Polymerization of Propylene with Vanadium Halides and Aluminum Alkyls

From the Istituto di Chimica Industriale del Politecnico, Milano, and Laboratorio Ricerche, Divisione Petrolchimica, Soc. Montecatini, Milano, Italy

By G. Natta, G. Mazzanti, D. De Luca, U. Giannini, and F. Bandini

SUMMARY:

The polymerization of propylene with VCl_3 and aluminum alkyls has been studied. The decrease of the polymerization rate with the increase of the polymerization temperature, in the presence of the catalytic system $VCl_3-Al(C_2H_5)_3$, is connected with the surface reduction of VCl_3 to VCl_2. When using $Al(C_2H_5)_2Cl$ at temperatures below 90 °C. no reduction of VCl_3 is detectable, and the rate of polymerization regularly increases with increasing temperature.

Using VCl_3 in combination with $Al(C_2H_5)_3$ the stereospecificity is higher than in the case of $Al(C_2H_5)_2Cl$, in contrast to catalytic systems based on violet $TiCl_3$.

ZUSAMMENFASSUNG:

Die Polymerisation des Propylens mit Mischkatalysatoren aus Vanadiumtrichlorid und aluminiumorganischen Verbindungen wird beschrieben. Der starke Abfall der Aktivität des aus VCl_3 und $Al(C_2H_5)_3$ hergestellten Katalysators mit steigender Temperatur wird mit der an der Oberfläche stattfindenden Reduktion des VCl_3 zu VCl_2 in Beziehung gesetzt. Verwendet man $Al(C_2H_5)_2Cl$ bei Temperaturen < 90 °C, so beobachtet man keine Reduktion des VCl_3, aber eine regelmäßige Abnahme der Polymerisationsgeschwindigkeit mit der Temperatur.

Im Gegensatz zu Beobachtungen am Katalysatorsystem aus violettem $TiCl_3$ ist die Stereospezifität mit VCl_3 höher, wenn man $Al(C_2H_5)_3$ statt $Al(C_2H_5)_2Cl$ als metallorganische Verbindung verwendet.

Although it is known[1] that propylene and α-olefins can be polymerized with the aid of catalysts prepared from organometallic compounds and transition metal salts (of the 4th, 5th and 6th group of the periodic table), the attention of researchers has been almost entirely directed to the catalysts based on titanium salts.

The investigations made have clarified several aspects of the polymerization mechanism, but a number of uncertainties still exist in relation to the actual nature of the catalyst.

Therefore, with regard to the polymerization of propylene, we considered it useful to extend our research also to catalytic systems containing compounds of other transition metals.

Some authors[2] recently compared the behaviour of the two catalytic systems $Al(C_2H_5)_2Cl-VCl_4$ and $Al(C_2H_5)_2Cl-TiCl_3$ in the polymerization of propylene and in the ethylene-propylene copolymerization.

As known, the violet modifications of $TiCl_3$ give rise to a highly stereospecific catalyst by interaction with $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$. All the violet forms show the same stereospecificity and the α modification can yield catalysts having a constant activity for a long time[3].

On the contrary, a bulky precipitate is formed by treating VCl_4 with $Al(C_2H_5)_3$ or with $Al(C_2H_5)_2Cl$[2]: it essentially consists of a mixture of vanadium halides (in which vanadium is present in the di- and trivalent state) complexed with aluminum alkylhalides, and it does not exhibit a detectable sharp diffraction by X-ray analysis. This catalyst, which has a composition that varies with varying reaction conditions (Al/V ratio, temperature and concentration of the reagents) is not stable with time and its activity decreases rapidly.

This behaviour is analogous to that observed for $TiCl_4$ which, by interacting with alkyl aluminum, gives rise to the formation of a mixture of products (not yet fully identified) having a catalytic activity that decreases rapidly with time[4].

Therefore, the comparison between VCl_4 and $TiCl_3$ seems of little interest to us: one of them is soluble and the other is completely insoluble in hydrocarbon solvents, and they react with organometallic compounds in a very different way.

On the contrary, the comparison between the catalytic properties of $TiCl_3$ and of VCl_3 in the presence of organometallic compounds of aluminum, seemed more useful to us because both salts are isomorphous crystalline solids, insoluble in hydrocarbon solvents.

