# Polymerization of propylene by the Ziegler catalysts systems $\alpha$-$TiCl_3/Al(C_2H_5)_3$ and supported $TiCl_4/Al(C_2H_5)_3$

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A comparison of the polymerization kinetics of propylene employing the Ziegler catalysts $\alpha$-$TiCl_3/Al(C_2H_5)_3$ and $TiCl_4/Al(C_2H_5)_3$ supported on the carrier $SiO_2$ containing the reducing system Cu/Mg has been established. The polymerization was carried out at 50°C and 5 atm in toluene medium and the time dependence of polymerization rates for different $|Al|/|Ti|$ ratios are presented. They suggest that in the temperature range 30°–100°C the $TiCl_4$ is reduced directly *in situ* to give $TiCl_3$ in its active form. The apparent activation energy for the polymerization reaction with the supported systems is about 9.5 kcal/mol. The molecular weight of the polypropylene and tacticity obtained by the supported catalyst is lower than that produced by $\alpha$-$TiCl_3/Al(C_2H_5)_3$. The kinetic peculiarities observed for the supported titanium catalysts are explained by the higher dispersity and defectivity of the formed crystalline $TiCl_3$, and also by side reactions of the $TiCl_4$ with the carrier.

## INTRODUCTION

It has been shown that in conventional heterogeneous, Ziegler polymerization catalysts based on transition metal halides (i.e. $\alpha$-$TiCl_3$) the active sites for polymerization are those structural defects such as edges, step faults and chlorine vacancies, where the hexacoordination of titanium ions in $\alpha$-$TiCl_3$ crystals would be incompletely satisfied[1,2]. Many potentially active sites are buried deep within the particles and blocked. High activity second generation of Ziegler catalysts has been discovered by deposition of the transition metal compounds on certain specific supports[3] in order to open the crystal structure and increase the active surface. The amount of the polymer formed per gram of catalysts is so high that the removal of residual catalyst is not necessary to produce satisfactory polymer for processing. Most of the studies on supported Ziegler catalysts are covered by patents[4,5], thus very little is published in the scientific literature[6–11].

One of the ways to ascertain whether or not the support takes part in the catalytic process, is to compare the validity of the kinetic relationship established for conventional Ziegler catalysts, with those for supported catalysts. In ethylene polymerization Zakharov *et al.*[6] found a good agreement between the kinetics for $SiO_2$ supported $TiCl_4$ catalysts with different compositions and $\alpha$-$TiCl_3$ heterogeneous Ziegler catalysts. However, Baulin *et al.*[7] found some differences when MgO and aluminium silica carriers for $TiCl_4$ were used.

This paper is mainly concerned with a comparison of the kinetics of the polymerization of propylene employing the $\alpha$-$TiCl_3/AlEt_3$ and supported $TiCl_4/AlEt_3$ catalysts with the purpose of finding out the state of the titanium ions in the supported catalysts.

## EXPERIMENTAL

### *Material and catalysts preparation*

Polymerization grade propylene from Phillips was freed from oxygen and moisture by passing through successive columns packed with BASF R-3-11 catalysts in the reduced state, KOH, molecular sieve and $AlEt_3$[12]. Analytical grade toluene was employed as solvent after carefully purifying it by reflushing over LiH under nitrogen. $\alpha$-$TiCl_3$, $TiCl_4$ and $AlEt_3$ purchased from Schuchardt München were used without further purification.

The carriers employed in the preparation of the support catalysts were silica gels with a surface area between 150–340 $m^2/g$. $SiO_2$ previously calcinated at 160°C for 6 h in air was treated with CuO and $Mg(OH)_2$ and then heated at 150°C for 5 h under a $H_2$ flow. It was then impregnated with excess $TiCl_4$ in a rotating evaporator at 30°–100°C for 15–40 h in nitrogen and the excess of $TiCl_4$ distilled off under pressure, giving a violet solid.

The catalysts were analysed for their Ti contents by spectrophotometric and gravimetric methods.

