

## Kinetic Studies of $\alpha$ -Olefin Polymerization

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### I. INTRODUCTION

The kinetic study of some organic syntheses has been, for over 15 years, one of the major research interests of the Industrial Chemistry Institute of the Milan Polytechnic. Kinetic work on catalytic hydrogenation, methanol synthesis and oxo-synthesis has been particularly fruitful in explaining apparent anomalies observed in the industrial development of these processes, and in clarifying their catalytic mechanism.<sup>1</sup>

In the polymerization field, we undertook a basic kinetic study on the products of  $n$  concurrent successive reactions, which, by 1945, had led to the solution of the resulting  $n$  differential equations.<sup>2</sup> Our application of this method to the anionic stepwise addition of ethylene oxide to alcohols showed that the reaction rate of each successive reaction step is higher than that of each initial step, owing to an activation attributable to the preceding highly exothermic reaction step.<sup>3</sup>

In 1952 we started work on the stepwise polymerization of ethylene by metal-organic compounds, as described by Ziegler<sup>4</sup> and began a kinetic study to determine the mechanism of the growth and termination reactions.<sup>5</sup> At first our main aim was to gain a sufficient understanding of these reactions to enable us to control and increase the molecular weight in the production of the polymers.

At the beginning of 1954 we succeeded in making the first regular, linear, head-to-tail polymers of  $\alpha$ -olefins. We attributed the heterogeneity of the raw polymers to the presence of macromolecules having different steric configurations, and devised methods for the separation of isotactic and atactic polymers.<sup>6</sup> After we had established both the structure of the isotactic polymers and the conditions under which we could control the stereospecificity of the catalytic systems, our experimental work turned to a thorough investigation of the nature of the catalysts and the polymerization kinetics. This new field of research has proved to be so wide that in the past four years the work has been divided between different groups of co-workers.

One group is particularly concerned with the chemical problems involved in the polymerization processes, e.g., the nature of the catalytic complexes and the improvement of their stereospecificity. By selecting particular catalytic systems, we have succeeded in synthesizing directly highly crystalline crude polymers (for instance, practically pure isotactic polymers)

or alternatively, with other systems, completely amorphous linear polymers of very high molecular weight.<sup>7</sup>

In the field of di-olefins, we have found processes with different kinds of stereospecificity, and have discovered classes of polymers previously unknown, *e.g.*, polymers with 1-2 linking and isotactic or syndiotactic structure.<sup>8</sup> In the case of butadiene, we have succeeded in preparing all four possible types of crystalline polymer, differing chemically and sterically, and have determined their crystalline structure. The 1,4-*cis* and 1,4-*trans* polymers were obtained with a very high degree of steric purity, enabling us to study their very interesting properties as well as their close analogies with the corresponding isoprene polymers.<sup>9</sup>

In the course of our work on the structure of the catalysts, we have been able to isolate crystallizable complexes containing metal-organic linkages and at least two different metal atoms, one of which is a transition metal.<sup>10</sup> Their crystalline structure has been accurately determined, and their catalytic behavior with different monomers investigated.<sup>11</sup>

In an attempt to extend coordination catalysis to vinyl monomers other than hydrocarbons, we have succeeded in obtaining isotactic polymers of aliphatic monomers containing oxygen,<sup>12</sup> silicon, tin,<sup>13</sup> and also of aromatic monomers containing halogen atoms.<sup>14</sup>

With another group of co-workers, I have begun a series of investigations on the structure of crystalline polymers, their physical properties, and the kinetics of the polymerization reaction. The kinetic study was extended to the stereospecific polymerization of  $\alpha$ -olefins and conjugated di-olefins both in systems which were heterogeneous throughout, and those which were, at least initially, homogeneous.

In this paper I will refer in detail to the system which we have studied most thoroughly, *viz.*, the polymerization and copolymerization of propylene.

## II. STEREOSPECIFICITY AND ACTIVITY OF POLYMERIZATION CATALYSTS

The heterogeneous nature of the catalysis in the stereospecific polymerization of  $\alpha$ -olefins, which we first suggested in 1954,<sup>15</sup> has been confirmed in our subsequent work.

The production of highly isotactic polymers (crude polymers containing over 85-95% of polymer not extracted by boiling heptane) was found to depend on the presence both of a catalyst and of a highly crystalline substrate (having a layer lattice).<sup>16</sup> Catalytic complexes containing transition metals and metal-organic groups, which alone do not polymerize the  $\alpha$ -olefins, are not stereospecific catalysts when adsorbed on the surface of amorphous substances, but become highly stereospecific when adsorbed on highly crystalline supports.<sup>17</sup> Furthermore, there are some insoluble crystalline compounds (having a layer lattice) which alone, or even in the presence of aluminum alkyls, cause virtually no polymeriza-

tion; but when added to soluble complexes (which again are inactive alone) yield stereospecific polymerization systems.<sup>18</sup> For example, certain crystalline compounds of metals in the eighth group of the Periodic System behave in this way (Table I).

TABLE I  
Stereospecificity of Propylene Polymerizations with  
Triethyl Aluminum and Different Titanium Compounds at 70–80°C.,  
Using *n*-Heptane as Solvent

Titanium compound	% polypropylene not extractable in boiling <i>n</i> -heptane
Violet $\text{TiCl}_3$	80–90
Brown $\text{TiCl}_3$	40–50
$\text{Ti}(\text{OC}_3\text{H}_7)_4$	Only traces
$\text{Ti}(\text{OC}_3\text{H}_7)_4$ on $\text{SiO}_2\text{—Al}_2\text{O}_3$	0–10
$\text{Ti}(\text{OC}_3\text{H}_7)_4$ on $\text{CoCl}_2$	35–45

The structure of the crystalline support is of great importance.  $\text{TiCl}_3$  was known to be dimorphous, but we have found that it can exist in three crystalline forms which we call  $\alpha$ ,  $\beta$ , and  $\gamma$ . Figure 1 indicates the struc-

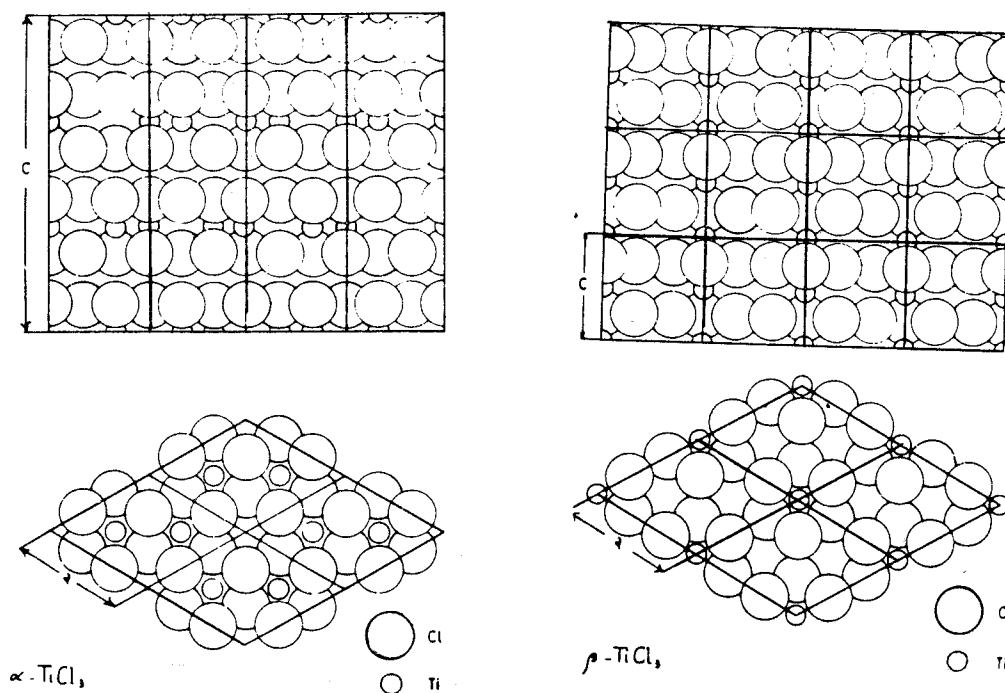


Fig. 1. Crystalline structure of  $\alpha$  (violet)- and  $\beta$  (brown)-  $\text{TiCl}_3$ .

tures of the  $\alpha$  (violet)<sup>19</sup> and pure  $\beta$  (brown)<sup>20</sup> forms. In the case of diolefins, the formation of polymers with predominantly 1,4-*cis* linking occurs only with the  $\beta$ -form, while the  $\alpha$ -form gives the 1,4-*trans* polymer. The  $\gamma$ -form also gives mainly 1,4-*trans* polymer.<sup>21</sup> In the case of  $\alpha$ -olefins, the  $\alpha$ -form leads to sterically purer polymers than do the other forms.

The stereospecificity also depends on the ionic radius of the metal-organic compounds. Metal-organic compounds of highly electropositive metals with a very small ionic radius give complexes with transition metal compounds which are more stable than corresponding complexes containing either less electropositive metal atoms or more electropositive metal atoms with a larger ionic radius (Table II).<sup>16,22</sup>

TABLE II  
Stereospecificity of Catalyst Prepared from a Sample of  
Violet  $\text{TiCl}_3$  and  $\text{Me}(\text{C}_2\text{H}_5)_n$   
(Temp. =  $75^\circ\text{C}$ .  $p_{\text{C}_3\text{H}_6} = 2.4 \text{ atm.}$ )

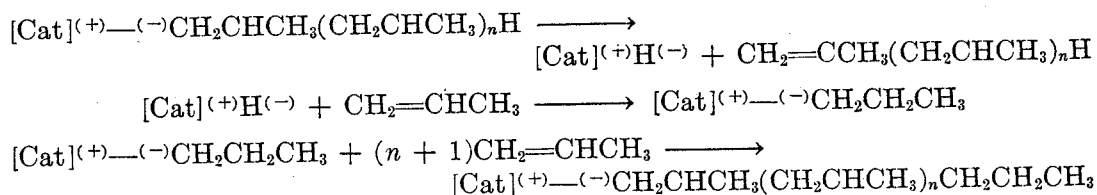
Me	Ionic radii of Me, A.	% polypropylene not extractable with boiling <i>n</i> -heptane
Be	0.35	94-97
Al	0.51	80-90
Mg	0.66	78-85
Zn	0.74	30-40

In our research on the kinetics of  $\alpha$ -olefin polymerization, the catalysts used were prepared from the  $\alpha$ -form of  $\text{TiCl}_3$  and of  $\text{Al}(\text{C}_2\text{H}_5)_3$ .

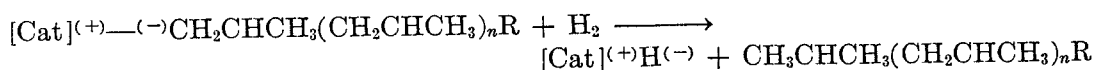
### III. STEREOSPECIFIC POLYMERIZATION OF PROPYLENE

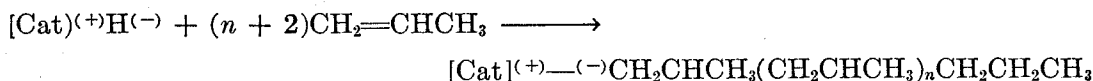
#### (a) Overall Rate of Polymerization

Our kinetic studies on the polymerization of propylene by highly stereospecific catalysts prepared from crystalline  $\alpha$ - $\text{TiCl}_3$  (violet) and aluminum alkyls have shown that the addition of propylene to the metal-organic complex is catalyzed, in the true meaning of the word, by the  $\alpha$ - $\text{TiCl}_3$ .<sup>23</sup> The polymerization of  $\alpha$ -olefins, under appropriate conditions (low temperature), may be considered as mainly a stepwise addition to a metal-organic compound. At high temperature the reaction can also become catalytic with respect to the metal-organic compound, since the polymeric alkyl dissociates and transfers to the catalytic complex a hydride ion capable of starting a new polymer chain.



When operating under a hydrogen pressure, the hydrogenation process is followed by the stepwise addition reaction.<sup>24</sup>





The whole process of polymerization turns out to be catalytic.