Therefore, in this paper we report the results obtained in the polymerization of propylene with the use of the catalytic systems $VCl_3-Al(C_2H_5)_3$ and $VCl_3-Al(C_2H_5)_2Cl$, and we compare them with the analogous catalytic systems based on $TiCl_3$.

Polymerization of Propylene with VCl_3 and $Al(C_2H_5)_3$

Fig. 1 shows the results obtained from kinetic runs of propylene polymerization with VCl_3 and $Al(C_2H_5)_3$, carried out at temperatures ranging from 40 to 90 °C. at a constant pressure and at the same monomer concentration.

The presence of an induction period is observed, the length of which tends to decrease with increasing polymerization temperature.
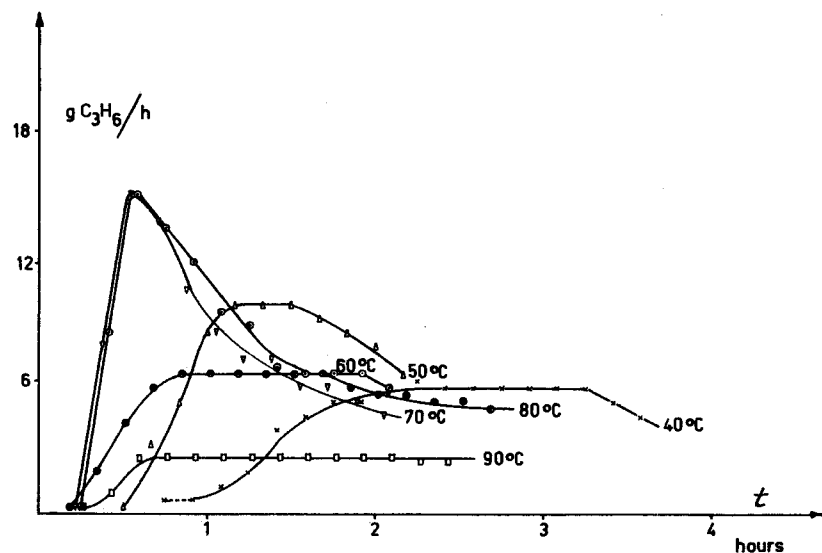
Fig. 1. Kinetic curves of propylene polymerization at constant monomer concentration and at different temperatures, in the presence of VCl_3 and $Al(C_2H_5)_3$.
Polymerization conditions: n-heptane = 200 ml.; $Al(C_2H_5)_3$ = 3.816 moles·10^{-3};
VCl_3 = 1.272 moles·10^{-3}; propylene = 0.765 mole/l.;
$\times$ = 40 °C., $\triangle$ = 50 °C., $\circ$ = 60 °C., $\triangledown$ = 70 °C., $\otimes$ = 80 °C., $\square$ = 90 °C.

Table 1. Reduction of VCl_3 with aluminum alkyls in n-heptane

VCl_3 mole/l.·10^3	Aluminum alkyl	Concentration mole/l.·10^3	Reaction condition temp. °C.	Reaction condition time min.	Weight-% of VCl_2 in the insoluble reaction product
12.7	$Al(C_2H_5)_3$	25.4	55	60	0
12.7	$Al(C_2H_5)_3$	25.4	60	60	2.10
12.7	$Al(C_2H_5)_3$	25.4	70	60	3.12
12.7	$Al(C_2H_5)_3$	25.4	80	60	4.05
12.7	$Al(C_2H_5)_3$	25.4	90	60	4.50
12.7	$Al(C_2H_5)_3$	25.4	95	60	4.76
12.7	$Al(C_2H_5)_3$	25.4	100	60	5.75
12.7	$Al(C_2H_5)_2Cl$	52,5	90	60	0
12.7	$Al(C_2H_5)_2Cl$	52.5	90	120	0
12.7	$Al(C_2H_5)_2Cl$	52.5	90	180	0

Even if it is difficult to compare the kinetic curves because only in the runs carried out at 40, 80, and 90 °C. the polymerization rate reaches a constant value for a certain length of time, it is yet evident that with increasing polymerization temperature above 70 °C. the polymerization rate decreases markedly.