### *Polymerization procedures and polymer characterization*

The polymerization procedure was mostly carried out at 50°C and 5 atm in a 1 litre glass reaction vessel, as reported previously[12]. The pressure of propylene and the temperature during the reaction were held constant. The experimental sequence was as follows. (a) The solid component of the catalytic systems was put in the reactor with 500 ml of previously purified solvent. (b) The required quantities of organo-aluminium cocatalysts were placed in a small container immediately above the solvent level. (c) By vigorously stirring, the $AlEt_3$ was freed by the solvent

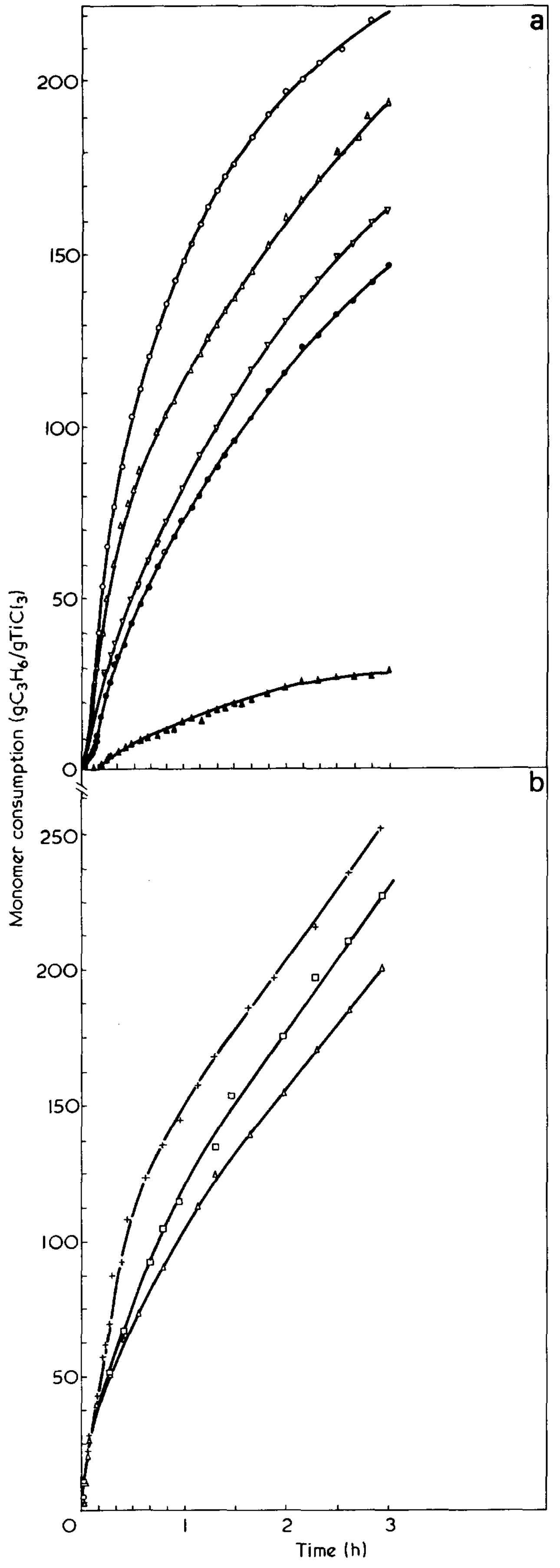


*Figure 1* (a) Monomer consumption for α-$TiCl_3/AlEt_3$ and (b) supported $TiCl_4/AlEt_3$ catalyst systems at various |Al|/|Ti| ratios: ▲, 2; ●, 3; □, 4; ▽, 5; △, 7; ○, 10; +, 16. (1 g $TiCl_3$/l in 500 ml toluene at 50°C and 5 atm)

and quickly mixed. This time was taken as the starting point of the reaction. The weight of the pressure bottle fitted to the reactor and containing the propylene was measured during polymerization and the difference in weight recorded.

The intrinsic viscosity of polypropylene was measured at 135°C in decalin containing 0.1% by wt of 2,6 di-terbutyl *p*-cresol. The molecular weight was calculated by the equation[13]:

$$|\eta| = 1.10 \times 10^{-4}\bar{M}_v^{0.80} \qquad (1)$$

The tacticity was determinated by the Hughes method[14]. Infra-red spectra in the region of 10.0 to 10.3 μm were obtained with a Perkin–Elmer model 577 spectrophotometer at room temperature.

## RESULTS

### *Polymerization rate*

The amounts of propylene used up in the polymerization reaction per weight unit of titanium as $TiCl_3$ are shown in *Figure 1* for conventional and supported catalysts. In both cases the propylene consumed depended on the |Al|/|Ti| ratio. However an initial build-up period is shown in the case of the conventional catalysts, while in the supported catalysts this occurs only at low ratios. The polymerization starts quickly at the beginning of the reaction for high ratios. This difference can be seen clearly in the time dependence of the polymerization rate shown in *Figure 2* and which was obtained by derivation from the curves in *Figure 1*. The kinetic curves for the conventional catalysts are of the 'decay' type, previously noted in the literature[15,16]. A build-up period is observed during which the polymerization rate increases rapidly to a maximum ($R_0$) and this is followed by the decay period where the rate decreases gradually to the stationary state ($R_\infty$). On the other hand, for the supported catalysts, only the decay period can be seen.

