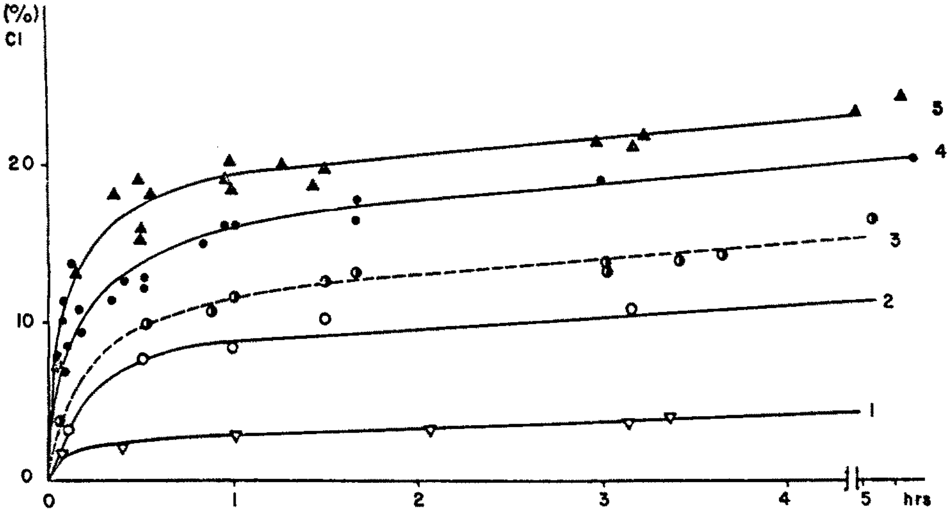

Fig. 1 The effect of components ratio on the time dependence of interaction reaction of α-$TiCl_3$ with $AlEt_3$. Al/Ti ratio; curve 1: 0.27; curve 2: 0.60; curve 3: 0.86; curve 4: 2-3; curve 5: 7.0

From Fig. 1 it can be seen that the conversion of the exchange reaction depends on the ratio of catalytic components. After an initial increase in the exchange reaction, the rate of conversion was not affected by reaction time. Also, starting from Al/Ti = 2-3 the exchange reaction is almost independent of further increase in Al/Ti. This corresponds to two moles of $AlEt_3$ for each gramatom of Cl exchanged, which is in agreement with the reaction scheme /1/.

The effect of temperature on the interaction reaction is shown in Fig. 2. Non-activated $TiCl_3$ at 50°C gave lower quantities of gaseous products (RH) than it would correspond to the total decomposition of the alkyltitanium component. This suggests that a part of the Ti-alkyl bonds remain undecomposed in the solid.

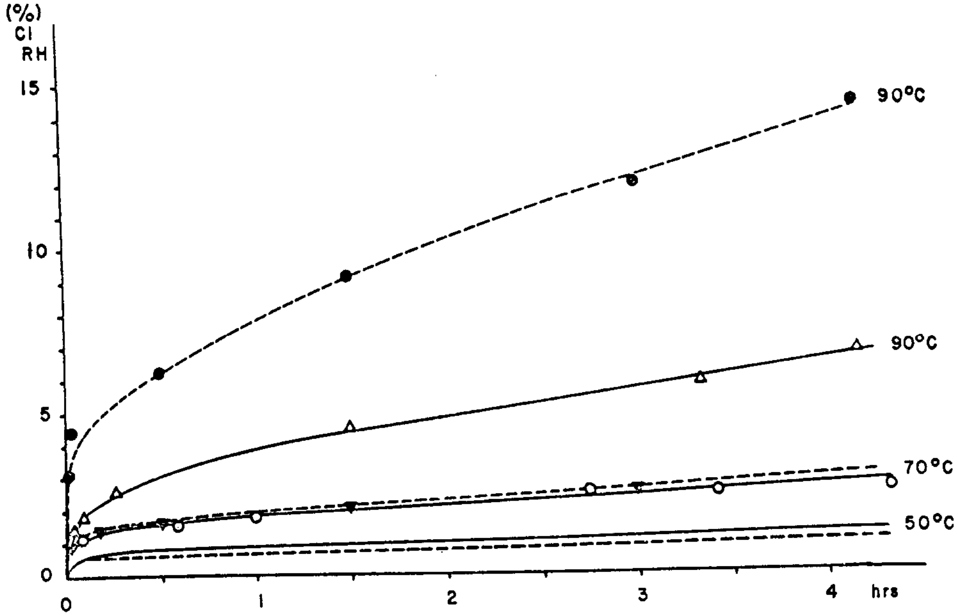

Fig. 2 The temperature dependence of the interaction between non-activated α-$TiCl_3$ and $AlEt_3$.
$S_{TiCl3} = 5\ m^2/g$; $TiCl_3 = 4.54$ mmole/l
—— $Cl_{ex} = Cl_1$; ---- RH

At higher reaction temperature (70°C), the rate of RH formation follows the rate of chlorine extraction from the solid phase. However, the rate of RH formation exceeds the rate of chlorine extraction at 90°C. The reaction would thus appear to follow the mechanism suggested by Rodriguez et.al. (1,2). It is known that an addition of electron donors (e.g. pyridiene) to the catalytic system formed by non-activated $TiCl_3$ and $AlEt_3$ can, depending on reaction conditions, either increase or inhibit the rate of polymerization (8).