At constant temperature and pressure, the rate of polymerization, after an initial settling period, becomes independent of time (Fig. 2). If the

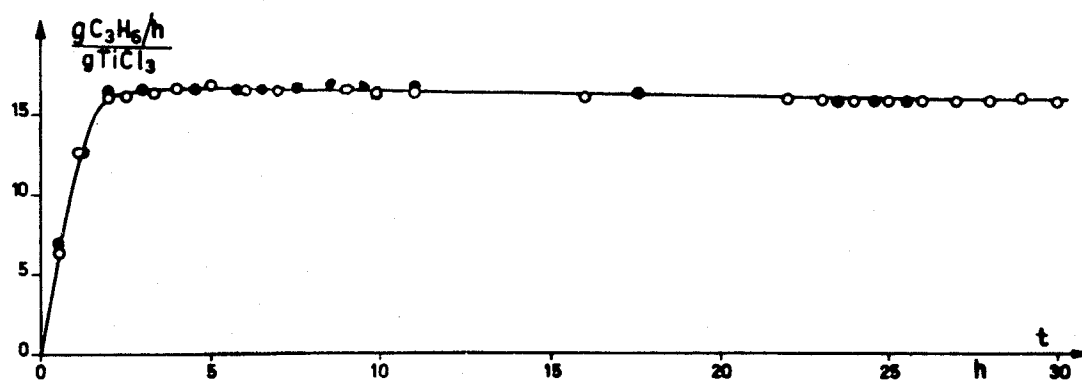


Fig. 2. Kinetic curve of the polymerization of propylene at constant temperature and pressure.

$\alpha\text{-TiCl}_3$ , g./l.	$\text{Al}(\text{C}_2\text{H}_5)_3$ , mole/l.	$t$ , °C.	$p_{\text{C}_3\text{H}_6}$ , mm. Hg
0.80	$4.45 \times 10^{-2}$	70	1450
1.00	$2.94 \times 10^{-2}$	70	1450

(Solvent = 250 ml. *n*-heptane)

$\text{TiCl}_3$  is in the form of relatively large crystals (*e.g.*, side  $\sim 10 \mu$ ), the activity increases during the settling period, and this fact is related to the phenomenon of cleavage of the large crystals. On the other hand, with finely dispersed  $\text{TiCl}_3$  the opposite effect occurs, the small crystals tending to coalesce. Using finely dispersed  $\text{TiCl}_3$  subsequently stabilized by heating, the rate of polymerization reaches a constant value in a few minutes (Fig. 3).<sup>25</sup>

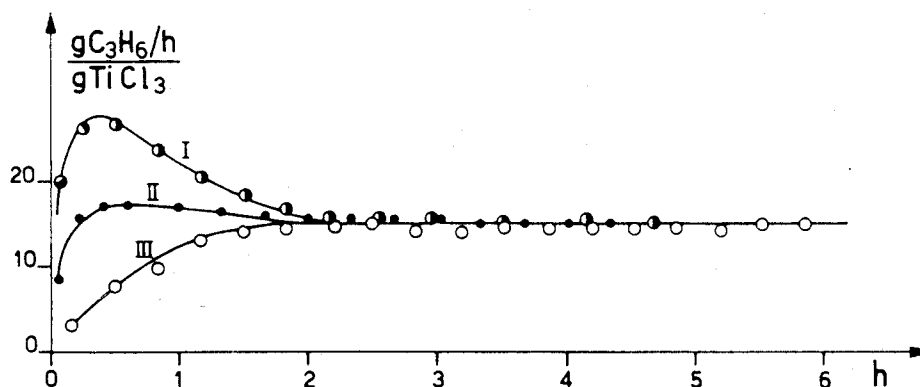


Fig. 3. Effect on the polymerization rate of previous physical treatments on a sample of  $\alpha\text{-TiCl}_3$ . (I)  $\text{TiCl}_3$  powdered and washed with anhydrous *n*-heptane. (II)  $\text{TiCl}_3$  powdered, washed with anhydrous *n*-heptane, and dried. (III)  $\text{TiCl}_3$  not powdered.  $t = 70^\circ\text{C}$ .  $p_{\text{C}_3\text{H}_6} = 1450$  mm. Hg.

Under steady-state conditions, the rate of polymerization of propylene by  $\alpha$ -TiCl<sub>3</sub> and Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> is independent of the Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> concentration, and is given by the following equation, deduced from data summarized in Figures 4, 5, and 6:

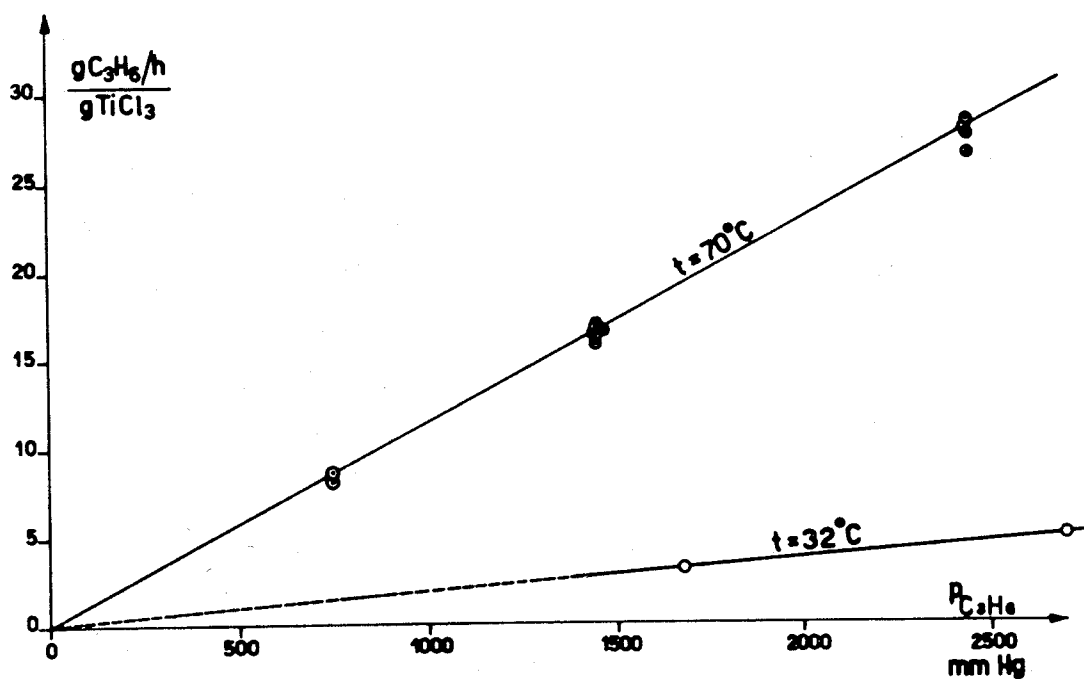


Fig. 4. Polymerization rate, in steady conditions, plotted vs. partial pressure of propylene. Quantities of  $\alpha$ -TiCl<sub>3</sub> vary from test to test from 0.8 to 20 g./l., and of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> from  $1.5 \times 10^{-2}$  to  $20 \times 10^{-2}$  mole/l. Solvent = 250 ml. *n*-heptane.

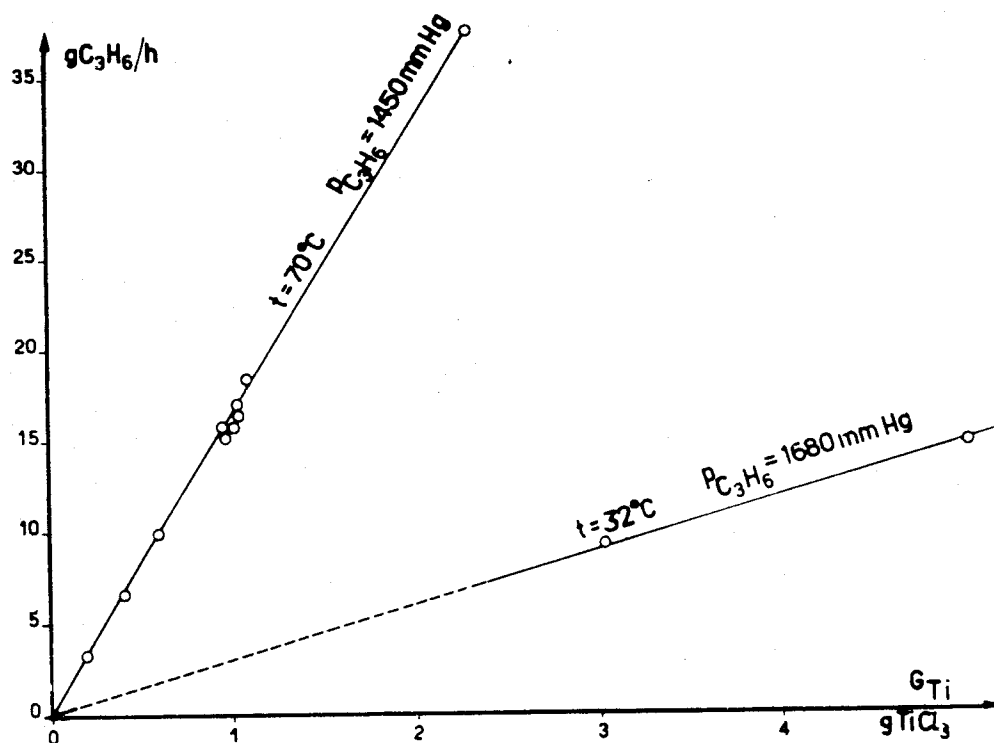


Fig. 5. Polymerization rate, in steady conditions, plotted vs. the quantity of  $\alpha$ -TiCl<sub>3</sub>. Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> concentration varies from test to test from  $1.5 \times 10^{-2}$  to  $20 \times 10^{-2}$  mole/l. Solvent = 250 ml. *n*-heptane.

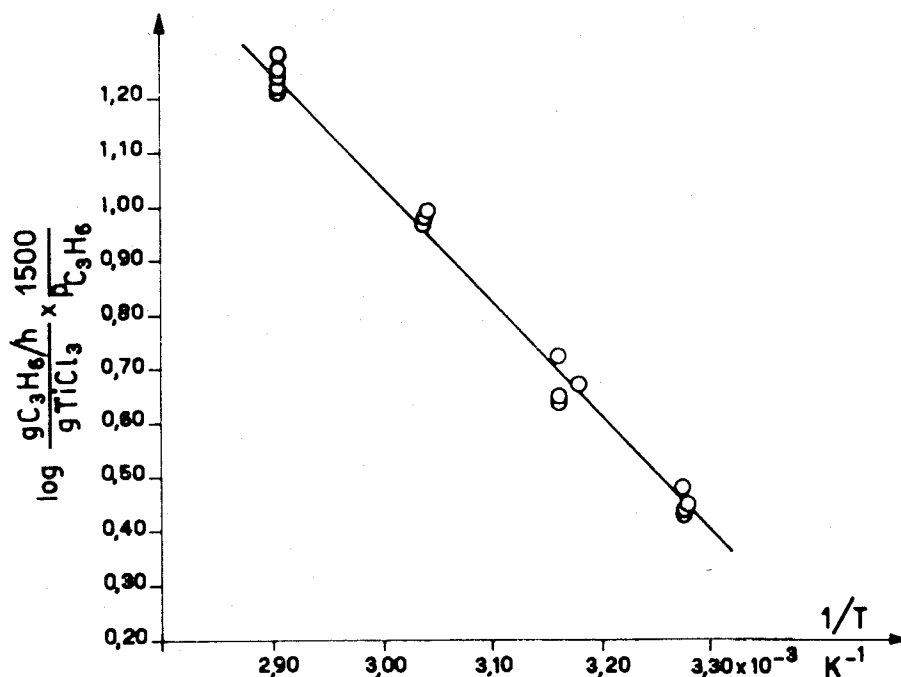


Fig. 6. Logarithm of the polymerization rate in steady conditions, plotted *vs.*  $1/T$ . The rate values were referred, with a proportionality relation, to a partial pressure of propylene of 1500 mm. Hg.

$$r = A e^{-E/RT} p_{\text{C}_3\text{H}_6} G_{\text{Ti}} \quad (1)$$

where

$r$  = rate of polymerization (g.  $\text{C}_3\text{H}_6$  polymerized/hr.)

$A = 10^{7.3}$

$E = 10,000$  cal./mole

$T = ^\circ\text{K.}$

$p_{\text{C}_3\text{H}_6}$  = partial pressure of propylene (atm.)

$G_{\text{Ti}}$  = g. of  $\text{TiCl}_3$  in the catalytic system.