The decay period has been defined by the following equations[17]:

$$\frac{dR}{dt} = k_3(R - R_\infty) \qquad (2)$$

$$\text{or} \quad \frac{R - R_\infty}{R_0 - R_\infty} = \exp(-k_3 t) \qquad (3)$$

$$\text{and} \quad \ln(R - R_\infty) = k_3 t + \ln(R_0 - R_\infty) \qquad (4)$$

where the constant $k_3$ may be considered as the constant of the first order rate law governing the rate of approach of $R$ to $R_\infty$.

The validity of equation (4) for conventional and supported catalysts is shown in *Figure 3*. The experimental results show good agreement with the theory for the conventional catalysts and for all |Al|/|Ti| ratios, while $k_3$ is independent of the $AlEt_3$ concentration. This is also in accordance with other observations[18]. The linear relationship $\ln(R - R_\infty)$ vs. $t$ is satisfied only by high |Al|/|Ti| ratios for the supported catalysts.

The equation proposed by Pasquon *et al.*[19] for the decay period in the propylene polymerization with active

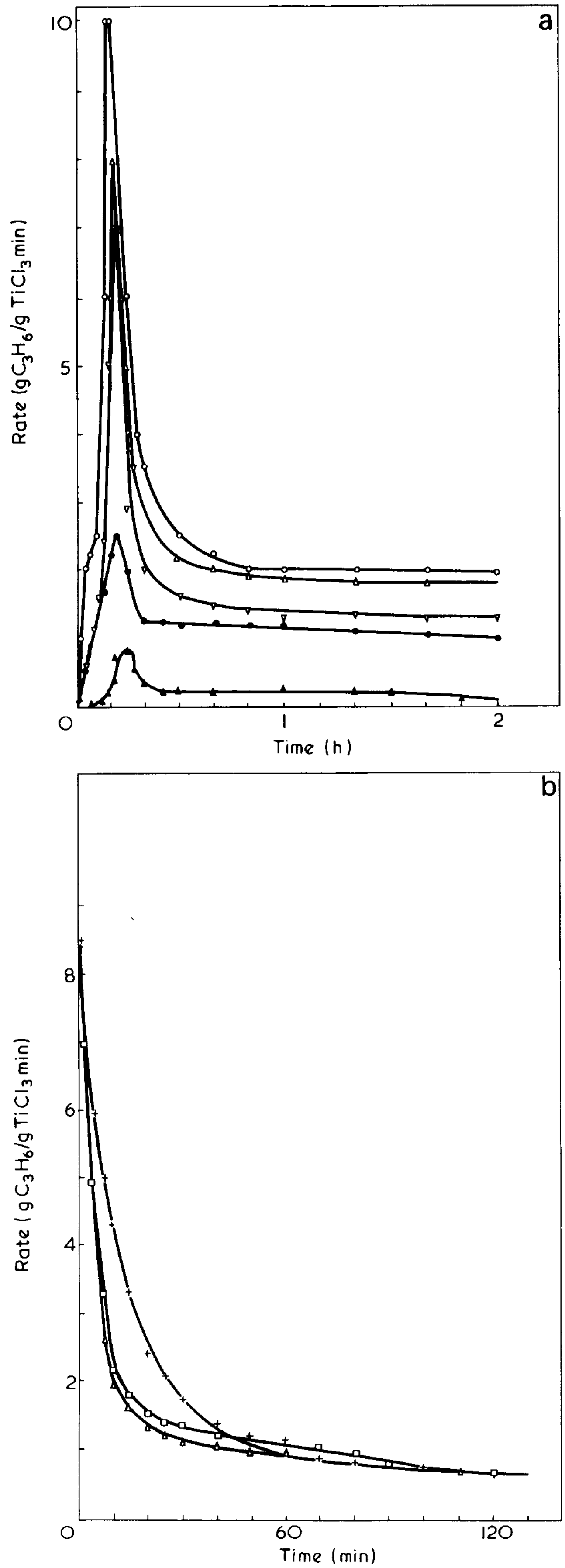


*Figure 2* (a) Kinetic curves obtained for α-$TiCl_3/AlEt_3$ and (b) supported $TiCl_4/AlEt_3$ catalyst systems at various |Al|/|Ti| ratios: ▲, 2; ●, 3; ▽, 5; △, 7; ○, 10; □, 11; +, 16. (1 g $TiCl_3$/l in 500 ml toluene at 50°C and 5 atm)