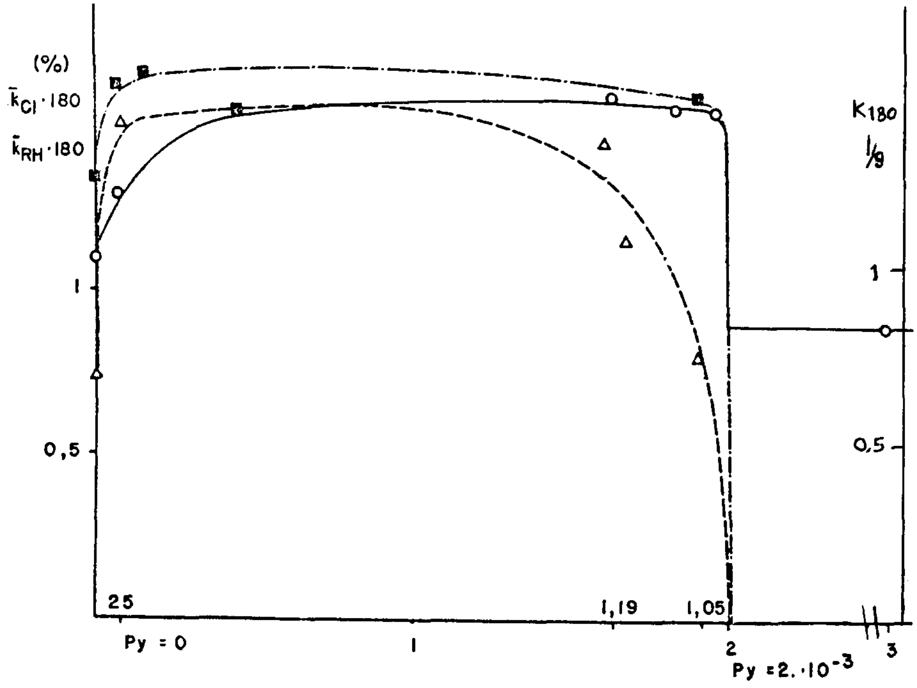

Fig. 3 The effct of pyridine on the interaction and polymerization of α-$TiCl_3$ with $AlEt_3$.
$s_{TiCl3} = 5\ m^2/g$; $TiCl_3 = 4.54$ mmole/l
Al/Ti = 2; t = 50°C; time = 180 min.;
polymerization: $TiCl_3 = 5.3$ mmole/l;
$M_o = 2.2$ mmole/l
□—·—·—·— Cl_{ex}; Δ - - - - RH; ○ ——— k average rate constant of polymerization.

From Fig. 3 it is clear that the increase in the rate of exchange reaction is followed by an increase in polymerization activity. At molar ratios Al/Py $\angle$ 1, polymerization is inhibited. Also the rate of interaction at Al/Py $\angle$ 1, as characterized by the formation of hydrocarbons (RH) is nearly equal to zero. As for as the exchange of chlorine is concerned, the reaction is rendered more complicated by secondary reactions by which a portion of Cl_{ex} is formed by the reaction with pyridine.

It was further shown that chemical reaction between the components also took part in the system $TiCl_3$-$AlEt_2Cl$, which is less active for propylene polymerization than the system using $AlEt_3$ as cocatalyst. From Fig. 4 it is obvious that gaseous hydrocarbons (RH) are also formed in this system. The quantity of RH increases with temperature, but, is substantially lower than $AlEt_3$ system. Also it is probable that the exchange reaction goes to a lower conversion.