This equation was verified for the  $\text{TiCl}_3$  used by us in the temperature range  $20$ – $70^\circ\text{C.}$  with reaction rates up to  $80$ – $100$  g. polymer/hr. per liter of solvent.<sup>23,25</sup>

### (b) Mechanism of Chain Termination

An analysis of the factors affecting the intrinsic viscosity of the mainly isotactic polypropylene fractions, and also the use of a radioactive aluminum alkyl, labeled with  $\text{C}^{14}$  (together with  $\alpha\text{-TiCl}_3$  in *n*-heptane), followed by a radioactive assay of the polymer, shows that the inverse degree of polymerization is given by the equation:

$$\frac{1}{x} = \frac{k_1 + k_2 p_{\text{C}_3\text{H}_6} + k_3 \sqrt{C_{\text{Al}}} + k_4 p_{\text{C}_3\text{H}_6} \sqrt{G_{\text{Ti}}}}{k_p p_{\text{C}_3\text{H}_6}} \quad (2)$$

where  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are the rate constants of the different chain-breaking processes causing termination,  $k_p$  is the propagation rate constant, and  $C_{\text{Al}}$

is the aluminum alkyl concentration. Equation (2) is easily deduced from the graphs shown in Figures 7-11.<sup>26,27</sup>

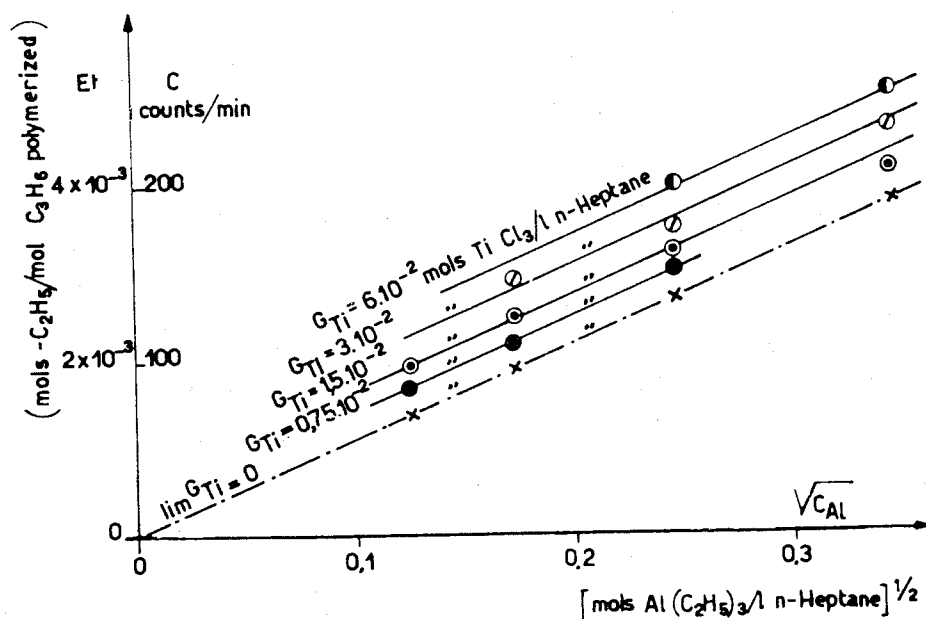


Fig. 7. Specific radioactivity (and corresponding value of  $-\text{C}_2\text{H}_5$  moles per mole of polymerized  $\text{C}_3\text{H}_6$ ) of the mainly isotactic polypropylene fraction, obtained with the reported quantities of  $\alpha\text{-TiCl}_3$  and radioactive  $\text{Al}(\text{C}_2\text{H}_5)_3$ , plotted vs. the square root of the aluminum alkyl concentration.  $t = 70^\circ\text{C}$ .  $p_{\text{C}_3\text{H}_6} = 450$  mm. Hg. Solvent = 100 ml.,  $n$ -heptane.

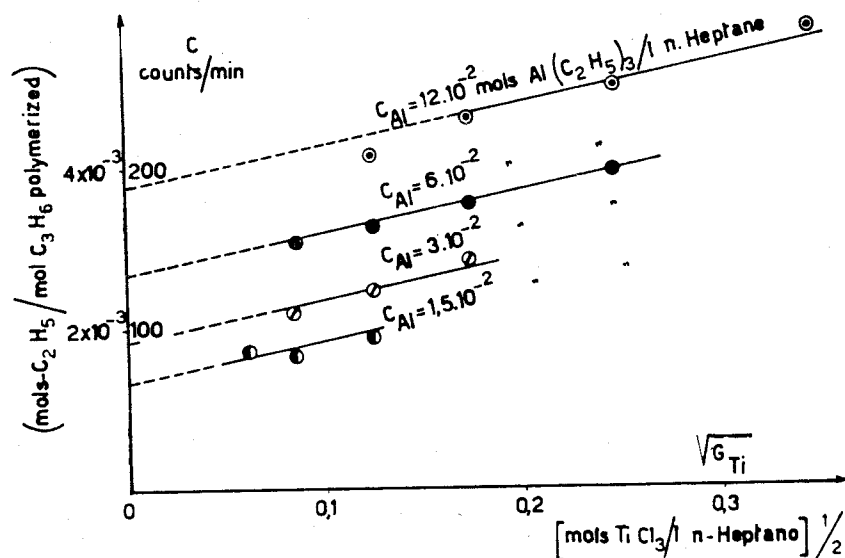


Fig. 8. Specific radioactivity (and corresponding value of  $-\text{C}_2\text{H}_5$  moles per mole of polymerized  $\text{C}_3\text{H}_6$ ) of the mainly isotactic polypropylene fraction, obtained with the reported concentration of radioactive  $\text{Al}(\text{C}_2\text{H}_5)_3$  and with  $\alpha\text{-TiCl}_3$ , plotted vs. the square root of  $\text{TiCl}_3$  concentration in  $n$ -heptane.  $t = 70^\circ\text{C}$ .  $p_{\text{C}_3\text{H}_6} = 450$  mm. Hg. Solvent = 100 ml.  $n$ -heptane.



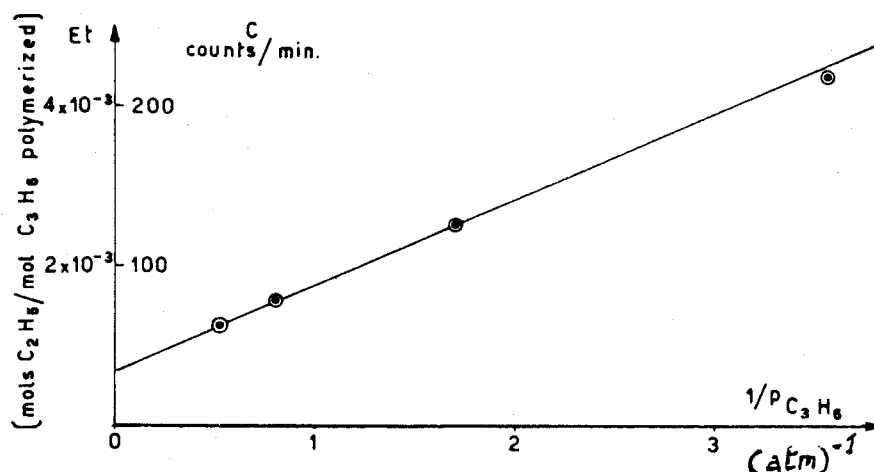


Fig. 9. Specific radioactivity (and corresponding value of  $-\text{C}_2\text{H}_5$  moles per mole of polymerized  $\text{C}_3\text{H}_6$ ) of the mainly isotactic polypropylene fraction, obtained with  $\alpha\text{-TiCl}_3$  and radioactive  $\text{Al}(\text{C}_2\text{H}_5)_3$ , plotted vs.  $1/p_{\text{C}_3\text{H}_6}$ .  $t = 70^\circ\text{C}$ .  $\text{TiCl}_3 = 1.5 \times 10^{-3}$  mole.  $\text{Al}(\text{C}_2\text{H}_5)_3 = 3 \times 10^{-3}$  mole. Solvent = 100 ml. *n*-heptane.

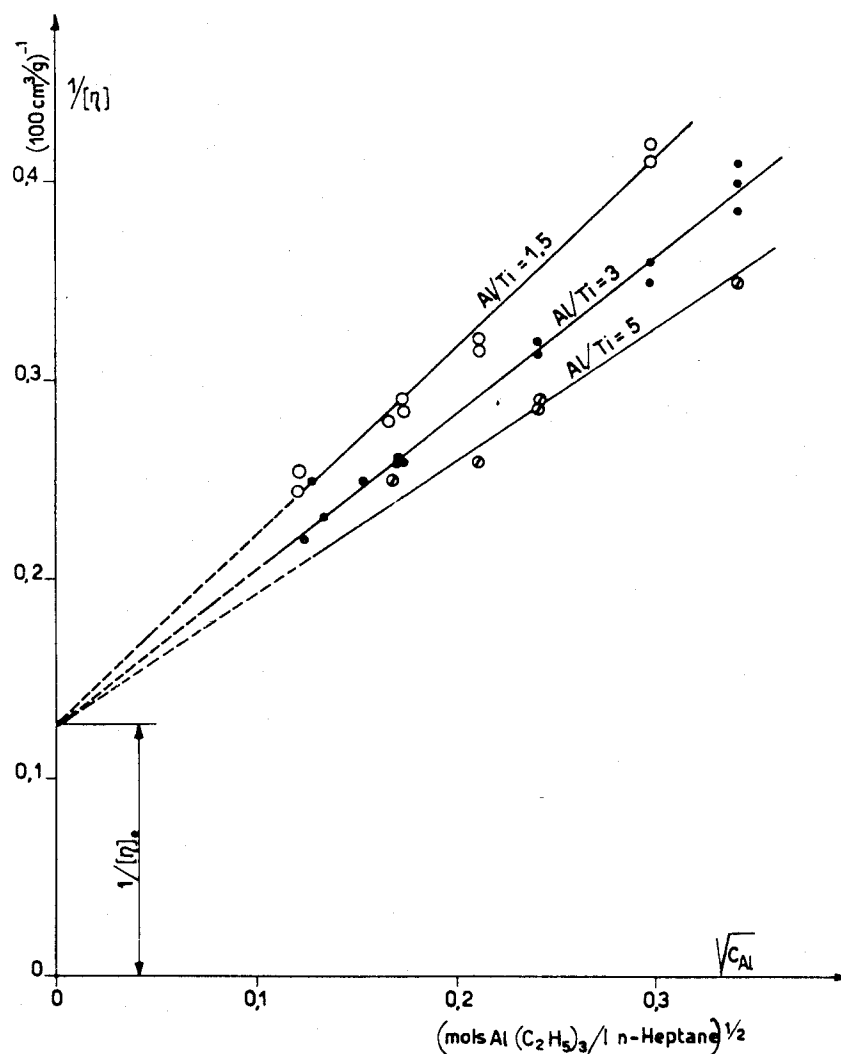


Fig. 10. Reciprocal of the intrinsic viscosity of the mainly isotactic polypropylene fraction, obtained with the reported pressure and  $\text{Al}(\text{C}_2\text{H}_5)_3/\alpha\text{-TiCl}_3$  ratios, plotted vs. the square root of the aluminum alkyl concentration.  $t = 70^\circ\text{C}$ .  $p_{\text{C}_3\text{H}_6} = 950$  mm. Hg. Solvent = 250 ml. *n*-heptane.