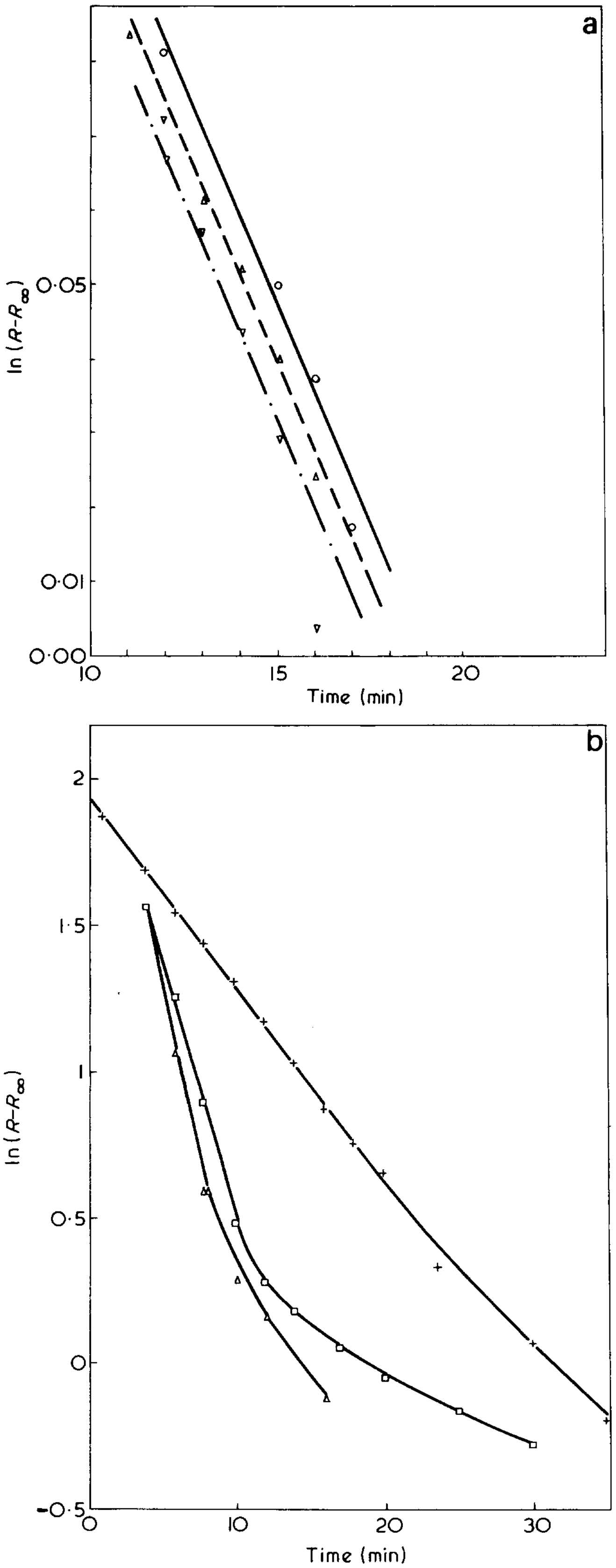


*Figure 3* (a) Kinetic data according to equation (4) for α-$TiCl_3$/$AlEt_3$ and (b) supported $TiCl_4/AlEt_3$ catalyst systems at various |Al|/|Ti| ratios: ▽, 5; △, 7; ○, 10; □, 11; +, 16. (1 g $TiCl_3$/l in 500 ml toluene at 50°C and 5 atm)

$TiCl_3/AlEt_3$ catalysts was modified by assuming that the monomer transfer through the polymer layer covering the catalyst surface was the rate determining step. Also by considering that the shape factor of the polymer layer