We tried to connect this inversion, observed in the activity of the catalyst above 70 °C. with a variation of the chemical nature of the catalyst.

Some hypotheses put forward for the polymerization mechanism are based on a surface alkylation of the transition metal halide; in the case of titanium, some organometallic derivatives have been isolated[5, 6], which also show a certain stability; on the contrary, analogous results have not been obtained in various attempts[7] to isolate analogous vanadium compounds because these are much more unstable and decompose rapidly to give lower valence compounds.

Therefore, it was reasonable to assume that the possible vanadium alkyl halides formed in the surface alkylation of VCl_3 might be decomposed more easily with the increase of temperature, with a consequent surface reduction of VCl_3 to VCl_2.

In order to confirm this hypothesis we studied the variation of the vanadium valency in the catalysts prepared from VCl_3 and aluminum triethyl at various temperatures and under the same conditions adopted for the polymerization (Fig. 1). As can be observed in Table 1, while at 50—60 °C. vanadium trichloride is only slightly reduced, at least under the reaction conditions adopted by us, the amount of VCl_2 increases markedly and continuously with an increase in temperature.

Since the activity of the catalytic system VCl_2—$Al(C_2H_5)_3$ is very low it can be realized how the activity of the catalyst decreases when the polymerization temperature and, consequently, the surface reduction of VCl_3 increase.

It can also be understood that the polymerization rate markedly decreases, though the percentage of vanadium dichloride formed is very low, considering that the reduction of vanadium trichloride occurs almost exclusively in correspondence with the formation of active centers on its surface and that the number of active centers is very low (e.g., in the case of the catalytic system $TiCl_3$—$Al(C_2H_5)_3$ it was found that the number of active centers varies from 1 to 7 mole-% with respect to $TiCl_3$)[8,9].

Heated to high temperature the catalyst undergoes a permanent transformation that modifies its activity; this is also proved by the fact that, if the catalyst has been previously heated to a temperature above that of polymerization, its activity is much lower than that found at the same temperature for an unaged catalyst (Fig. 2).
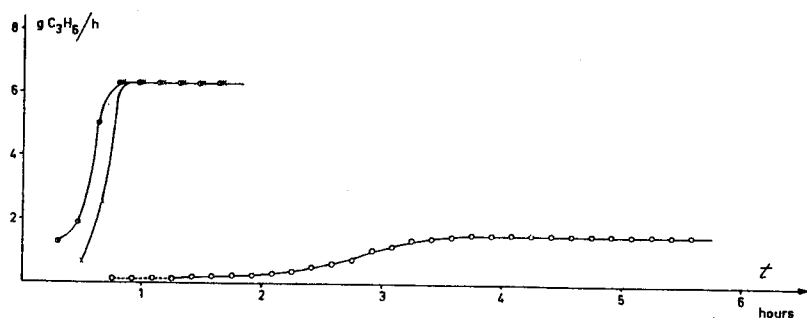
Fig. 2. Kinetic curves of propylene polymerization at constant monomer concentration in the presence of an aged catalyst

Polymerization conditions: n-heptane = 200 ml.; $Al(C_2H_5)_3$ = 3.816 moles$\cdot 10^{-3}$; VCl_3 = 1.272 moles$\cdot 10^{-3}$; propylene = 0.645 mole/l.

× = Polymerization at 50 °C., unaged catalyst; ◑ = Polymerization at 50 °C., catalyst aged for 3 hrs. at 50 °C.; ○ = Polymerization at 50 °C., catalyst aged for 3 hrs. at 90 °C.

The irregular behaviour of the kinetics of the polymerization at 50, 60, and 70 °C., detectable from the curves reported in Fig. 1, which show a high initial polymerization rate, then decrease rapidly, can be discussed by considering the following hypotheses:

a) the decrease in rate is mainly due to a continuous decrease, during the polymerization, of the diffusion rate of the monomer to the surface of the catalyst. This decrease in the diffusion rate of the monomer should be due to a conglobation of the catalyst by the polymer formed on its surface.

b) The catalyst undergoes a variation with time so that the active centers previously formed disappear and consequently the catalytic activity decreases.