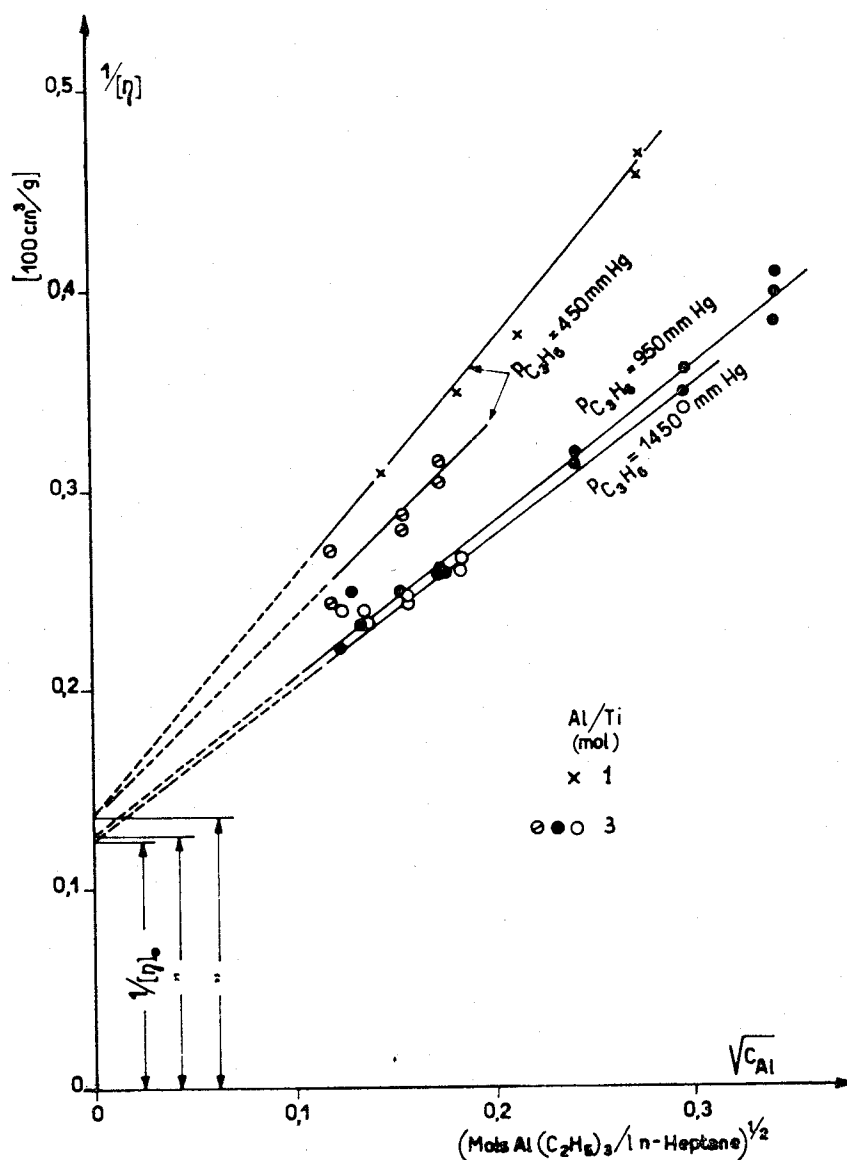


Fig. 11. Reciprocal of the intrinsic viscosity of the mainly isotactic polypropylene fraction, obtained at 70°C. At the reported pressure and  $\text{Al}(\text{C}_2\text{H}_5)_3/\alpha\text{-TiCl}_3$  ratios, plotted vs. the square root of the aluminum alkyl concentration.

Using aluminum tri-ethyl labeled with  $\text{C}^{14}$ , we have been able to detect termination reactions which depend on the aluminum alkyl concentration, and on the quantity of  $\text{TiCl}_3$  present.<sup>27</sup> Both processes involve the incorporation of ethyl groups derived from the aluminum alkyl into the polymer chain. The quantity of ethyl groups (Et) introduced per unit weight of polymer is given by the following equation, which is derived directly from the graphs shown in Figures 7-9:

$$\text{Et} = \frac{k_3 \sqrt{C_{\text{Al}}} + k_4 p_{\text{C}_3\text{H}_6} \sqrt{G_{\text{Ti}}}}{k_p p_{\text{C}_3\text{H}_6}} \quad (3)$$

The terms appearing in the numerator of eq. (3) are, theoretically, equal to the corresponding terms in eq. (2). The relation between reactions introducing ethyl groups and chain termination is demonstrated by the

increase of the inverse molecular weight with increase of the aluminum alkyl concentration and of the quantity of  $\text{TiCl}_3$  in the system (Fig. 10).

As  $C_{\text{Al}}$  and  $G_{\text{Ti}}$  tend to a limiting value of zero,  $1/[\eta]$  tends to a limiting value different from zero (Fig. 10). This limiting value  $1/[\eta]_0$  decreases slowly to an asymptotic value when the pressure is increased (Fig. 11).

Below  $70^\circ\text{C}$ . the temperature has only a minor effect on the molecular weight (Fig. 12). It would therefore appear that the activation energies

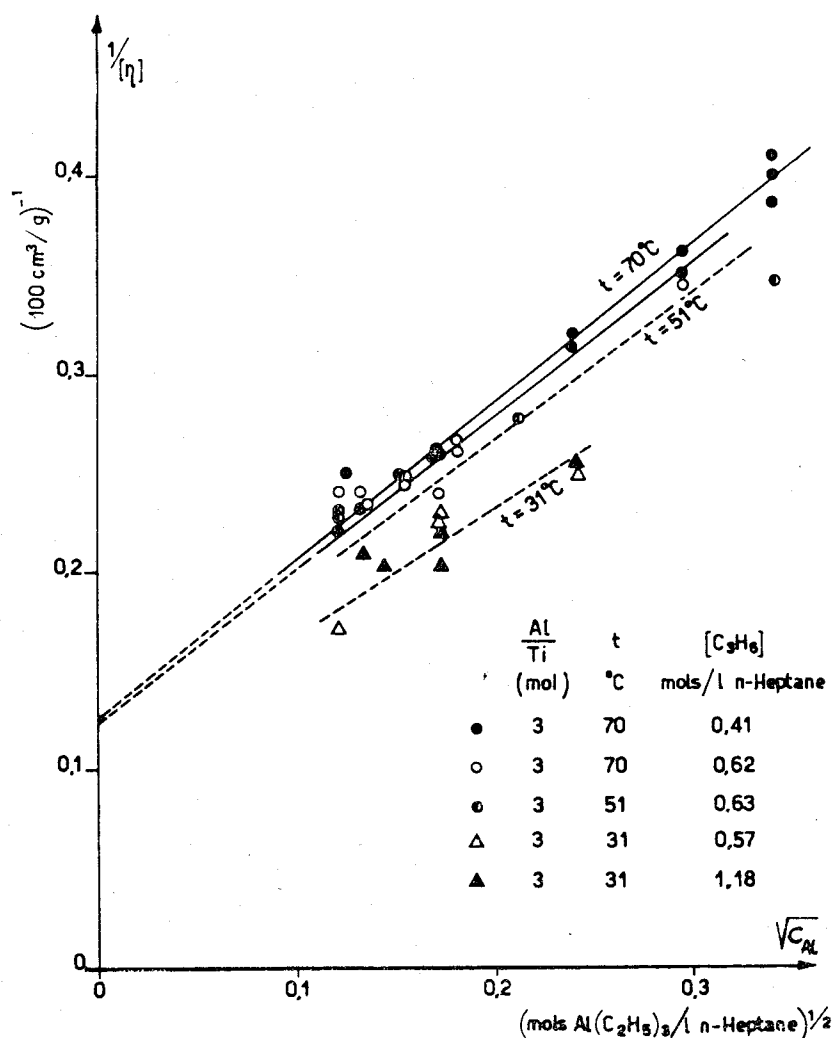


Fig. 12. Reciprocal of the intrinsic viscosity of the mainly isotactic polypropylene fraction, obtained at the reported temperature and olefin concentrations, plotted vs. the square root of the aluminum alkyl concentration.

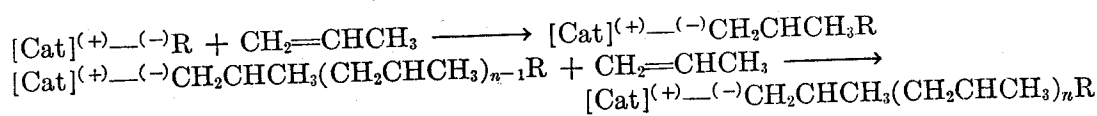
of the more important termination reactions do not differ greatly from that of the propagation process. Under the conditions of our experiments, none of the chain termination reactions seems to lower the overall rate of polymerization.

The mechanism which we have proposed for the complete polymerization reaction is shown in Table III.

TABLE III

Reaction Schemes for the Propylene Polymerization Process with  
Stereospecific Catalysts

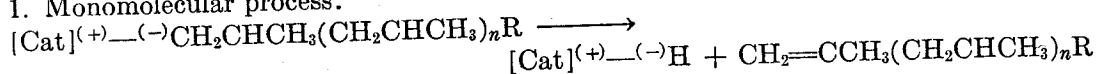
(a) *Initiation and propagation*



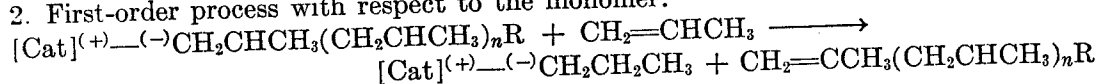
where R = H, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub> or other polymeric alkyl groups

(b) *Termination*

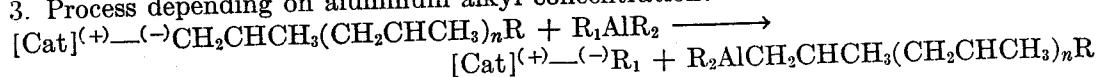
1. Monomolecular process:



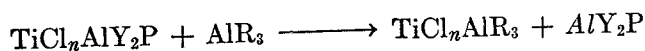
2. First-order process with respect to the monomer:



3. Process depending on aluminum alkyl concentration:



or:



where Y = alkyl and P = polymeric chain.

The termination reaction, which is first order with respect to monomer concentration, may be considered as a chain transfer to the monomer, but an alternative mechanism with many stages cannot be excluded. One possibility is a monomolecular dissociation of the growing polymer chain, with transfer of a hydride ion to the catalytic complex. Such a hydride, reacting with the monomer, should give an alkyl group and initiate a new chain.

The termination reaction of order 1/2 with respect to the aluminum alkyl concentration has been interpreted as an exchange of alkyl groups between the growing polymer chain and the aluminum alkyl in solution.

The nature of the termination reaction which involves the quantity of TiCl<sub>3</sub> present is not yet completely clear, but it is connected with an exchange of alkyl groups between the growing polymer chain and alkyl compounds in solution containing ethyl groups derived from the tri-ethyl aluminum.

A comparison of the inverse intrinsic viscosity ([η], which varies with the degree of polymerization, (eq. 2)) with the number of ethyl groups (Et) found in the polymer [eq. (3)] supports our hypothesis concerning the termination mechanism. At a given pressure, the result should be as follows:

$$1/x = B + \text{Et} \quad (4)$$

where B = constant, or 1/x is a unique and monotonous function of Et. In Figure 13, 1/[η] is shown as a function of Et.

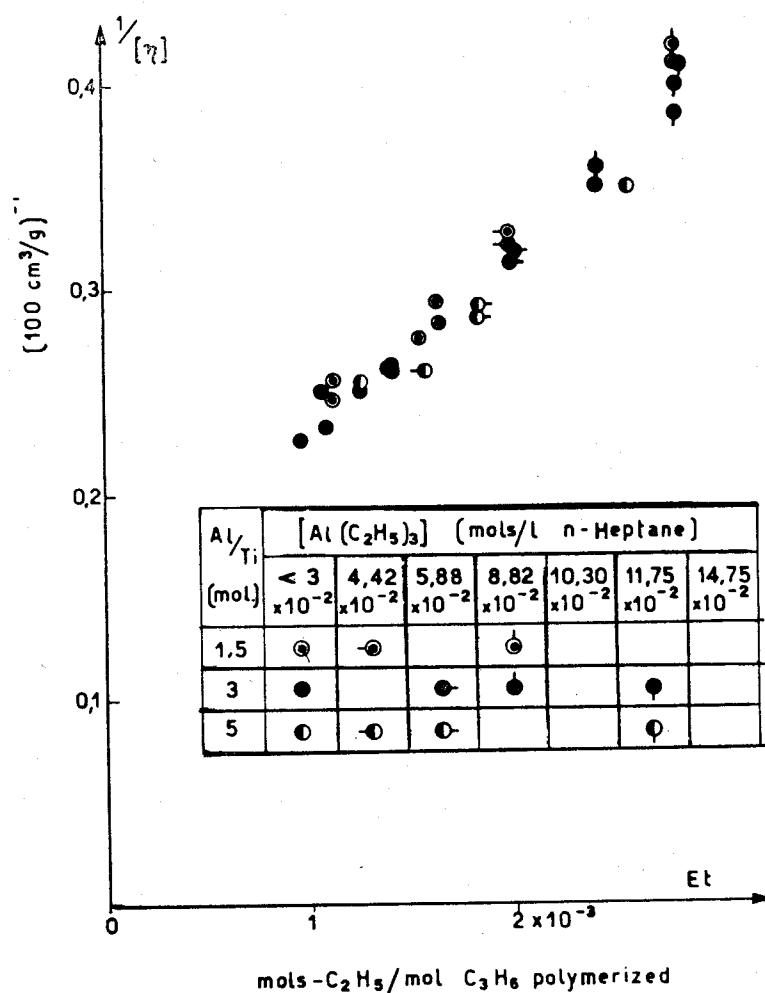


Fig. 13. Reciprocal of the intrinsic viscosity of the mainly isotactic polypropylene fraction, obtained with  $\alpha$ -TiCl<sub>3</sub> and Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, as a function of the moles of —C<sub>2</sub>H<sub>5</sub> bound to the polymer.

