

## The Kinetics of the Stereospecific Polymerization of $\alpha$ -Olefins

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## I. Introduction to Anionic Coordinated Polymerization of $\alpha$ -Olefins

### A. GENERALITIES

Considerable interest has been shown in the new processes of stereospecific polymerization, not only so far as they concern the production of new classes of polymers, having unusual characteristics and improved properties, but also because they are representative of a peculiar new type of heterogeneous catalysis, of great interest from the practical and the theoretical points of view (1-5).

The discussion of kinetic work will be here preceded by a summarized description of the chemical nature of the polymerization, to which we have attributed a mechanism of anionic coordinated type. Such a definition of the reaction mechanism depends upon the fact that the catalyst is a complex in which, generally, a transition metal acts as a coordinating agent and that a carbon atom, which belongs to the extremity of a growing polymeric chain, is coordinated to such a complex and, in the activated state, it possesses a negative charge.

The stereospecific polymerization of  $\alpha$ -olefins takes place only in the presence of heterogeneous catalytic systems, including a crystalline substrate (formed by halides of transition metals, such as  $\text{TiCl}_3$ ,  $\text{TiCl}_2$ ,  $\text{VCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{CoCl}_2$ , etc.) and a suitable metallorganic compound (5).

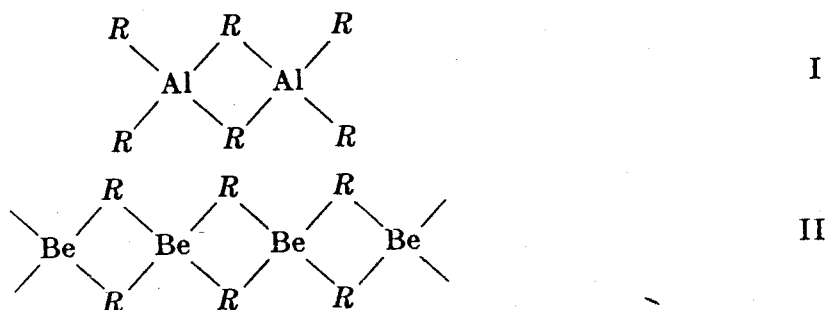
Such metallorganic compound or coordination complex contains an electropositive metal for which the carbon-metal bond may be considered at least partly polarized, so that the carbon atom has a partially ionic character and behaves as a carbanion.

The above-mentioned metallorganic compounds must have the property of forming complexes with the halides of transition metals. It is required, in order to get catalytic complexes, that the metal of metallorganic compounds be able to create a strong localized electric field; therefore, metals having a very small ionic diameter (below 1 Å.) jointly with a very electropositive character are to be used. For such reasons, metals such as Ca,

Ba, Sr, K, Rb, Cs, although they have high electropositivity, cannot be employed, their ionic radius being too large, whereas other metals such as B, with a small ionic radius, are not so suitable, because they show an insufficient electropositivity (5, 6).

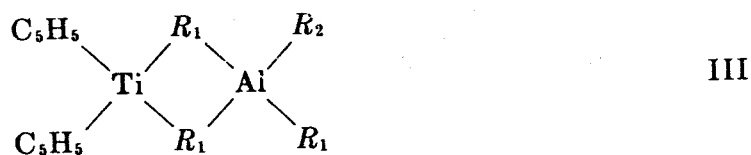
The most suitable metallorganic compounds are those of Al or Be, since these metals are characterized by small ionic radius [for instance,  $\text{Al}(\text{C}_2\text{H}_5)_3$ ,  $\text{AlCl}(\text{C}_2\text{H}_5)_2$ ,  $\text{Al}(\text{iC}_4\text{H}_9)_3$ ,  $\text{Be}(\text{C}_2\text{H}_5)_2$ ]. Less efficiency is shown by certain metallorganic complexes containing Zn, Li, etc. (5, 6.)

The formation of prevailingly electron-deficient complexes between transition metals of low valency and metallorganic compounds of metals having small ionic radius has been clearly shown. The electron-deficient metallorganic compounds



where  $R$  is an alkyl group, polymerize ethylene to low-molecular-weight polymers (7).

Crystallizable complexes containing transition metals of the following general formula have been isolated:



where  $R_1$  is a halide or an alkyl group and  $R_2$  is an alkyl group. They polymerize ethylene to high-molecular-weight polymers (8).