The first hypothesis can be excluded by observing the data of Fig. 3, which shows the kinetic polymerization curves corresponding to different monomer concentrations. A decrease in the polymerization rate with time is observed in both cases, independently of the amount of polymer found, even at a lower monomer concentration.

With regard to the second hypothesis, it must be pointed out that the variation of the catalyst with time is strictly connected with the polymerization process and occurs only during the polymerization. In fact, by comparing the kinetic curves of two polymerizations carried out at 60 °C. and under the same conditions, but operating in one case in the presence of a catalyst aged for two hours at 60 °C., the only difference observed is a decrease of the induction period (Fig. 3).
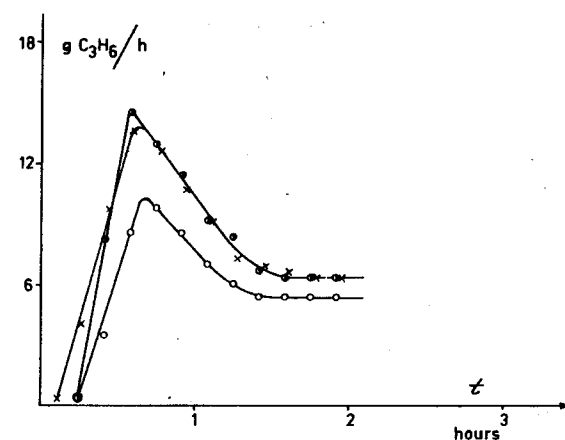

Fig. 3. Kinetic curves of the propylene polymerization at constant pressure in the presence of VCl_3 and $Al(C_2H_5)_3$ at different monomer concentration

Polymerization conditions: n-heptane = 200 ml.; VCl_3 = 1.272 moles$\cdot 10^{-3}$; $Al(C_2H_5)_3$ = 3.816 moles$\cdot 10^{-3}$; T = 60 °C.

◑ = total pressure = 825 Torr; × = total pressure = 825 Torr, catalyst aged for 2 hrs. at 60 °C.; ○ = total pressure = 760 Torr
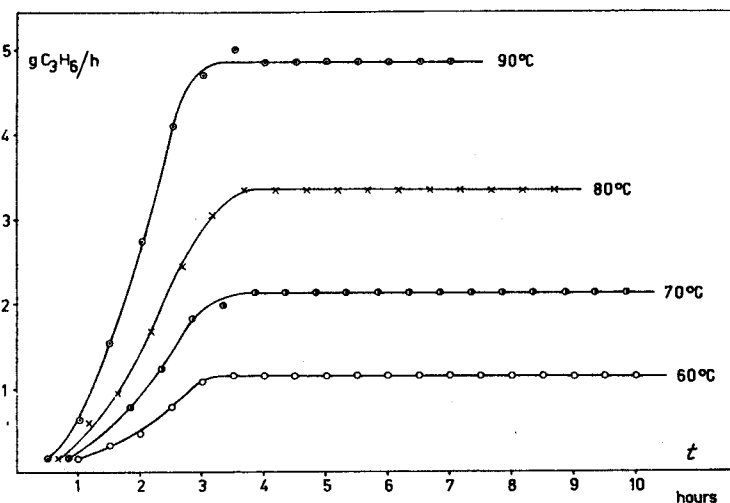

Fig. 4. Kinetic curves of propylene polymerization at constant pressure in the presence of VCl_3 and $Al(C_2H_5)_2Cl$ at different temperatures

Polymerization conditions: n-heptane = 200 ml.; $Al(C_2H_5)_2Cl$ = 12.72 moles$\cdot 10^{-3}$; VCl_3 = 3.18 moles$\cdot 10^{-3}$; propylene = 1,785 mole/l.

○ = 60 °C.; ◑ = 70 °C.; × = 80 °C.; ⊙ = 90 °C.