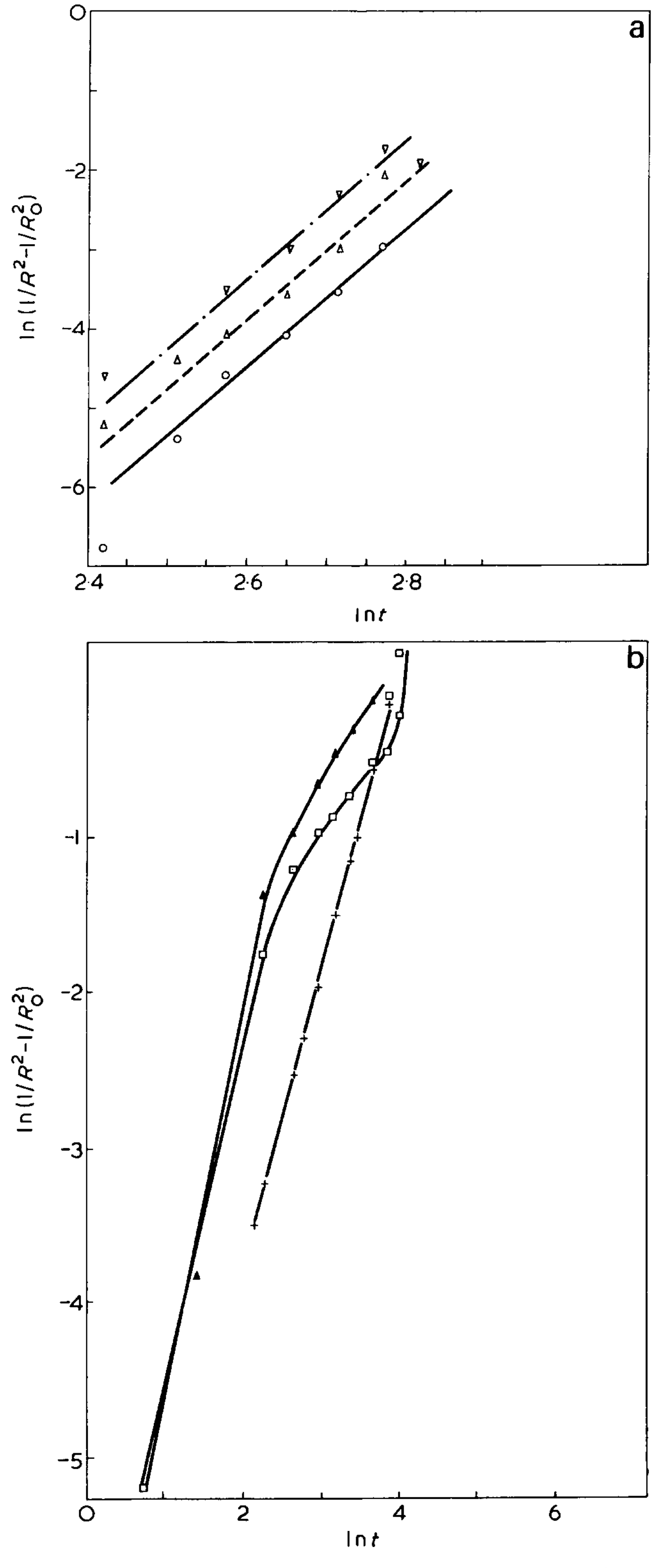


*Figure 4* (a) Kinetic data ccording to equation (5) for α-$TiCl_3$/$AlEt_3$ and (b) supported $TiCl_4$/$AlEt_3$ catalyst systems at various |Al|/|Ti| ratios: ▽, 5; △, 7; ○, 10; □, 11; +, 16. (1 g $TiCl_3$/l in 500 ml toluene at 50°C and 5 atm)

depends on time, we deduced the following equation[12]:

$$\ln \frac{1}{R^2} - \frac{1}{R_0{}^2} = \ln k/G^2|M| + 5 \ln t \qquad (5)$$

where, $k$ is a constant, $G$ is the mass of catalyst and $|M|$ is the monomer concentration. This modified equation fits very well with the experimental results for both catalytic systems, as can be observed in *Figure 4*. Again for the supported catalysts the agreement is established only for high ratios.

The activation energy obtained by temperature dependence of the stationary polymerization rate ($R_\infty$) and at high concentrations of $AlEt_3$ for the supported catalysts was about 9.5 kcal/mol (see *Figure 5*). Furthermore the time dependence of polymerization rate for supported catalysts depends on the carrier surface area, as shown in *Figure 6*. The amount of polymer per gram of catalyst was 320 when the surface area of the carrier was 320 $m^2/g$ and the activity found for α-$TiCl_3$ was 210, both at a polymerization time of 3 h (see *Figure 7*).