### B. STEREOSPECIFICITY OF CATALYSTS

The metallorganic compounds (I, II) employed in presence of a heterogeneous phase containing an amorphous compound of a low-valency, strongly electropositive transition metal, generally polymerize  $\alpha$ -olefins to amorphous polymers. In a similar fashion, the soluble reaction products of such metallorganic compounds with compounds of transition metals, chemisorbed on amorphous substrates, polymerize  $\alpha$ -olefins to amorphous polymers (6, 9).

The same compounds (I, II) employed in presence of solid crystalline halogenated compounds of some transition metals behave as stereospecific

TABLE I  
*Stereospecificity of Catalytic Systems:  $\alpha$ -TiCl<sub>3</sub>-M(C<sub>2</sub>H<sub>5</sub>)<sub>n</sub>*  
*t = 75°, p<sub>C<sub>2</sub>H<sub>4</sub></sub> = 2.4 atm.)*

Metal of the metal alkyl compound	Ionic radii of the metal, A.	Polypropylene not extractable in boiling <i>n</i> -heptane %
Be	0.35	94-96
Al	0.51	80-90
Mg	0.66	78-85
Zn	0.74	30-40

catalysts and polymerize the  $\alpha$ -olefins to crystalline polymers (5, 9). A greater stereospecificity is shown by catalysts containing metallorganic compounds of metals with very small ionic radius (see Table I) (5, 6).

Complexes of type III and also traces of soluble halides of strongly electropositive transition metals, being able to form complexes with metallorganic compounds of the type I, II, increase the activity of the stereospecific catalysts formed by the action of metallorganic compounds on crystalline substrates (10, 11). They can also polymerize in a stereospecific way in the presence of crystalline substrates of transition metals (for instance, CoCl<sub>2</sub>) which are not by themselves sufficiently electropositive, (when used in the presence of metallorganic compounds) to polymerize the  $\alpha$ -olefins (10, 11).

The stereospecific catalysts polymerize  $\alpha$ -olefins, giving linear polymers, by head-to-tail addition containing long sequences of monomeric units, whose carbon atoms show the same relative steric configuration. The non-stereospecific catalysts, on the contrary, give chains whose monomeric units follow each other in a random or not ordered way as far as it concerns the relative steric configuration. Each molecule of  $\alpha$ -olefin, at the moment of polymerization, may give rise to two types of monomeric enantiomorphous units, which differ only for the steric configuration, one being the mirror image of the other one (Fig. 1).

Only the heterogeneous catalysts, and in particular those acting on a crystalline substrate, contain active centers, each of which makes an asymmetric synthesis, as it converts the monomer molecules which do not yet contain atoms of asymmetric carbon, at the moment of the polymerization, into monomeric units having all the same steric configuration (12, 5).

An asymmetric structure has been ascribed to such active centers, that justifies their behavior as catalysts of asymmetric synthesis (6).

In a heterogeneous not optically active catalyst there is the same probability that an active center shows a given steric structure or the enantiomorphous one; it follows that one half of the present active centers will cause a given configuration of monomeric units (for instance, right-handed) and the other half will cause the opposite configuration (left-handed).

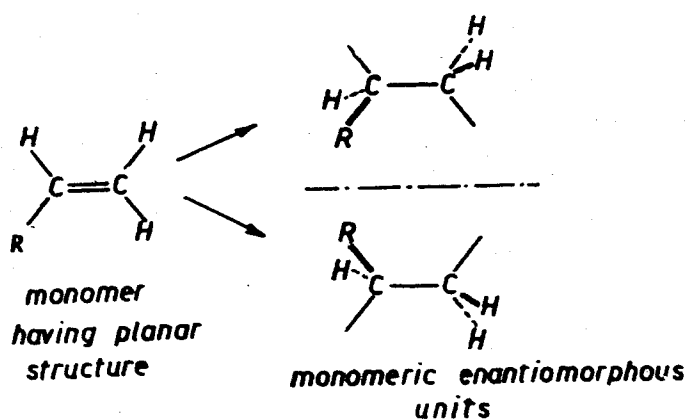


FIG. 1.

There will be in a raw polymer the same number of chains, whose monomeric units show, with regard to a certain terminal group, a given structure (for instance, right-handed) and the same number with the opposite steric structure (left-handed).

The raw polymers of this type have been called isotactic and may in general crystallize (1). They differ for this reason from atactic polymers, in which the monomeric units follow in the same chain with random steric configuration and are unable to crystallize.