### (c) Determination of the Active Centers by Radiochemical Methods

The number of active centers in the catalytic systems  $\alpha$ -TiCl<sub>3</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and  $\alpha$ -TiCl<sub>3</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl, used in the polymerization of propylene, was determined by using a sample of powdered  $\alpha$ -TiCl<sub>3</sub> and aluminum alkyls labeled with C<sup>14</sup>. Two methods were used for this evaluation: (1) Direct measurement of the adsorption of radioactive aluminum alkyl on TiCl<sub>3</sub>, and (2) determination of the active centers by kinetic methods.

To determine the number of active centers resulting from the adsorption of aluminum alkyls on  $\alpha$ -TiCl<sub>3</sub>, the following procedure was adopted<sup>28</sup>: treatment of crystalline TiCl<sub>3</sub> at a given temperature with a solution of aluminum alkyl, and filtration followed by repeated washing of the solid at a given temperature with anhydrous benzene, until the filtrate was no longer radioactive.

The TiCl<sub>3</sub> thus obtained, on treating with acid, yields free C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. This shows that during the treatment of the TiCl<sub>3</sub> with aluminum alkyls, complex formation which is at least partially irreversible occurs on the surface of the crystalline substrate.

In another series of experiments,  $\text{TiCl}_3$  which had been treated with labeled aluminum alkyl and subsequently washed with anhydrous hydrocarbon, was used to polymerize propylene (and also ethylene) after the further addition of nonradioactive aluminum alkyl. This last addition is not indispensable for the formation of the catalyst and the initiation of polymerization. The polymer obtained is radioactive, and the total number of  $-\text{C}_2\text{H}_5$  groups found in the polymer does not depend on either the duration of the polymerization or on the amount of nonradioactive aluminum alkyl added. This confirms our previous hypothesis as to the nature of the catalyst.<sup>29</sup>

Below  $60^\circ\text{C}$ . the number of ethyl groups found in the polymer is lower than the total number of ethyl groups adsorbed on the  $\text{TiCl}_3$  as measured by gas evolution. This can be attributed to two different types of adsorption. At a temperature of  $70^\circ\text{C}$ . the number of ethyl groups found in the polymer corresponds to the total amount adsorbed on the  $\text{TiCl}_3$  (Table IV), and we may therefore assume that at this temperature the ethyl

TABLE IV

Determination of the Number of Active Centers on a Powdered Sample of  $\alpha\text{-TiCl}_3$  from Adsorption Data of Labeled  $\text{C}^{14}$  Aluminum Alkyl Compounds, Followed by Polymerization of Propylene

( $\text{TiCl}_3 = 0.5$  g. Aluminum alkyl compound = 0.5 ml. Solvent = 30 ml. *n*-heptane)

Aluminum compound	Adsorption temperature, $^\circ\text{C}$ .	Time of adsorption, hr.	Solvent	Temperature washing with anhydrous solvent, $^\circ\text{C}$ .	Moles of $\text{C}_2\text{H}_5$ adsorbed per mole of $\text{TiCl}_3$	
					Total alkyl groups remaining on $\text{TiCl}_3$ after washing	Number of alkyl groups on active centers (pre-adsorbed alkyl groups found in the polymer)
$\text{Al}(\text{C}_2\text{H}_5)_3$	-18	$1/2$	<i>n</i> -Heptane	-18	$17.0 \times 10^{-3}$	n.d.
$\text{Al}(\text{C}_2\text{H}_5)_3$	-18	3	"	-18	$45.0 \times 10^{-3}$	$9.3 \times 10^{-3}$
$\text{Al}(\text{C}_2\text{H}_5)_3$	20	$1/2$	Benzene	20	$48.2 \times 10^{-3}$	$10.1 \times 10^{-3}$
$\text{Al}(\text{C}_2\text{H}_5)_3$	46	$1/2$	"	46	$17.7 \times 10^{-3}$	$10.5 \times 10^{-3}$
$\text{Al}(\text{C}_2\text{H}_5)_3$	70	$1/2$	"	20	$10.5 \times 10^{-3}$	$10.8 \times 10^{-3}$
$\text{Al}(\text{C}_2\text{H}_5)_3$	70	$1/2$	"	70	$6.2 \times 10^{-3}$	$6.7 \times 10^{-3}$
$\text{Al}(\text{C}_2\text{H}_5)_3$	100	$1/2$	Toluene	100	$3.0 \times 10^{-3}$	$3.0 \times 10^{-3}$
$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	70	$1/2$	<i>n</i> -Heptane	20	$3.0 \times 10^{-3}$	$3.1 \times 10^{-3}$

groups found in the polymer correspond to the number of active centers initially present on the  $\text{TiCl}_3$  surface. The results obtained for both systems are shown in Table IV. The same value for the number of active centers was found over the entire range of temperatures investigated (about 1 mole per 100 moles of  $\text{TiCl}_3$  in the  $\text{Al}(\text{C}_2\text{H}_5)_3/\alpha\text{-TiCl}_3$  system). The number of active centers found in the  $\alpha\text{-TiCl}_3/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  system at

70°C. is less than the number found in the system  $\alpha$ -TiCl<sub>3</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>. This can be correlated with the different activities observed in the two systems. All of the data on polymer radioactivity have been corrected for radioactive contamination.

In the treatment of  $\alpha$ -TiCl<sub>3</sub> with aluminum alkyl, traces of radioactive products are formed, probably polyethylene. Small quantities of ethylene can be formed by disproportionation of the —C<sub>2</sub>H<sub>5</sub> radicals liberated when the aluminum alkyl reacts with traces of TiCl<sub>4</sub> present in the  $\alpha$ -TiCl<sub>3</sub>. The radioactivity due to this contamination is much lower than the radioactivity due to the active centers (Table V).

TABLE V

Radioactive Contamination, in the Treatment of a Powdered Sample of  $\alpha$ -TiCl<sub>3</sub> with Labeled C<sup>14</sup>Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, Independent from Adsorbed Alkyl Groups

(TiCl<sub>3</sub> = 0.5 g. Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> = 0.5 ml. Solvent = 30 ml. *n*-heptane)

Treatment temperature, °C.	Radioactive contamination, as —C <sub>2</sub> H <sub>5</sub> moles per TiCl <sub>3</sub> mole	Ratio between the radioactivity of contamination and the radioactivity of alkyls adsorbed on active center from the data of Table IV, %
—18	$1.8 \times 10^{-3}$	19.5
20	$1.3 \times 10^{-3}$	13
46	$1.2 \times 10^{-3}$	11.5
70	$1.6 \times 10^{-3}$	15

#### (d) Determination of the Active Centers by Kinetic Methods

The method of determining active centers described in the previous section only applies to those centers present on the TiCl<sub>3</sub> surface after treatment with aluminum tri-ethyl and repeated washing with the solvent prior to polymerization. These centers do not necessarily correspond to the centers present during steady-state polymerization. In fact, depending on the size of the TiCl<sub>3</sub> crystals, the polymerization may show an initial settling period, lasting for some minutes, during which there is a variation in the surface area of the TiCl<sub>3</sub>, and consequently in the number of accessible active centers.

We have been able to calculate the total number of active centers taking part in the polymerization by a kinetic method, which can be summarized as follows: Each catalytic complex initiating polymerization can be written as [Cat]·R, where [Cat]·R is the catalytic complex bound to the crystalline substrate of TiCl<sub>3</sub>, and R is the alkyl group derived from the metal-organic compound initially added as part of the catalytic system.

The monomer molecules enter across the [Cat]—R bond, thus separating from the active center the R group, which remains as the terminal group of the first molecule of polymer produced by this active center. If R is present in the catalytic complex at the start of polymerization, the total

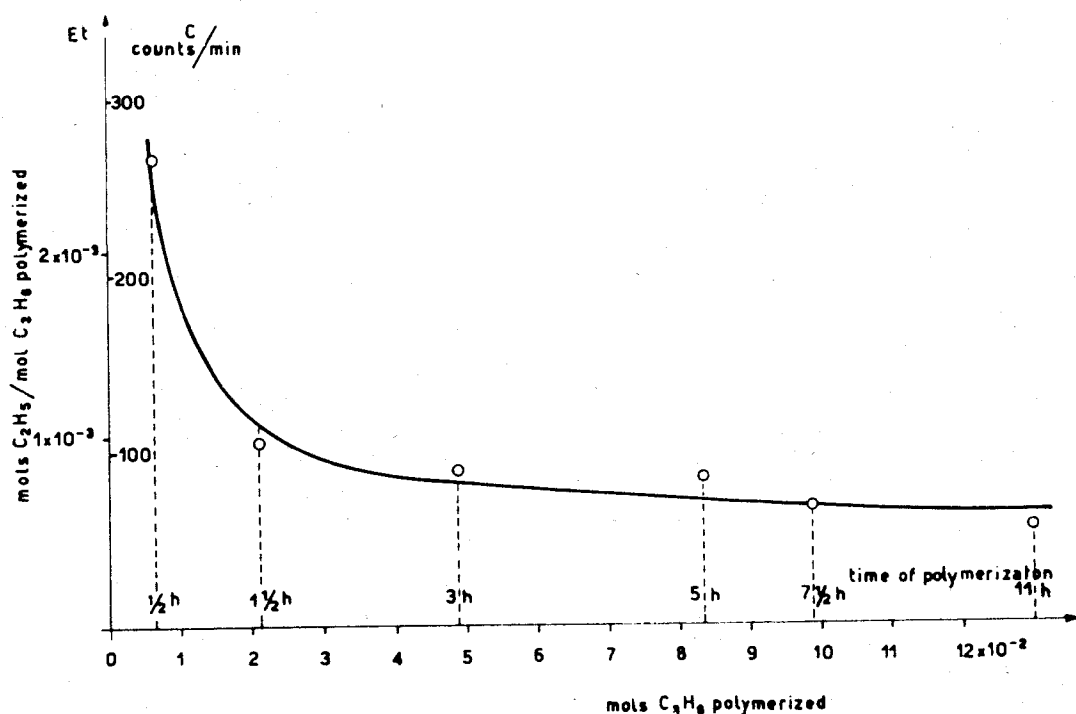


Fig. 14. Specific radioactivity (with the corresponding value of  $-\text{C}_2\text{H}_5$  moles per mole of polypropylene) plotted vs. the quantity of polypropylene obtained at different times of polymerization.  $t = 70^\circ\text{C}$ .  $p_{\text{C}_3\text{H}_6} = 450$  mm. Hg.  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} = 0.6$  ml.  $\text{TiCl}_3 = 0.3$  g. Solvent = 100 ml. *n*-heptane.

number of R groups found in the polymer should be the same as the number of active centers. However, in the polymerization of propylene by the system  $\text{Al}(\text{C}_2\text{H}_5)_3/\alpha\text{-TiCl}_3/n\text{-heptane}$ , we have observed that R also enters, at a constant rate, into macromolecules formed under steady-state conditions, presumably as a result of some chain-termination reaction. Thus, in steady conditions, some of the growing chains will have an R group at one end, while others will have a  $-\text{C}_3\text{H}_7$  endgroup, introduced by the various termination or transfer processes which involve the linkage of a monomeric molecule to the active center. Because of this, in some of our experiments with radioactive aluminum alkyl, a variation of the ratio: (R groups found in the polymer/total number of polymer molecules) was observed as the polymerization time increased. This enables us to evaluate the number of active centers taking part in the polymerization process.

It has been shown<sup>30</sup> that in the systems which we have examined, the number of ethyl groups found in the polymer per mole of propylene polymerized is given by the following equation:

$$\text{Et} = \frac{C^* + \Sigma r_1 t}{r_p t} \quad (5)$$

where

Et = "moles" of ethyl groups found in the polymer for each mole of propylene polymerized.

$\Sigma r_1$  = rates of the termination reactions which introduce ethyl groups derived from the aluminum alkyl as terminal groups in the polymer chains.



$r_p$  = rate of propagation of the growing polymer chain.  
 $C^*$  = number of active centers.  
 $t$  = polymerization time.

This equation can only be used to determine the number of active centers when  $\Sigma r_1$  is sufficiently low in comparison with  $C^*$ . This condition has been shown to hold in the system  $\alpha$ -TiCl<sub>3</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl/*n*-heptane.<sup>33</sup> On the other hand, systems containing tri-ethyl aluminum gave excessively high values of  $\Sigma r_1$ .