### *Polypropylene molecular weight and tacticity*

The molecular weight of polymers produced with α-$TiCl_3$ and supported $TiCl_4$ decreases gradually with the |Al|/|Ti| (see *Figure 8*). This indicates that $AlEt_3$ acts as a chain transfer agent[20]. The molecular weight of the polypropylene obtained by the supported catalysts is approximately one half of that produced by conventional catalysts. This is probably partly due to a higher concentration of active centres on the surface of catalysts produced by depositing $TiCl_4$ on the carrier[10,11].

The concentration effect of the $AlEt_3$ on stereospecificity of both catalyst systems can be observed in *Figure 9* and agree with previous observations[21,22]. The polypropylene isotacticity obtained by the supported catalysts is lower than that of the conventional catalysts. In the polymerization of propylene by heterogeneous catalysts, the high activity and the stereoselectivity are usually countercurrent[3].

## DISCUSSION

In works previously referred to, supported titanium catalysts for the ethylene polymerization are obtained by the following methods: (a) supporting $TiCl_4$ on $SiO_2$ giving a brown colour and reducing with $AlEt_3$ in the reaction medium[6]; (b) supporting $TiCl_4$ on $SiO_2$ and reducing by

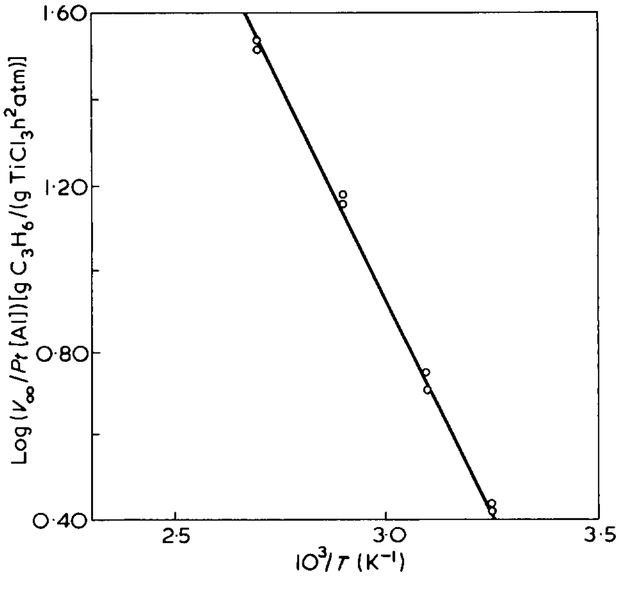


*Figure 5* Arrhenius plot of the stationary rate for the supported $TiCl_4$/$AlEt_3$ catalyst

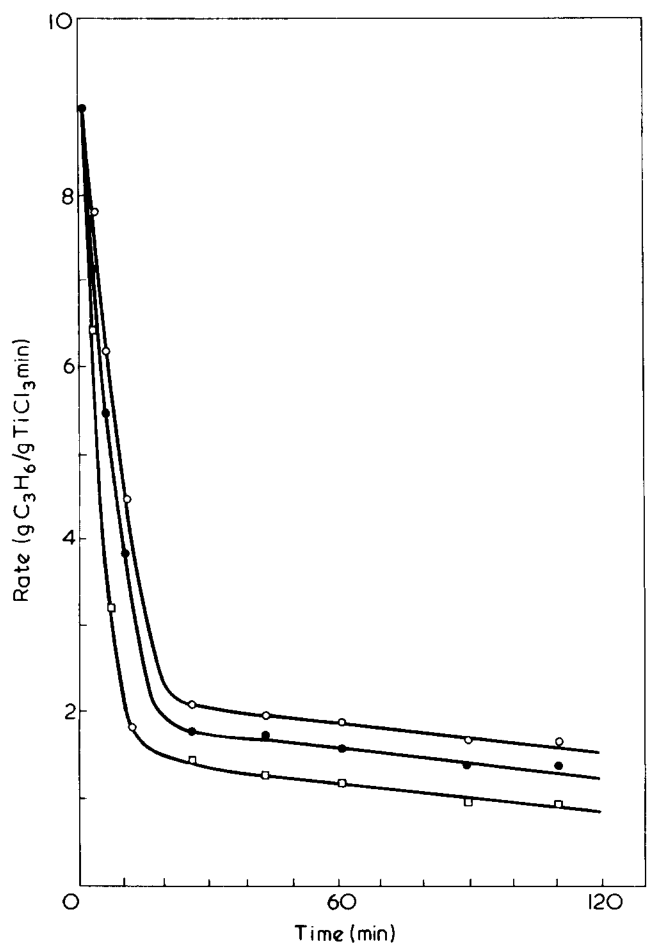


*Figure 6* Dependence of the kinetic data on time at various specific surface areas of the supported $TiCl_4/AlEt_3$: □, 250 $m^2/g$; ●, 290 $m^2/g$; ○, 320 $m^2/g$