In an isotactic chain having a very great length (considered as being of infinite length), there will be no more asymmetric carbon atoms because the asymmetry of the tertiary carbon atoms, which was due to the different structure or length or configuration of the two parts of the chain linked to it, disappears (5). Such carbon atoms show, however, the same steric configuration of the tertiary carbon atoms which follow or precede them, and this makes them different from atactic polymers (5, 13, 14).

Before the discovery of stereospecific catalysis, all the known polymers of  $\alpha$ -olefins were unable to crystallize, because their structure was chemically irregular (for instance, not rigorously linear or not rigorously head-to-tail) and because it was sterically irregular (15).

A difference of structure between isotactic and atactic polymers exists independently of their physical state. If we could, in fact, stretch on a horizontal plane a sterically regular segment of the main chain of an isotactic polymer of the type  $(\text{CHR}=\text{CH}_2)_n$ , the  $R$  groups linked to the tertiary carbon atoms would range themselves all over or under such plane, whereas in an atactic polymer they would be arranged in a random way, partly over and partly under it (Fig. 2).

The chains of isotactic polymers (in which the dimensions of  $R$  are much greater than those of the hydrogen atom) have the tendency to assume a helicoidal configuration with a pitch which depends on the dimensions of the  $R$  group. There is evidence that a helicoidal structure has the tendency to exist also (at least partially) in the amorphous state. It is detectable,

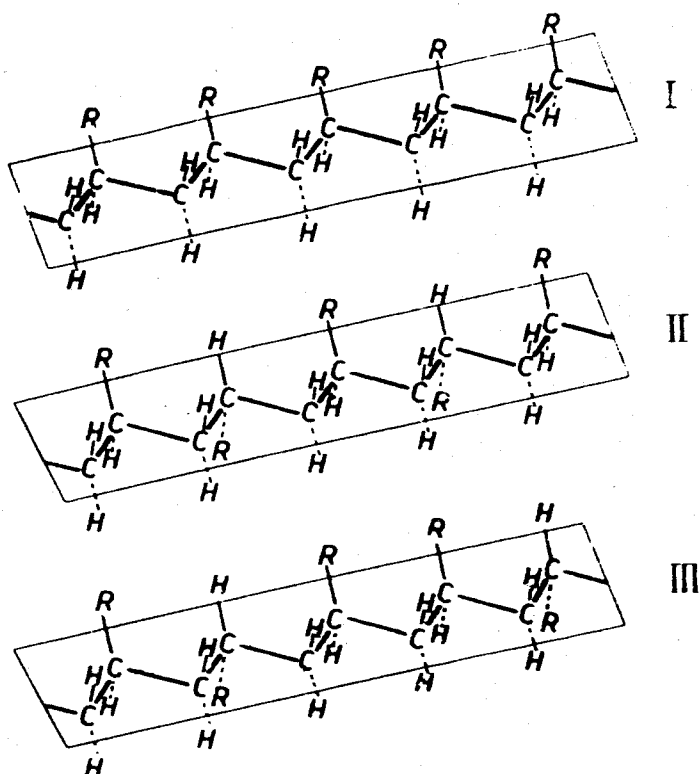


FIG. 2. Chains of stereoisomeric poly- $\alpha$ -olefins supposing the main chain stretched on a plane. I. Isotactic. II. Syndiotactic. III. Atactic.

however, in the crystalline state. In the crystals we may find macromolecules of isotactic polymers with a helix-shaped arrangement, which is ternary (in the case of polypropylene, polystyrene, modification I of polybutene, etc.), quaternary (in the case of poly-3 methyl-butene-1), or heptenary (in the case of poly-4-methylpentene-1, etc. (Fig. 3) (16, 17).

The helices may show a right- or left-handed winding (independent of the steric configuration of the tertiary carbon atoms. In the crystal lattice of many isotactic polymers, there may be found a chain packing, characterized by the fact that each right-handed chain is surrounded by left-handed chains and vice versa (Fig. 4) (18, 19). To the high regularity of structure must be ascribed the exceptional properties of isotactic polymers (high melting point, high mechanical characteristics, possibility to form films or fibers made of oriented crystals having high tensile strengths). To them is attributed the great interest arisen in the fields of plastics and synthetic fibers (5).

### C. MECHANISM OF STEREOSPECIFIC POLYMERIZATION

The process may be ascribed to the coordinated anionic type. Such a process which leads to the addition of a molecule of monomer in a polymeric chain, may be considered as divided into several consecutive steps.