Specific radioactivities, corrected for radioactive contamination, together with the corresponding values of Et found in polymerizations using the  $\alpha$ -TiCl<sub>3</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl/*n*-heptane system, are shown in Figure 14. These experimental values tend toward an asymptotic value corresponding to the ratio  $\Sigma r_1/r_p$ . They agree with the curve shown, which was calculated assuming that:

$$C^* = 6.3 \times 10^{-3} \text{ moles } -\text{C}_2\text{H}_5/\text{mole TiCl}_3$$

Using the same catalytic system at the same temperature, the two methods used to determine the number of active centers, *viz.*, radiochemical adsorption and kinetic measurements, lead to values of the same order of magnitude. A comparison of the highest value obtained by the kinetic method (about 0.6%, expressed as moles  $-\text{C}_2\text{H}_5$  per mole of TiCl<sub>3</sub>) with that obtained by the adsorption method (about 0.3%) is evidence that not all the active centers taking part in the polymerization are initially present on the surface of the catalyst used [*i.e.*,  $\alpha$ -TiCl<sub>3</sub> treated with Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and washed repeatedly].

#### (e) Variation in the Molecular Weight of the Polymer as a Function of Reaction Time

In any polymerization process, the number-average degree of polymerization of the total polymer produced after a time  $t$  is given by the equation:

$$x = \frac{\int_0^t r_p dt}{C^* + \int_0^t \Sigma r_t dt} \quad (6)$$

where  $\Sigma r_t$  is the termination rate of growing chains. If all of the rates are independent of time, then:

$$x = r_p t / (C^* + \Sigma r_t t) \quad (7)$$

Under conditions where  $\Sigma r_t$  is sufficiently small, and  $C^*$  not, therefore, negligible in comparison with  $\Sigma r_t t$ , a variation of  $x$  with reaction time is detectable. Figure 15 shows the results of some preliminary experiments on the polymerization of propylene with the system  $\alpha$ -TiCl<sub>3</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>/*n*-heptane, operating at a temperature of 15°C. and a partial pressure of propylene of 200 mm. Hg.

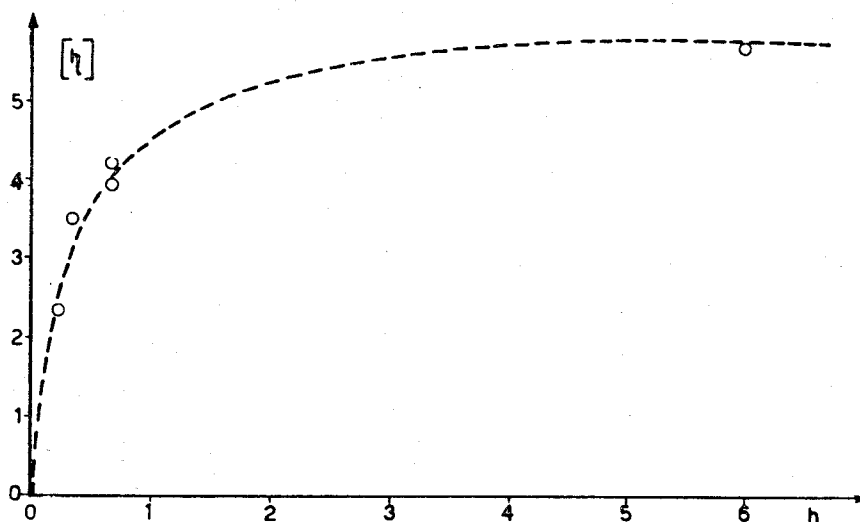


Fig. 15. Intrinsic viscosity of the mainly isotactic polypropylene fraction, plotted *vs.* the polymerization time.  $t = 15^\circ\text{C}$ .  $p_{\text{C}_3\text{H}_6} = 200 \text{ mm. Hg}$ .  $\alpha\text{-TiCl}_3 = 1 \text{ g}$ .  $\text{Al}(\text{C}_2\text{H}_5)_3 = 0.8 \text{ ml}$ . Solvent: 250 ml. *n*-heptane.

Knowing  $x$  as a function of time enables us to calculate  $C^*$ . In order to obtain the  $x$  values from viscosity data, we must have a relation between the intrinsic viscosity of the polymer and its number-average degree of polymerization.

**(f) Attempt to Determine a Relation between the Intrinsic Viscosity and the Number-Average Degree of Polymerization by a Radiochemical Method**

A combination of eqs. (2) and (3) gives:

$$\frac{1}{x} = \frac{1}{x_0} + \text{Et} \quad (8)$$

On the basis of the results shown in Figure 13, we can assume that, over the range in question, the following relationship holds approximately:

$$\frac{1}{[\eta]} = \frac{1}{[\eta]_0} + K\text{Et} \quad (9)$$

Eliminating Et between eqs. (8) and (9), we have:

$$\frac{1}{x} - \frac{1}{x_0} = \frac{1}{K} \left[ \frac{1}{[\eta]} - \frac{1}{[\eta]_0} \right] \quad (10)$$

where  $x_0$  and  $[\eta]_0$  are, respectively, the number-average degree of polymerization and the intrinsic viscosity of the polymer, obtained by extrapolating the experimental values to the limiting conditions  $C_{\text{Al}} = 0$ , and  $G_{\text{Ti}} = 0$ . Since

$$1/x_0 = 1/K[\eta]_0 \quad (11)$$

it follows from eq. (10) that:

$$x = K[\eta] \quad (12)$$

From the results shown in Figure 13, which refer to the mainly isotactic polypropylene fraction (representing about 90% by weight of the total

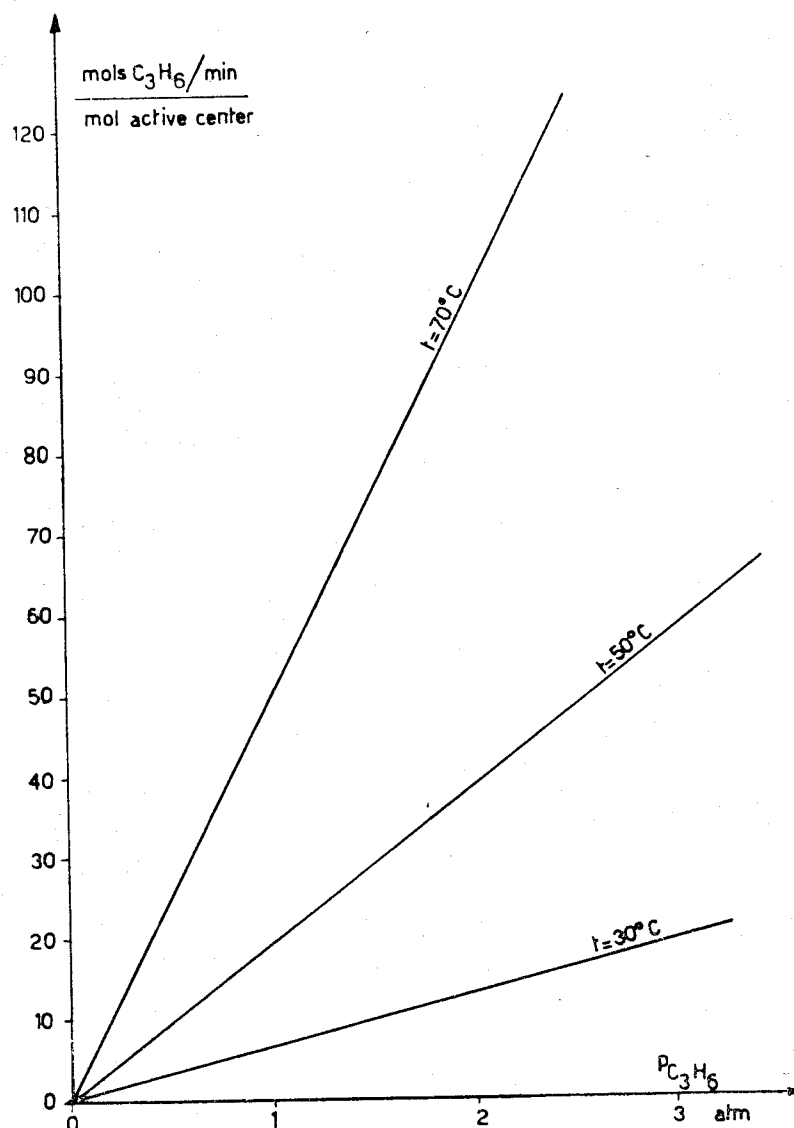


Fig. 16. Mean growth rate of the chains of polypropylene with a catalytic system:  $\alpha\text{-TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$ .

polymer) obtained with the system  $\alpha\text{-TiCl}_3/\text{Al}(\text{C}_2\text{H}_5)_3/n\text{-heptane}$ , the following approximate results emerge:

$$x = 90[\eta]$$

or

$$M_n = 3800[\eta]$$

The number-average molecular weight, determined in this way, is very much lower than the viscometric molecular weight (determined on the

assumption that the known relations for polyethylene are also valid for propylene). The very low value ( $<0.1$ ) found for the ratio between the number-average and the viscometric molecular weights shows that the polymer has a wide molecular weight distribution.

### (g) Average Life-Time of the Growing Chains

Knowing the number of active centers and the overall rate of polymerization, we can calculate the mean growth rate of the chains on each active center. We have assumed that in the system  $\alpha\text{-TiCl}_3/\text{Al}(\text{C}_2\text{H}_5)_3/n\text{-heptane}$ , the number of active centers is independent on the temperature in the range  $30\text{--}70^\circ\text{C}$ ., and is equal to 1 mole per 100 moles  $\text{TiCl}_3$ . The resulting average growth rates are shown in Figure 16.

It is also possible to determine the average life-time of each macromolecule if the rates of the different termination processes are known. The rate at which the alkyl complexes undergo chain scission can be deduced directly from eq. (3), in which all the factors are known. The rate of the other termination reaction can be determined from the graph shown in Figure 10, with the aid of eq. (3). The average life-time of the growing chains, determined in this way, under various conditions of polymerization, is given in Figure 17.<sup>31</sup>

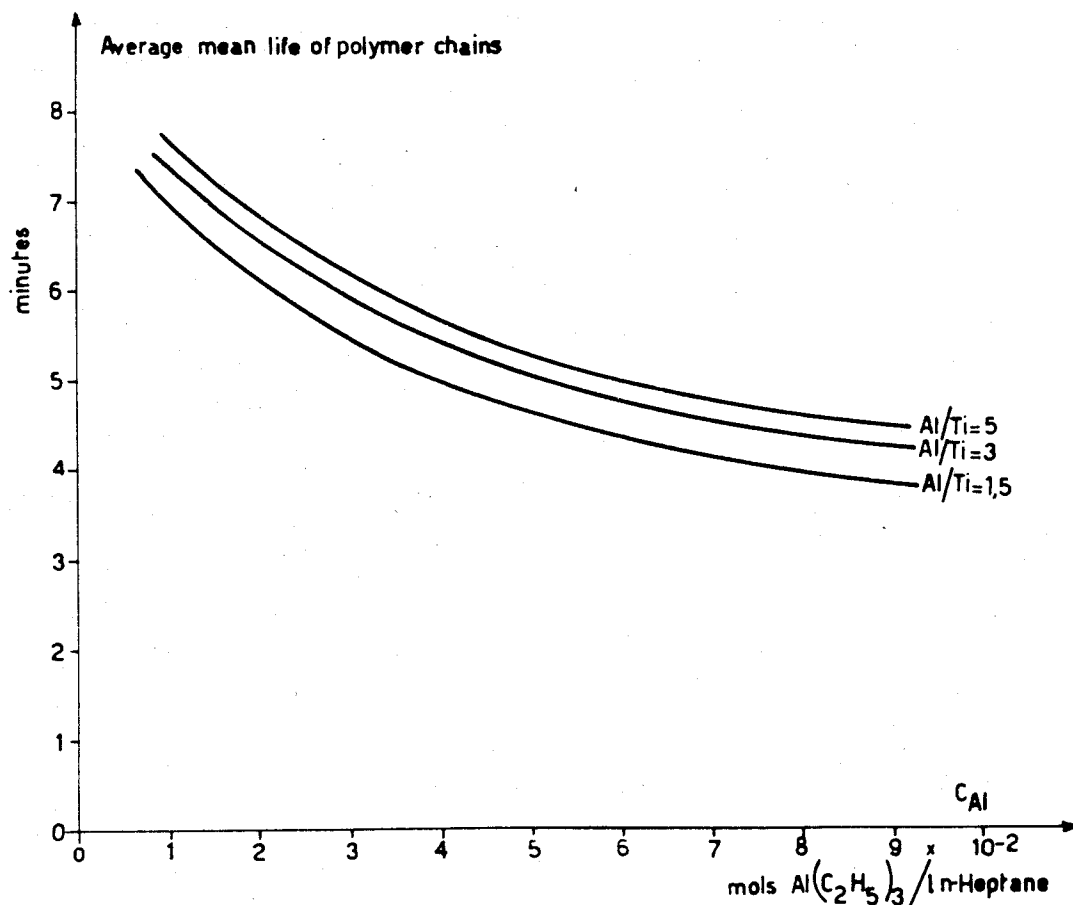


Fig. 17. Average mean life of the chains of polypropylene growing on the active centers of a catalytic system:  $\alpha\text{-TiCl}_3\text{--Al}(\text{C}_2\text{H}_5)_3$ .  $t = 70^\circ\text{C}$ .  $p_{\text{C}_3\text{H}_6} = 950 \text{ mm. Hg}$ .