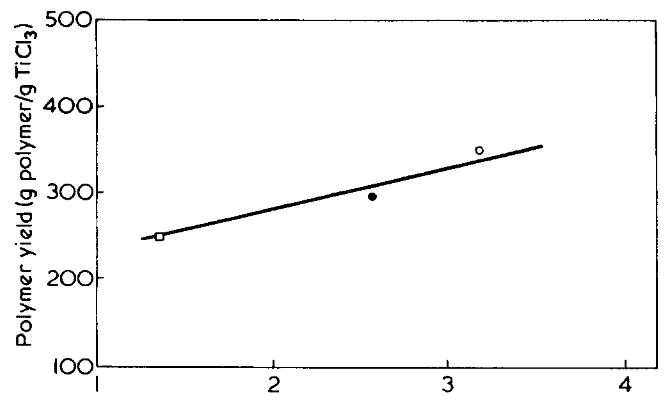
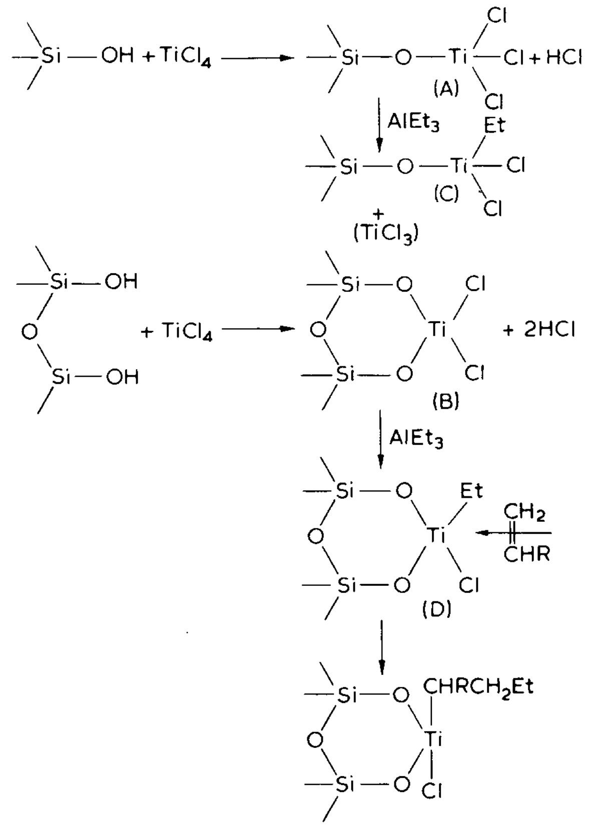


*Figure 7* Relationship between polymer yield and specific surface area for the supported $TiCl_4/AlEt_3$ catalyst

adding $AlEt_3$ prior to interaction with the reaction medium[5]; (c) supporting $TiCl_4$ on $Al_2O_3$[7] and (d) supporting $TiCl_4$ on MgO[6]. This last system was also employed for the propylene polymerization[8]. On the other hand, to prepare industrial Ziegler catalysts for heterogeneous polymerization of propylene using $TiCl_4$, the procedure is normally to reduce it, at high temperatures, *in situ* to $TiCl_3$ in its active violet forms $\alpha$, $\gamma$ or $\delta$[23]. With the support based on $SiO_2$ containing the reducing system Cu and Mg the violet colour is obtained—probably due to the formation of active $TiCl_3$ directly at low temperatures. It is reasonable to assume that for the supported catalysts, $TiCl_3$ is formed by and according to the same kinetic relationships as for conventional $\alpha$-$TiCl_3$. The apparent activation energy for the supported catalysts is similar to that reported by Natta *et al.*[15] for $\alpha$-$TiCl_3/AlEt_3$ (10 kcal/mol). The most important differences between conventional and supported catalysts can be explained by the presence of side reactions of the $TiCl_4$ and organo-aluminium compounds with the support surface as follows:



The hydroxyl group contained in the silica surface reacts with $TiCl_4$ giving single surface hydroxyls (Type A sites) and interacting surface hydroxyls (Type B sites)[24,25]. By adding the solution of organo-aluminium compound and under similar conditions corresponding to those used in carrying out the polymerization an alkylation of the Types A and B sites takes place, producing the Types C and D sites[26]. In addition, the decomposition of the initially formed surface complex by breaking the surface bond of the titanium ion to the support, leads to the formation of crystalline titanium trichloride[25,27].