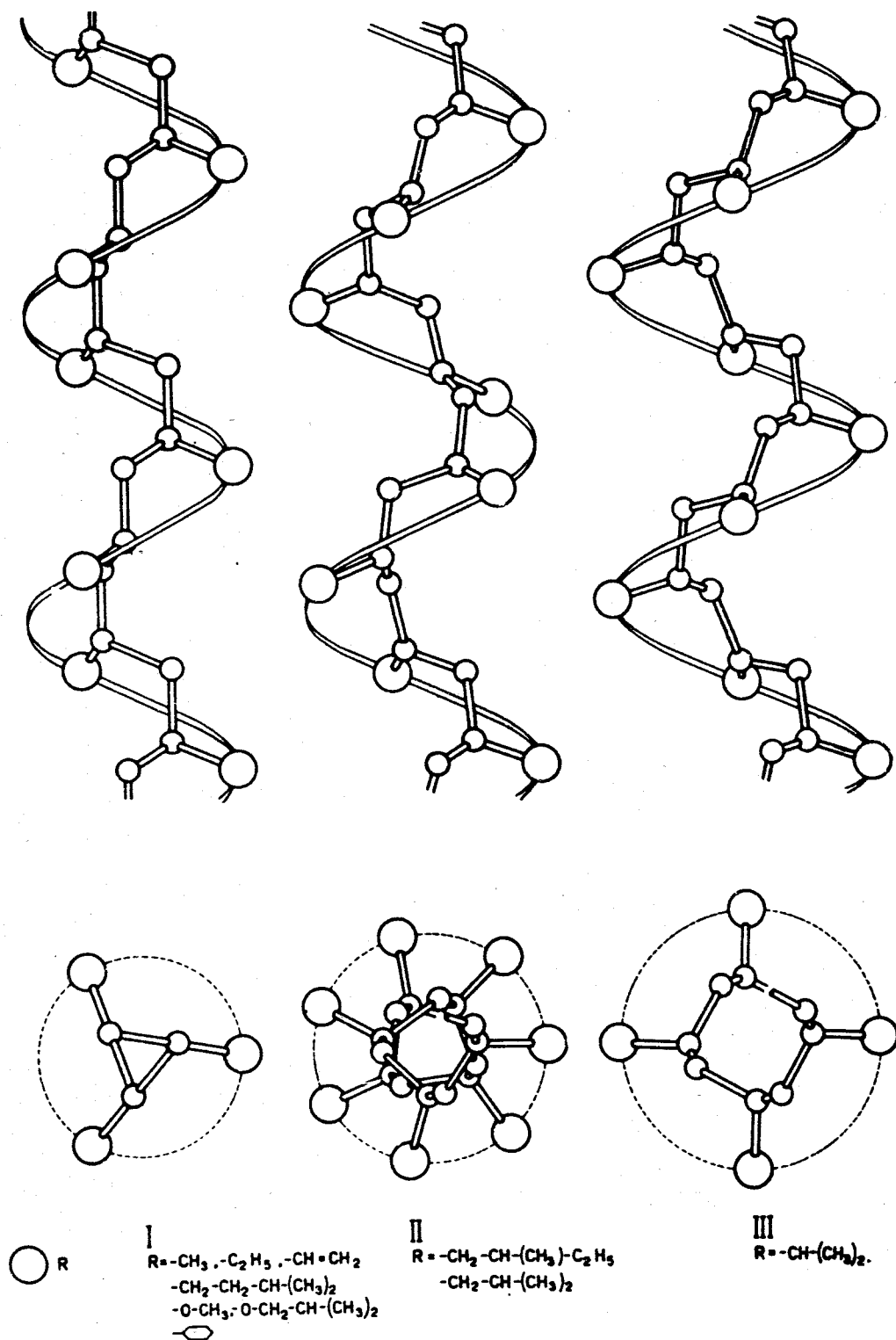
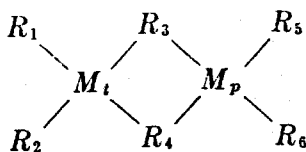


FIG. 3. Chains of isotactic polymers.

The electron-deficient catalytic complex, containing a transition metal, has the tendency to attract the olefin molecule, whose  $\pi$ -electrons tend to compensate the deficiency of electrons of the complex.