Polymerization of Propylene in the Presence of VCl_3 *and* $Al(C_2H_5)_2Cl$

When in the catalytic system $Al(C_2H_5)_3$–VCl_3 triethylaluminum is substituted by aluminum diethylmonochloride, the rate of the propylene polymerization (at constant monomer concentration) increases with the rise of temperature and, under the temperature conditions considered, it keeps constant in time (Fig. 4). This different behaviour of the two catalytic systems can be explained by the lower alkylating activity of $Al(C_2H_5)_2Cl$ compared with $Al(C_2H_5)_3$; while at 90°C., VCl_3 is reduced to the extent of approximately 4–5% by triethyl aluminum (0.0254 mole/l.) in 1 hr. a reduction does not occur with aluminum diethylmono-chloride; even in longer times and with a higher concentration of aluminum alkyl, no detectable reduction to V^{II} by titration with Ce^{IV} is observed.
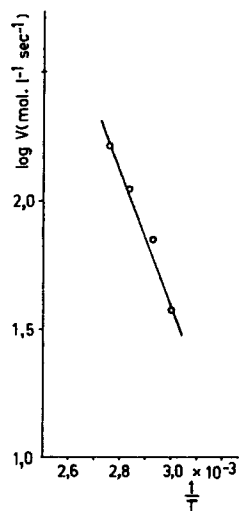
Fig. 5. Logarithm of the polymerization rate of propylene with VCl_3 and $Al(C_2H_5)_2Cl$ *vs.* the inverse of the absolute temperature. Polymerization conditions are those reported in Fig. 4

From the diagram of Fig. 5 drawn from Fig. 4, in which the logarithm of the reaction rate is reported, under constant rate conditions, as a function of the inverse of the absolute temperature, an approximate value of the activation energy of 11 kcal./mole is observed.

Properties of the Polymers Obtained

Fig. 6 reports the percentage of the X-ray crystallinity of the crude polymer, obtained with the use of the catalytic system VCl_3–$Al(C_2H_5)_3$, *vs.* the polymerization temperature.

The constant value of crystallinity with the variation of temperature is a result of two effects. In fact, by fractionating the polymer by boiling *n*-heptane extraction, the solvent insoluble polymer fraction decreases with the increase of the polymerization temperature (Fig. 7), while the X-ray crystallinity of this fraction increases simultaneously (Fig. 6).
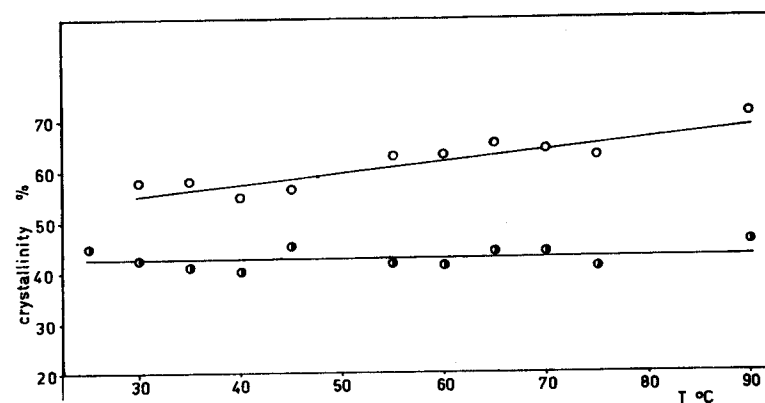
Fig. 6. X-ray crystallinity of polypropylene obtained with VCl_3 and $Al(C_2H_5)_3$ *vs.* polymerization temperature. Polymerization conditions are those reported in Fig. 1