According to Ballard *et al.*[26,28] the Types C and D sites can take part in the polymerization through the complexing of the olefin with the metal centre followed by a four-centre insertion reaction. Chain termination occurs easily by $\beta$-hydrogen abstraction and low molecular weights can be obtained.

At high |Al|/|Ti| ratios a larger quantity of $TiCl_3$ is obtained and the validity of the kinetic relationship for supported catalysts, when compared with the conventional catalysts is readily established[5,7].

The presence of the build-up period for the $\alpha$-$TiCl_3$ based catalysts is usually explained by the break-up of the titanium trichloride crystalline particles increasing the ac-

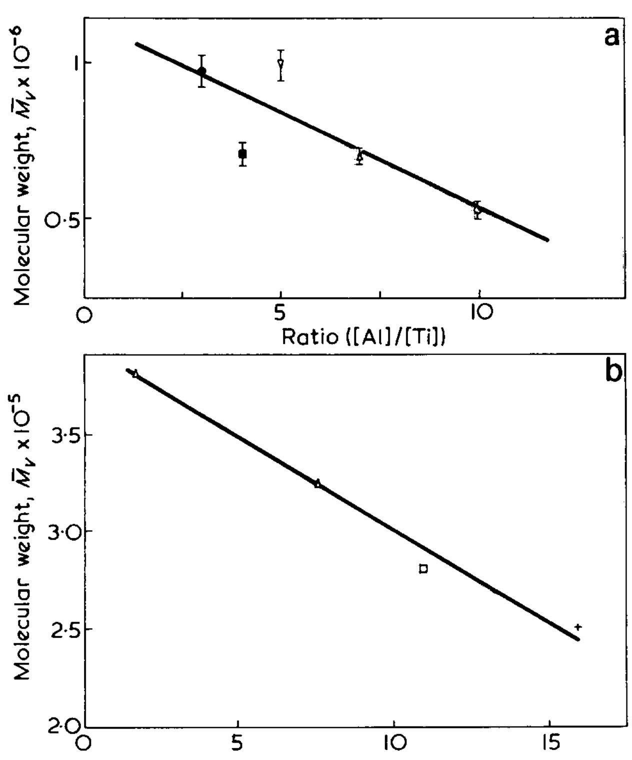


*Figure 8* Dependence of viscosity-average molecular weight on |Al|/|Ti| ratios for (a) $\alpha$-$TiCl_3/AlEt_3$ and (b) supported $TiCl_4/AlEt_3$ catalyst systems

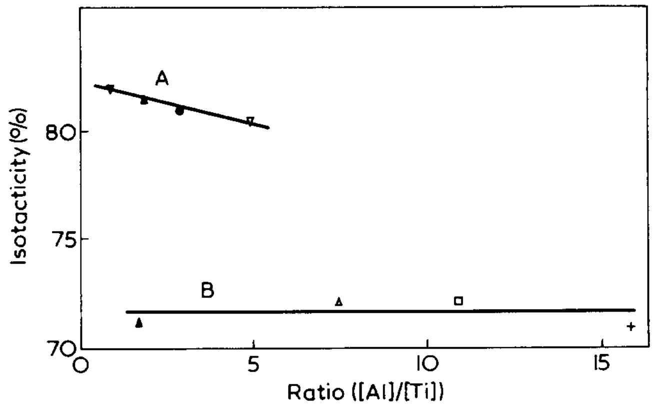


*Figure 9* Dependence of isotacticity on |Al|/|Ti| ratios for (a) $\alpha$-$TiCl_3/AlEt_3$ and (b) supported $TiCl_4/AlEt_3$ catalyst systems

tive sites number during the polymerization[15,29]. By dry milling this period is sharply reduced or may not be seen at all. The absence of the build-up period for the supported catalysts can be taken as evidence of the fine dispersion states of the titanium trichloride on the supported surface.

Finally the stereoselectivity loss of the supported catalysts can be explained by the modification of the crystalline defect morphology due to the crystal opening by deposition of the transition metal.

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