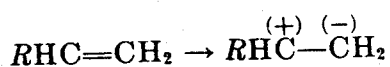
The catalytic complexes may possess a type of structure as follows:



where  $M_t$  is the transition metal and  $M_p$  is the strongly electropositive metal to which the alkyl groups are bound.

Only when such a complex is chemisorbed or lies on the surface of a crystalline lattice made of a compound of a transition metal does the catalyst act in a stereospecific way in the polymerization of  $\alpha$ -olefins.

In the first reaction step, the olefin is strongly polarized by the catalyst, as follows:



At the same time, a dissociation of ionic type of the bridge bond takes place. The bridge bond  $M-R-M$  is, in fact, weaker, as demonstrated by

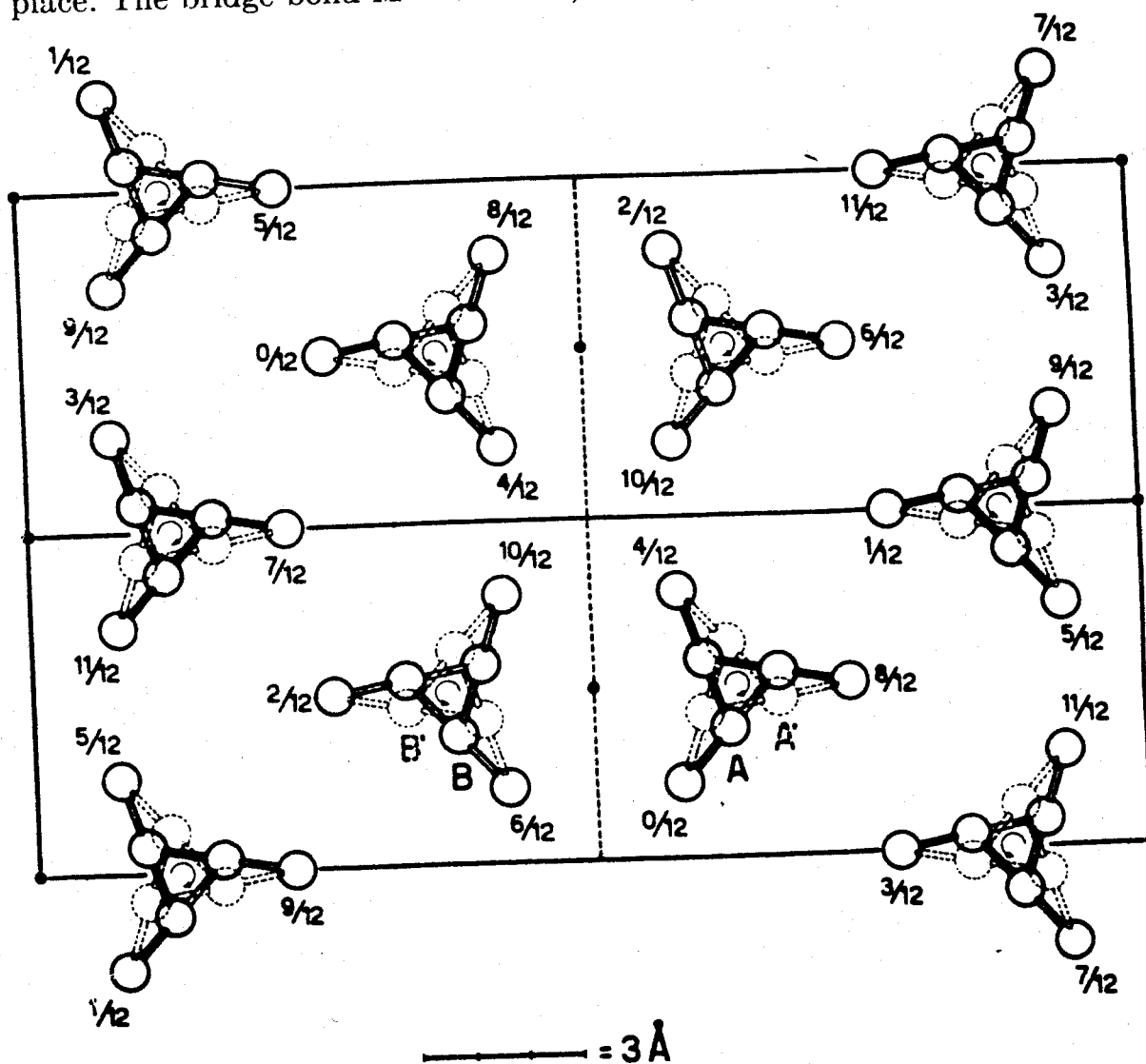


FIG. 4. Projection of the crystalline polypropylene lattice, on a plane perpendicular to the axis of the polymeric chains.