We have also tried to calculate the number of active centers from the variation of the intrinsic viscosity with reaction time.<sup>31</sup> The results obtained using this method are of the same order of magnitude, but the values are lower than those obtained by the method previously described (0.2%  $\text{—C}_2\text{H}_5$  per mole  $\text{TiCl}_3$  instead of 1%). Calculation of the number of active centers from the variation of intrinsic viscosity with reaction time is necessarily indirect, since the determining factor is the rate of propagation of the polymer chains; only if all the growing chains had the same propagation rate would it be possible to obtain the same value as that resulting from direct measurements.

The propagation rate of the mainly isotactic crystalline fraction, and of isotactic chains with a high molecular weight, appears to be higher than the propagation rate of the amorphous chains, which always have a lower molecular weight. We can therefore assume that not all of the active centers have the same polymerization rate: the centers with higher rates should produce polymer chains of higher molecular weight. Since the intrinsic viscosity of a polymer is mainly determined by the higher molecular weight fractions, the number of active centers deduced from the variation of the intrinsic viscosity with reaction time is, to a large extent, governed by the propagation rate of the high molecular weight chains. In this case, the number of active centers obtained from viscosity measurements is lower than the true value.

#### IV. COMPARISON OF THE REACTIVITIES OF $\alpha$ -OLEFINS AND ETHYLENE BY A KINETIC STUDY OF THEIR COPOLYMERIZATION

Kinetic investigations on the polymerization and copolymerization of  $\alpha$ -olefins can be useful in clarifying the influence of the structure of different monomers on their response to this type of coordination catalysis, and in forecasting their behavior in copolymerization. In this section, we wish to summarize very briefly the results we have obtained on the copolymerization of ethylene and propylene.

The problems involved were by no means simple, since in addition to known difficulties arising from the ionic character of the polymerization, there were others due to the differing activities of the different parts of the typical heterogeneous Ziegler catalyst. In our researches we have concentrated on the preparation of catalysts having a composition and physical structure as homogeneous as possible, to avoid the presence of active centers having different reactivity ratios with respect to the two monomers to be copolymerized. One class of catalysts which proved to have these requirements is that of highly dispersed catalysts, which, with  $\alpha$ -olefins, produce mainly atactic, noncrystallizable polymer.<sup>32</sup> It should be said, however, that under suitable experimental conditions we have also succeeded in preparing homogeneous copolymers using other classes of catalysts; for instance, those obtained starting from solid crystalline hal-

ides of transition metals, virtually containing only one type of active center, which is effective in polymerizing both  $\alpha$ -olefins and ethylene.

Another difficulty was the much higher reactivity of ethylene compared with  $\alpha$ -olefins in anionic copolymerization. This has been overcome by using a continuous-flow method, with a high rate of flow of a gaseous mixture of monomers, in proportions very different from those desired in the copolymer.<sup>32</sup> Only under these conditions has it been possible to prepare true copolymers, free from homopolymers.

The composition of the copolymers has been established to within a very close approximation by using ethylene labeled with  $C^{14}$ . Another method of analysis which we have used for ethylene-propylene copolymers is based on measuring the intensity of the absorption band at  $7.25\ \mu$ , working in carbon tetrachloride solution. Using these methods, we have been able to show that the composition of the ethylene-propylene copolymers prepared using highly dispersed catalysts does not depend on either the concentration of the catalyst, the aging time of the catalyst, the duration of the polymerization, or on the ratio moles aluminum tri-alkyl/moles halide used in the preparation of the catalyst.<sup>32</sup>

As an example of our results, Figure 18 shows the variation in composi-

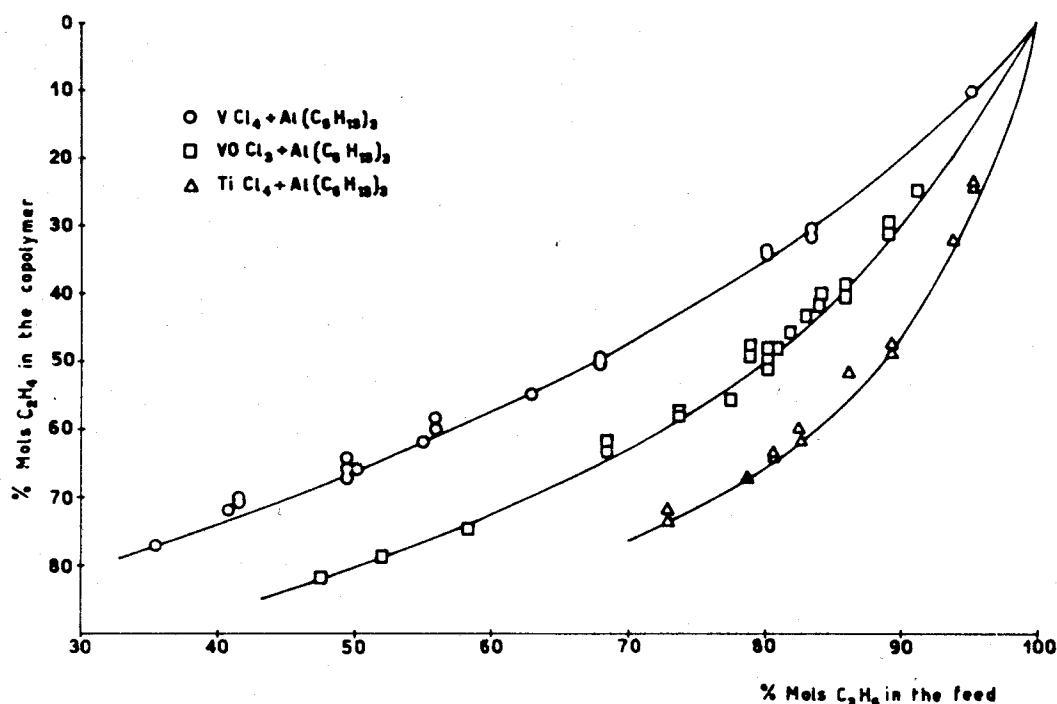


Fig. 18. Composition of ethylene-propylene copolymers obtained with different catalysts, corresponding to different compositions of the feed.

tion of the ethylene-propylene copolymers with varying composition of the gaseous feed mixture, using catalysts prepared respectively from  $VOCl_3$ ,  $VCl_4$ , and  $TiCl_4$ . At high rates of flow, the copolymer composition is independent of the feed rate, and we have been able to determine the variation of copolymer composition with variation of the ratio moles propylene

in solution/total moles of both monomers in solution.<sup>33,34</sup> The results are shown in Figure 19.

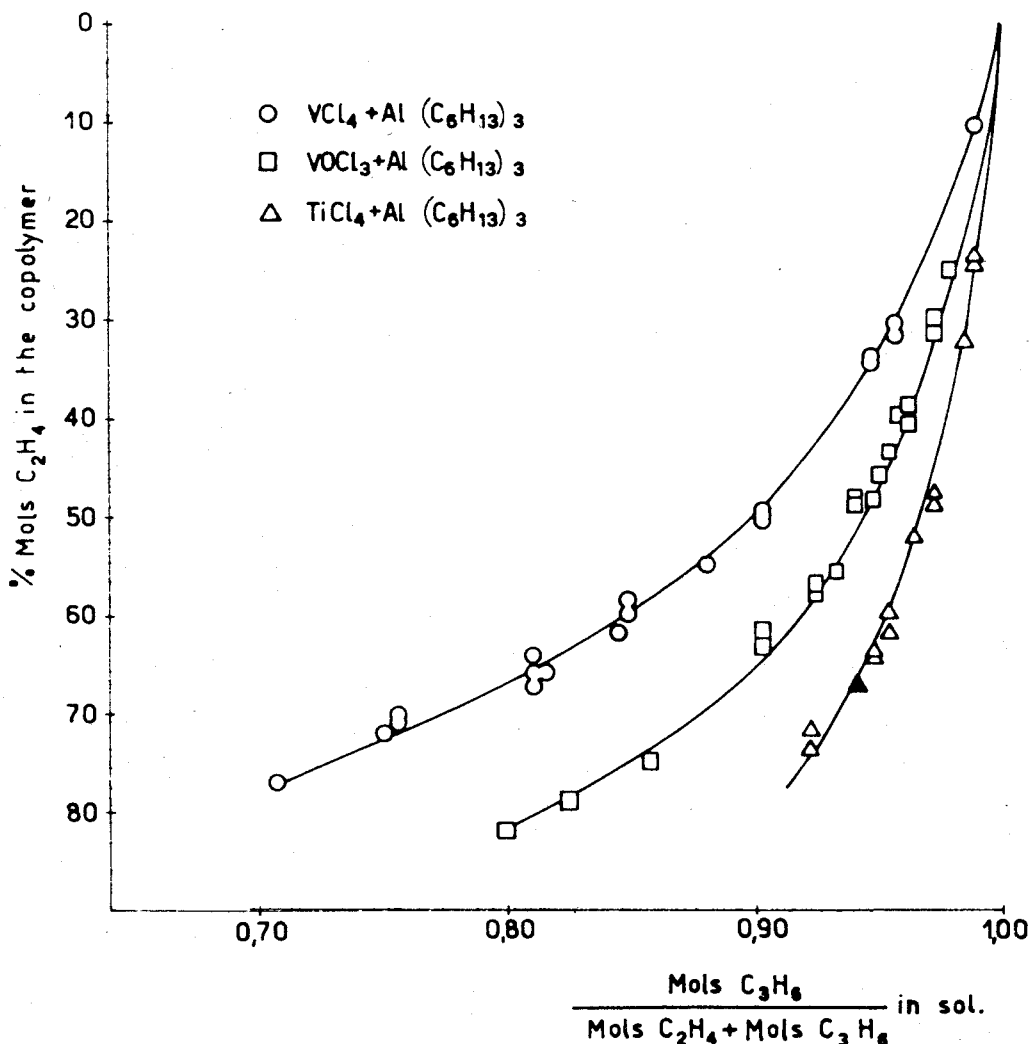


Fig. 19. Composition of ethylene-propylene copolymers obtained with different catalysts, referred to the ratio between the moles of dissolved propylene and the total moles of the two monomers in solution.

We have applied to these results the copolymerization equation proposed by Alfrey and Goldfinger, which, in the case of ethylene-propylene copolymerization can be written as follows:

$$\frac{m_{C_3H_6}}{m_{C_2H_4}} = \frac{M_{C_3H_6} r_{C_3H_6} M_{C_3H_6} + M_{C_2H_4}}{M_{C_2H_4} r_{C_2H_4} M_{C_2H_4} + M_{C_3H_6}}$$

The reactivity ratios  $r_{C_3H_6}$  and  $r_{C_2H_4}$  were determined using the experimental data of Figures 18 and 19, which give the mole percentages  $m_{C_2H_4}$  and  $m_{C_3H_6}$  of the two monomers present in the copolymer, and the corresponding molar concentrations  $M_{C_2H_4}$  and  $M_{C_3H_6}$  of the monomers in solution. The calculation has been carried out both by the method of Lewis and Mayo,<sup>35</sup> and also by the method of Fineman and Ross.<sup>36</sup> Values of

the reactivity ratios found for different catalytic systems are given in Table VI.

TABLE VI

Reactivity Ratios in Ethylene-Propylene Copolymerization in the Presence of Different Catalysts

(Temperature = 25°C. Solvent = *n*-heptane<sup>a</sup>)

Catalyst	$r_{C_2H_4}$	$r_{C_3H_6}$	$r_{C_2H_4} r_{C_3H_6}$
$Al(C_6H_{13})_3 + TiCl_4$	$37.36 \pm 1.31$	$0.032 \pm 0.001$	1.20
$Al(C_6H_{13})_3 + VOCl_3$	$17.95 \pm 0.27$	$0.065 \pm 0.002$	1.15
$Al(C_6H_{13})_3 + VCl_4$	$7.08 \pm 0.20$	$0.088 \pm 0.003$	0.63

<sup>a</sup> Monomer reactivity ratios are referred to molar fraction of the monomer in solution.