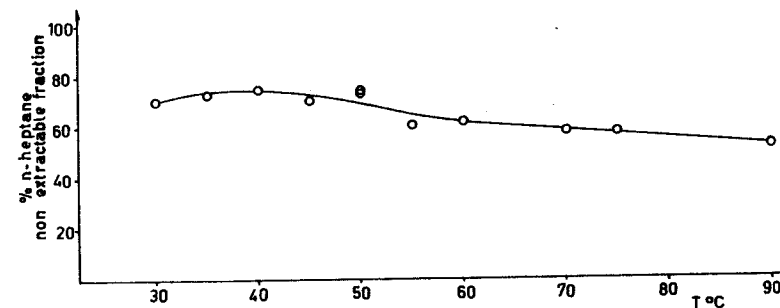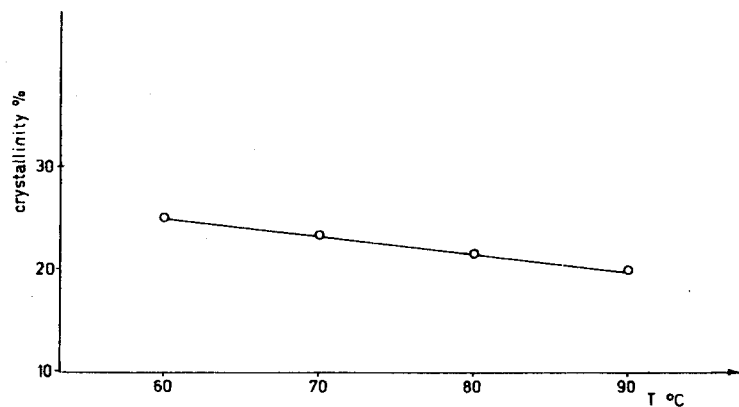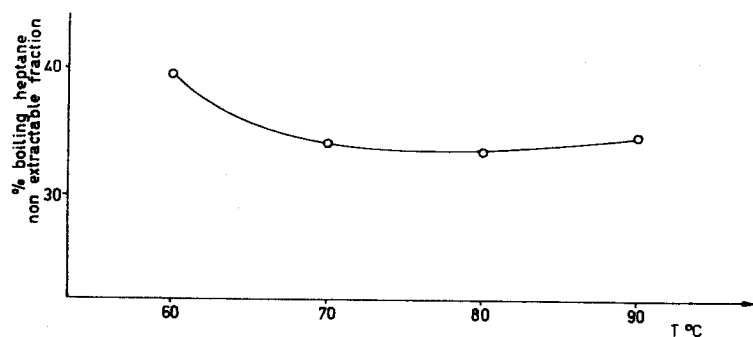◑ = crude polymer;   ○ = insoluble polymer in boiling *n*-heptane

Fig. 7. Percentage of non extractable polypropylene in boiling *n*-heptane as a function of the polymerization temperature. Polymerization conditions are those reported in Fig. 1

This can be explained by taking into account the higher rate of crystal-
ration shown by the isotactic macromolecules having the same steric
rity but a lower molecular weight.

As the molecular weight decreases with increasing polymerization
nperature, the isotactic fractions produced at higher temperature show
ligher crystallinity at X-rays, even if their steric purity is the same.
The polymers prepared with the aid of catalysts obtained from
l_3–Al$(C_2H_5)_2$Cl show, at the same polymerization temperature, a much
ver X-ray crystallinity and residue to the n-heptane extraction than
polymers obtained from VCl$_3$ and Al$(C_2H_5)_3$, (Figs. 8 and 9). This
s already been observed recently by other authors[10]. This behaviour
in contrast to observations with catalysts prepared from the violet

. 8. X-ray crystallinity of polypropylene obtained with VCl$_3$ and Al$(C_2H_5)_2$Cl *vs.* poly-
merization temperature. Polymerization conditions are those reported in Fig. 4

. 9. Percentage of insoluble polymer in boiling n-heptane *vs.* polymerization temperature.
Polymerization conditions are those reported in Fig. 4

modifications of TiCl$_3$ for which the polymers obtained with Al$(C_2H_5)_2$Cl
are sterically more regular than those prepared with Al$(C_2H_5)_3$[11].

We now are searching for an explanation of this difference; since now
we can point out that an analogous behaviour is observed also for com-
pounds of other metals of the 5th group.

Some authors[2] have observed the formation of soluble complexes be-
tween vanadium halides and aluminum halides or alkylhalides; if soluble
compounds of this type were formed in the reaction between VCl$_3$–
Al$(C_2H_5)_2$Cl, they could be responsible for the formation of the amorphous
polymer.