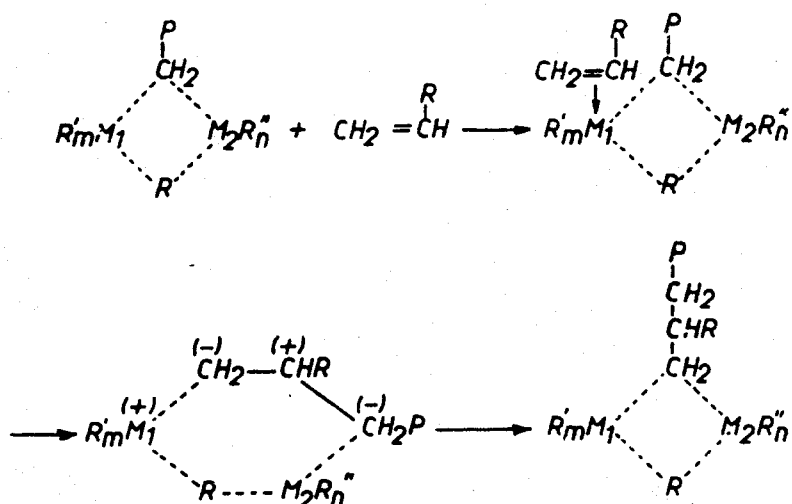
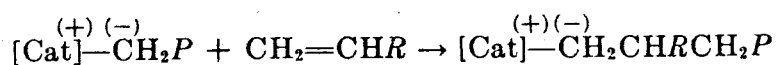


FIG. 5. Hypothesis of addition of a monomer molecule on the bond between the catalytic complex and the growing chain, in the anionic coordinated polymerization.

the greater length of this bond between metal and  $R$  group compared with the bonds between side groups  $R$  and the metal. This was observed by X-ray examination of different complexes, containing bridge bonds (20, 21).

The introduction of a monomeric unit occurs between the electronegative  $-CH_2$  at the chain end and the electropositive metal. A new  $-CH_2$  group deriving from the new monomeric unit, comes and substitutes in the complex the  $-CH_2$  group of the previous monomeric unit (see Fig 5). The reaction of polyaddition is represented by the following equation:



The termination of the growing polymeric chain may occur through several different processes, mostly by chain transfer. Either the process of chain transfer with the monomer, or the reaction of dissociation to hydride, leads to the formation of terminal vinylidenic groups, whose presence was noticed in the olefin polymers, obtained with the previously described catalysts (22).

The chain termination processes will be described in detail in the following sections, dealing with the kinetic study of polymerization process.

#### D. INFLUENCE OF THE CRYSTALLINE SUBSTRATE ON THE STEREOSPECIFIC POLYMERIZATION

The stereospecificity depends not only upon the electropositivity and the ionic radius of the metal which belongs to the metallorganic compound, used for the preparation of the catalyst, but also upon the lattice structure of the crystalline substrate made of the transition metal compound (5).

Besides the chemical composition, the crystalline structure of the substrate exerts a great influence on the stereospecificity of the catalyst.