The reactivity ratios of the two monomers differ greatly, and their product is remarkably close to unity, in agreement with the general results found for ionic copolymerization. The reactivity of propylene is much lower than that of ethylene, as might be expected in an anionic copolymerization, because of the presence of an electron-releasing methyl group in the propylene molecule. The fact that the reactivity ratios depend on the type of catalyst used is a further confirmation of the ionic mechanism of these polymerizations.

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### Synopsis

The kinetics of chain growth and chain transfer processes in the stereospecific polymerization of propylene, using catalytic systems such as  $\text{—TiCl}_3\text{—Al}(\text{C}_2\text{H}_5)_3$  and  $\text{—TiCl}_3\text{—AlCl}(\text{C}_2\text{H}_5)_2$ , has been examined. The number of active centers present on the catalyst surface has been determined radiochemically by kinetic and adsorption measurements, using aluminum labeled with  $\text{C}^{14}$ . The mean life of macromolecules was determined by radiochemical determination of terminal groups, and the relationships between intrinsic viscosity and number-average molecular weight were found. Kinetic research into ethylene-propylene copolymerization enabled us to determine the different reactivity ratios of the monomers.

### Résumé

On a étudié la cinétique de la propagation et du transfert de chaîne dans la polymérisation stéréospécifique du propylène en utilisant des systèmes catalytiques tels que  $\text{TiCl—Al}(\text{C}_2\text{H}_5)_3$  et  $\text{TiCl}_3\text{—AlCl}(\text{C}_2\text{H}_5)_2$ . On a déterminé le nombre de centres actifs sur la surface du catalyseur par une méthode radiochimique, au moyen d'aluminium marqué de  $\text{C}^{14}$ . On a fait des mesures de cinétique et d'adsorption. On a examiné la durée de vie moyenne des macromolécules par une mesure radiochimique des groupes terminaux. On a constaté une relation entre la viscosité intrinsèque et le poids moléculaire moyen en nombre. L'étude cinétique de la copolymérisation d'éthylène-propylène nous a permis de déterminer les rapports de réactivité des monomères.

## Zusammenfassung

Die Kinetik der Kettenwachstums- und Kettenübertragungsreaktion bei der stereospezifischen Polymerisation von Propylen mit Katalysatorsystemen wie  $\text{—TiCl}_3\text{—Al(C}_2\text{H}_5)_3$  und  $\text{—TiCl}_3\text{—AlCl(C}_2\text{H}_5)_2$ , wurde untersucht. Die Anzahl der aktiven Zentren, die an der Katalysatoroberfläche vorhanden sind, wurde radiochemisch, durch kinetische und Adsorptionsmessungen mit  $\text{C}^{14}$ -markierten Aluminiumverbindungen, bestimmt. Die mittlere Lebensdauer der Makromoleküle wurde durch radiochemische Endgruppenbestimmung ermittelt; die Beziehungen zwischen Viskositätszahl und dem Zahlenmittel des Molekulargewichts wurden erhalten. Kinetische Untersuchungen auf dem Gebiet der Äthylen-Propylen copolymerisation erlaubten eine Bestimmung der Copolymerisationsparameter der Monomeren.

## Discussion

**G. M. Burnett and P. J. T. Tait (Aberdeen):** We have studied the rates of polymerization of styrene in *n*-heptane solution using  $\text{TiCl}_3$  as catalyst in conjunction with either  $\text{AlEt}_2\text{Cl}$  or  $\text{AlEt}_3$ . The main significant results are:

- (1) Rate is proportional to the amount of  $\text{TiCl}_3$ , which can be interpreted as proportional to the surface area.
- (2) Rate is proportional to monomer concentration.
- (3) Rate is independent of  $\text{AlEt}_3$  concentration over about a tenfold range and down to the lowest conveniently measurable concentrations. This may be interpreted as demonstrating the formation of a surface complex for which very little  $\text{AlEt}_3$  would be required.
- (4) Rate is markedly depressed by the addition of small quantities of *n*-propyl alcohol.
- (5) An approximate determination of the activation energy gives a value of about 8 kcal./mole for the overall process.

**F. Danusso (Milan):** I agree with the results on styrene polymerization in the presence of  $\text{TiCl}_3$  reported by Dr. Burnett. Our equivalent and more extended data, also in the presence of  $\text{TiCl}_4$ , were communicated in my own lecture during the Prague Symposium, September 1957 (published in *Collection Czech. Chem. Commun.*, 1958).

**K. Vesely (Czechoslovakia):** In studying the mechanism of Ziegler-Natta polymerization, we followed the rate by means of a dilatometric method, and the results are reproducible. The reaction is monomolecular with respect to propylene and  $\text{TiCl}_3$ .

As to the molecular weights, they are all in the same range, though the rates are very different. I believe the role of the solvent in the chain transfer is important.

For instance, in the case of ethylene polymerization catalyzed by  $\text{AlEt}_3\text{—TiCl}_4$ , there is a linear relation between intrinsic viscosity and solubility temperature of the polymer in the series: cyclohexane, xylene, kerosene, *n*-heptane.

In following up our work on termination reactions in ionic polymerizations, we are studying the influence of small amounts of polar substances. Very interesting is the behavior of substances which do not react, for steric reasons, with  $\text{AlEt}_3$ . For instance, the polymerization rate of propylene was not changed by addition of 40 mole-% of tributylamine to  $\text{AlEt}_3$ , but the intrinsic viscosity was increased from 280 to 450 ml./g.

We are interpreting these results as a selective sorption of tributylamine on the reactive dipole, which thus protects the reaction center against termination by the solvent.

**C. van Heerden (Geleen, Netherlands):** This contribution to the discussion is not a personal one, but is done in the name of a number of research people of the Central Laboratory of the Dutch State mines.

Most people agree that in the Ziegler-Natta catalyst systems for the polymerization of olefins one has to deal with a reaction which is very similar to the "aufbaureaction" found by Ziegler on Al and other metal alkyls.

Professor Natta introduced the concept of a  $\text{TiCl}_3$ -aluminum alkyl complex where

this aufbaureaction probably takes place on the Al—C bond. Some time ago it was stated in a paper by Ludlum (in the *Journal of the American Chemical Society*) that it is perhaps more probable that the aufbaureaction takes place on a Ti—C bond.

We believe that at the moment there are rather strong arguments in favor of the Ti—C bond.

TiCl<sub>3</sub> forms an active system with a large number of different metal alkyls, including Al-alkyls. In a Belgium patent Hoechst mentioned that TiCl<sub>3</sub> also forms an active system with tetravalent titanium alkyl halides. We found in our laboratory that the combination of TiCl<sub>3</sub>Me and brown TiCl<sub>3</sub>, obtained by thermal decomposition of the same TiCl<sub>3</sub>Me, is one of the most active systems, so here we have a system in which only Ti—C bonds can occur.

It seems that the essential role of the metal alkyls is not their ability for complex formation, nor their capacity as a reduction agent.

All metal alkyls can easily exchange their alkyl groups for the chlorine atoms of metal chlorides, and it seems to be a reasonable assumption, which, as far as we know, is not in disagreement with any experimental fact, that the active center for the polymerization is a trivalent Ti—C bond on the surface of solid TiCl<sub>3</sub>, obtained by exchange of a surface chlorine atom for an alkyl group of the metal alkyl. This assumption is very simple and worth investigating.

The Ti—C bond in tetravalent TiCl<sub>3</sub> alkyl seems to be too stable to give a rapid aufbaureaction under the mild conditions of low-pressure ethylene polymerization. A solution of TiCl<sub>3</sub>Me in the absence of TiCl<sub>3</sub> does not give the aufbaureaction, or at least the rate is very small in comparison with the polymerization rate in Ziegler-Natta systems.

Until a few years ago Ti-alkyl compounds were not known and assumed to be very unstable. Only recently Ti-alkyls were isolated. In our laboratory Dr. de Vries found that only those Ti-alkyl chlorides are unstable which can decompose in a bimolecular reaction by disproportionation of two alkyl groups to an olefin and an alkane. For this reason TiCl<sub>3</sub>Me and TiCl<sub>3</sub>-neopentyl are stable as a consequence of the absence of  $\beta$ -H-atoms.

This disproportionation is also the essential step in the reduction of TiCl<sub>4</sub> by metal alkyls. The alkyl only exchanges a chlorine atom for an alkyl group, and the resulting tetravalent Ti-alkyl chloride only decomposes in a bimolecular reaction if a disproportionation of two alkyl groups is possible. For instance, AlMe<sub>3</sub> or AlMe<sub>2</sub>Cl does not reduce TiCl<sub>4</sub>.

For the trivalent Ti-alkyls by surface alkylation of TiCl<sub>3</sub>, which we assumed to be the active center for polymerization, the same disproportionation reaction must be expected. Here, however, the alkyl groups are fixed on the surface of the solid TiCl<sub>3</sub> and therefore cannot react with each other.

**G. Natta (Milan):** Dr. van Heerden, referring to a paper of Noulta *et al.*, criticized our statement that in the Ti-Al catalyst the polymer chain growth is on the aluminum atom. We would like to summarize very briefly our views on the catalytic action of titanium and aluminum as published by us [*J. Polymer Sci.*, **26**, 120 (1957); *Chimica e industria (Milan)*, **39**, 1032 (1957)]. The metallo-organic complexes of Ti containing only one Ti atom, such as (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, do not promote ethylene polymerization at the temperatures (below 150°) and pressure (below 60 atm.) we have used.

By reacting (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> with a trialkyl or triarylaluminum, complexes containing Ti and Al have been obtained which polymerize ethylene.

As in certain complexes, Ti and Al are bonded by Cl bridges or by alkyl group bridges (G. Natta, P. Pino, and G. Massanti, Paper presented at XVI International Congress of Pure and Applied Chemistry). It appears very difficult to establish which bond is involved in the propagation step of the polymerization. Moreover, the fact that the groups originally bound to Al have been found as terminal groups in the polymer chains and that a large number of the macromolecules after the polymerization are still bound to Al, supports the hypothesis that the polymer chains grow from aluminum atoms.

By reacting  $(C_5H_5)_2Ti(C_6H_5)_2$  with  $TiCl_4$ , we have obtained insoluble complexes which contain more than one Ti atom and are catalytically active both in the polymerization of ethylene and propylene. In this case there is no doubt that the polymer chains grow from the Ti atoms, other metallic atoms being absent, but the catalyst shows an activity that is lower than that of the Ti-Al catalysts.

We think that our experiments clearly show that the catalysts for ethylene polymerization are metallo-organic complexes containing more than one metal atom; the most active catalysts contain different metal atoms but catalysts can be prepared which contain more than one atom of the same transition metal, in the absence of any other metallic atom.

**A. Gilchrist** (*I.C.I. Alkali Division, Northwich*): Professor Natta has emphasized in both of his papers presented to this Conference that it is the most highly crystalline catalysts which produce the most regular polymers. Surface corrosion of an originally highly crystalline catalyst reduces stereospecificity. It is not obvious why this should be so if polymerization occurs at *isolated* sites on the edges of the basal planes of the crystal layer lattice. (G. Natta, paper presented at the International Meeting on the Chemistry of Coordination Compounds, Rome, September 1957.) On the other hand, such observations follow at once from any theory in which the center of polymerization moves along the layer surface of the crystalline catalyst. The freer the surface from defects and dislocations, the longer can the polymer continue uninterrupted regular growth.

**S. R. Palit** (*Calcutta*): I should like to draw the attention of all workers using metal compounds as catalysts for polymerization to a series of three papers published from my laboratory *circa* 1950 on the effect of metals on polymerization. We demonstrated that metallic soaps, such as oleates and laurates of Fe, Co, and Al, are powerful catalysts for the polymerization of styrene and methyl methacrylate. This work conclusively established that in homogeneous solutions these metals are good initiators by a mechanism not well understood, and in considering any theory of the action of the recently developed catalysis by metallo-organic compounds, this fact has also to be taken into consideration.

The rate curve of, say, methyl methacrylate polymerization by ferric laurate is similar to that found by Professor Bawn, a sharp maximum being obtained at a certain concentration of the ferric soap. This type of self-retardation is also met with in other cases.