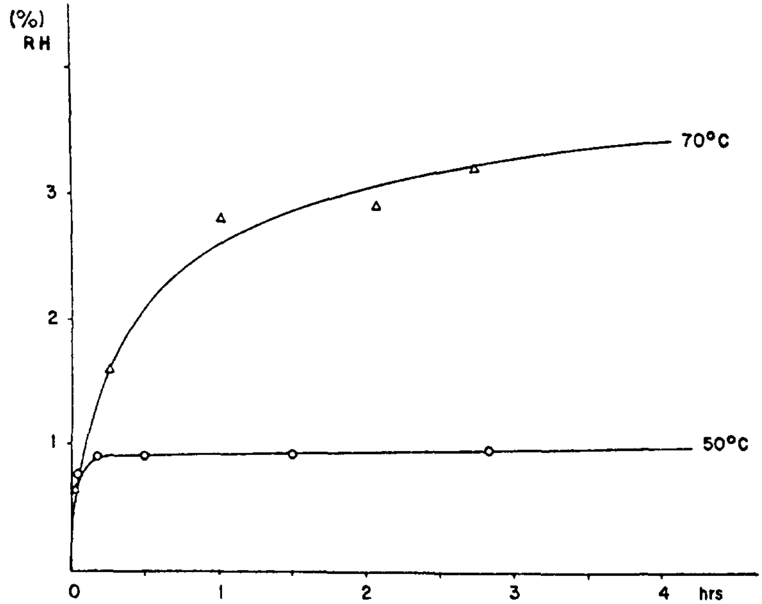

Fig. 4 The time and temperature depends on the gaseous products formation during the interaction between activated $TiCl_3$ and $AlEt_2Cl$
s_{TiCl3} = 80 m^2/g; $TiCl_3$ = 4.54 mmole/l
t = 70°C; Al/Ti = 8.6 t = 50°C; Al/Ti = 1

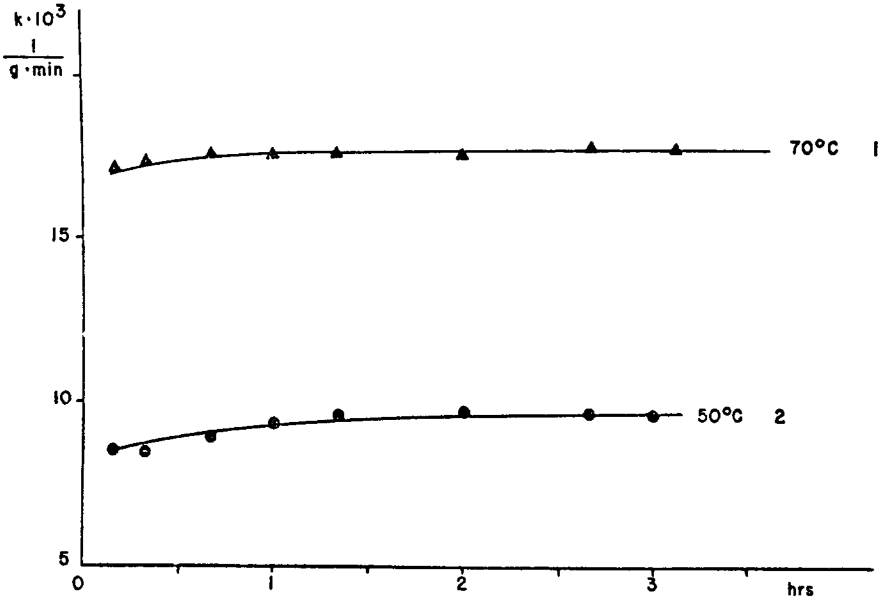

Fig. 5 The time and temperature dependence on the average rate constant of polymerization k in the system formed by activated $TiCl_3$ and $AlEt_2Cl$
S_{TiCl3} = 80 m²/g;
t = 70°C; $TiCl_3$ = 0.73 mmole/l; Al/Ti = 6.7
M_o = 2.09 mmole/l
t = 50°C; $TiCl_3$ = 0.90 mmole/l; Al/Ti = 6.1
M_o = 2.16 mmole/l

The dependence of the polymerization rate constant on time, at the same temperature used for the interaction reaction, is shown in Fig. 5. It may be stated that the increase of polymerization rate closely corresponds to the increase in RH formation. A chemical reaction is also observed in the system $TiCl_3$ - $AlEtCl_2$. Although its rate is very low compared to the system with $AlEt_3$, no polymerization activity is observed. This is because $AlEtCl_2$ ia also an inhibitor of stereospecific polymerization. Addition of an electron donor (e.g. pyridine) to the above system can increase the polymerization activity.

CONCLUSIONS

It has been shown that the polymerization systems, based on titanium trichloride and ethylaluminium compounds in heptane, involves a chemical interaction between the catalytic components. It must be noted, however, that the exchange reaction is not the only necessary condition which must be fulfilled in order that a formation of active centers take place. It is further necessary that this reaction occur on potentially suitable sites and that the growth of these sites be not limited.

ACKNOWLEDGMENT

The authors wish to express their thanks to Research Institute of Macromolecular Chemistry, Brno, Czechoslovakia for the opportiunity to perform the experimental work. The valuable discussions with Dr. J. Ambroz and Dr. J. Mejzlik in the course of experimental work is highly appreciated.

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Accepted June 20, 1989 K