For instance, the halides of the type  $MX_n$  which crystallize with layer

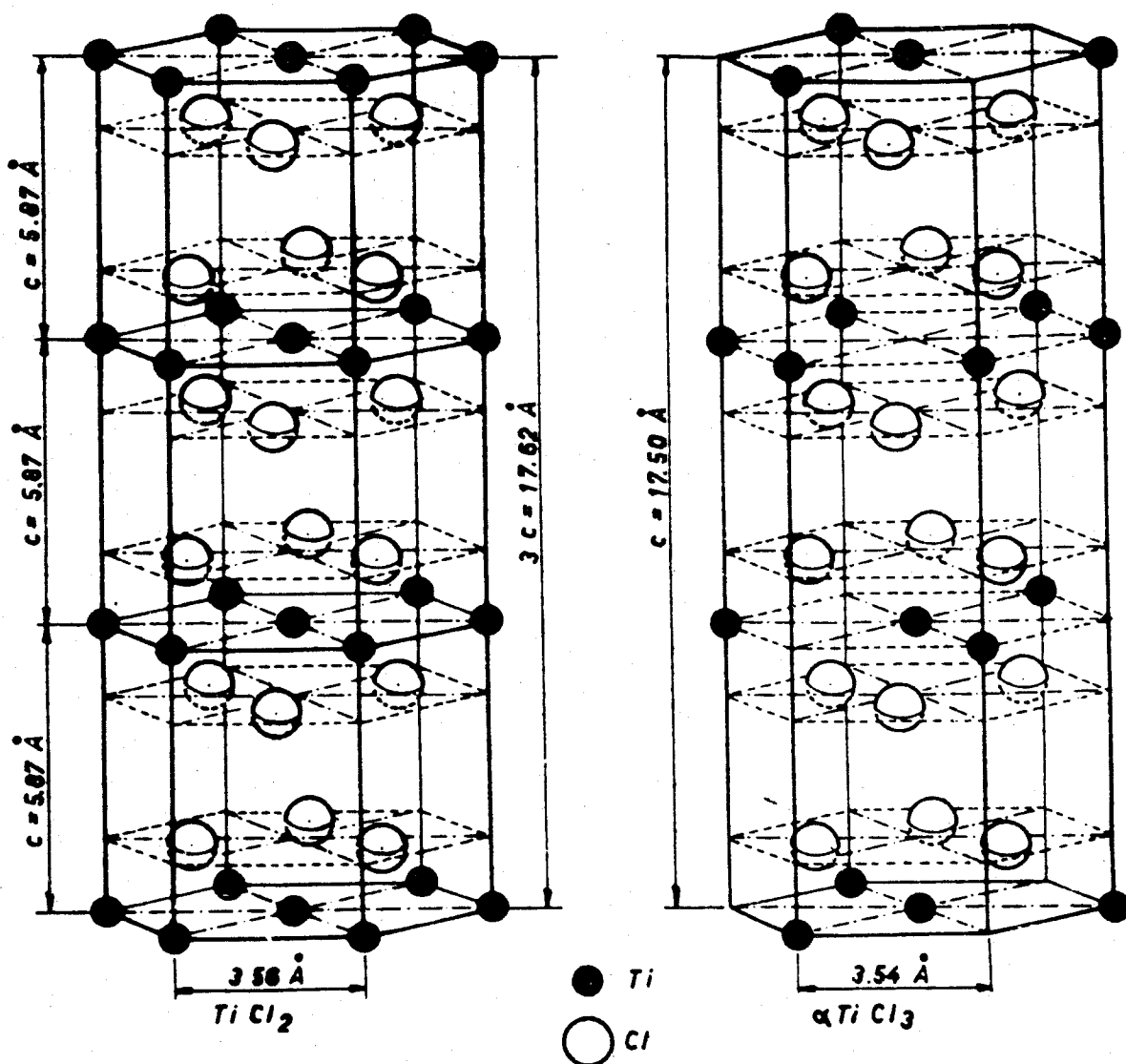


FIG. 6.  $\alpha\text{-TiCl}_3$  and  $\text{TiCl}_2$  crystalline lattices.

lattice ( $\alpha\text{-TiCl}_3$ ,  $\text{TiCl}_2$ ,  $\text{VCl}_3$ , etc.) (Fig. 6) (23, 24) are all suitable for the preparation of stereospecific catalysts (9, 5, 25, 26).

In the case of  $\text{TiCl}_3$  the less crystalline forms obtained at low temperature by precipitation from solution of  $\text{TiCl}_4$  and alkylaluminum are less stereospecific than the well-crystallized forms obtained at high temperature (5).  $\text{TiCl}_3$  crystallizes in three forms at least (27), and the greatest stereospecificity is given by the  $\alpha$ -form.

For this reason the catalytic systems, which we have mostly employed for studies of stereospecific polymerization of  $\alpha$ -olefins, are those made using  $\alpha\text{-TiCl}_3$ .

## II. Over-All Kinetics of Polymerization Process

### A. CATALYTIC SYSTEMS USED

As already stated in the first chapter, several catalytic systems show a certain stereospecificity in the  $\alpha$ -olefin polymerization.

These systems may be differentiated either by the nature of the compound of the transition metal or by the type of the metallorganic compound used for their preparation.

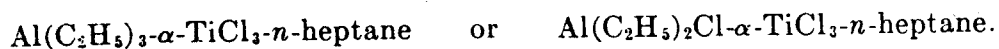
The behavior of the different catalytic systems (containing transition metal crystalline compounds) in the  $\alpha$ -olefin polymerization, except for the different degree of stereospecificity, may be connected with a definite kinetic scheme. This was shown by experimental work performed at the Institute of Industrial Chemistry of the Milan Polytechnic.