The change of the intrinsic viscosity of the residue of the heptane ex-
traction with varying polymerization temperature are reported in Figs.
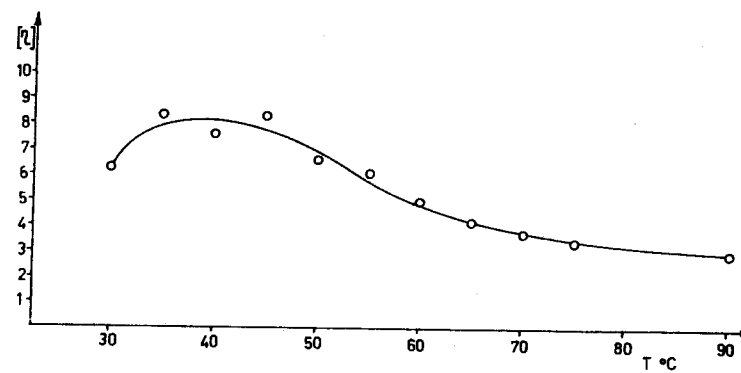10 and 11. The intrinsic viscosity increases when the polymerization

Fig. 10. [η] of insoluble polypropylene in boiling n-heptane, obtained in the presence of
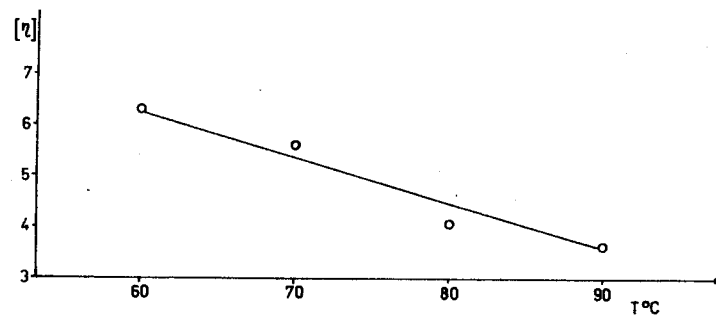VCl$_3$ and Al $(C_2H_5)_3$ *vs.* polymerization temperature

Fig. 11. [η] of insoluble polypropylene in boiling n-heptane, obtained in the presence of
VCl$_3$ and Al$(C_2H_5)_2$Cl as a function of the polymerization temperature

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temperature decreases, using either $Al(C_2H_5)_3$ or $Al(C_2H_5)_2Cl$ as organo-metallic compound.

Conclusions

In the polymerization of propylene with VCl_3 and $Al(C_2H_5)_3$ a decrease of the polymerization rate, due to the surface reduction of VCl_3 to VCl_2 is observed above 70 °C. Moreover, while $TiCl_3$ with $Al(C_2H_5)_2Cl$ yields more stereospecific catalysts than with $Al(C_2H_5)_3$, the polypropylenes obtained in the presence of VCl_3 and $Al(C_2H_5)_2Cl$ show a lower crystallinity than those prepared in the presence of VCl_3 and $Al(C_2H_5)_3$.

Experimental Part

Materials

VCl_3, a Stauffer commercial product, was purified by hot extraction with anhydrous benzene under nitrogen. Triethylaluminum was prepared according to Ziegler[12] and had the following properties: $Al(C_2H_5)_3 = 95\%$; $Al(C_2H_5)_2OC_2H_5 = 5\%$. Aluminum diethyl-monochloride was prepared according to Grosse and Mavity[13] and had an $Al(C_2H_5)(OC_2H_5)Cl$ content of about 5%.

Determination of bivalent and trivalent vanadium: it was observed that when using the redox methods of analysis described in the literature[14], errors can occur due to the possible oxidation of V^{II} present in the sample, at the expense of the hydrogen ions of the acid aqueous solution in which the sample is usually introduced before performing the redox titration. For this reason it was necessary to set up a particular procedure for the potentiometric dosage with standardized solutions of ceric sulfate in order to exclude the above mentioned oxidative phenomena[15].

[η] was determined in tetralin solution at 135 °C. using viscosimeters of the Desreux-Bischoff type.

The degree of crystallinity of the polymers was determined by X-rays, according to Natta and co-workers[16].

Polymerization Runs

Kinetic runs, carried out at constant temperature and pressure for the whole length of the run, were performed in a 550 ml. flask, equipped with buckets stirrer, connected with a manometer and a feeding tank.

The amount of olefin consumed in the reaction was determined by pressure variations vs. time, measured in the feeding tank in which the olefin was maintained in the gaseous state; it was thermostatized by circulating water.

Pressure in the reaction flask was kept constant by a regulation valve placed between the flask and the feeding tank.

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