When the compound of the transition metal is changed (e.g.,  $\alpha$ -TiCl<sub>3</sub>,  $\beta$ -TiCl<sub>3</sub>), generally, the molecular weight of the resulting polymer changes. Also the nature of the alkyl group of the metallorganic compound influences the stereospecificity and the molecular weight of the polymer obtained (28).

The nature of the olefin exerts a certain influence on the rate constant of the over-all polymerization. This is connected with factors of steric character and to the more-or-less enhanced electron-releasing character of the alkyl group bound to the vinyl group which may influence several steps of the over-all polymerization process.

Although the catalysts containing beryllium alkyl are more stereospecific than those with alkylaluminum (5, 6), nevertheless the greater part of our kinetic measurements were performed using alkylaluminum compounds, since they represent a special practical interest due to the higher availability, and lower toxicity compared with the corresponding beryllium compounds.

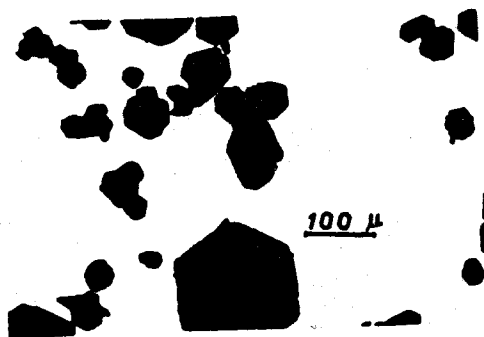
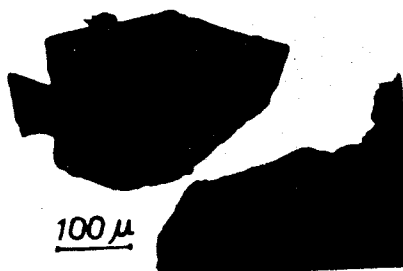
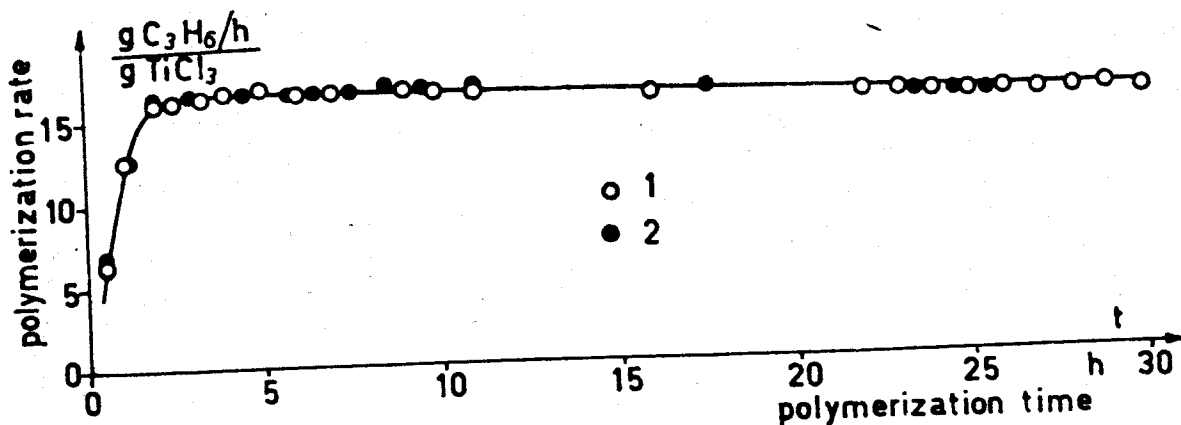
The results summarized in this paper have been obtained using the catalytic systems:



The kinetic measurements reported in the following sections are concerned with the polymerization of propylene; the results obtained with this monomer can, however, be extended to other olefins (e.g., normal: butene-1, pentene-1, or branched). For this reason, although we limit ourselves to recording measurements made with one monomer only and with two types of catalytic system, we have given the most general title to this paper.

## B. INFLUENCE OF THE SIZES OF $\alpha$ -TiCl<sub>3</sub> CRYSTALS ON THE POLYMERIZATION RATE. ADJUSTMENT PERIOD

The  $\alpha$ -TiCl<sub>3</sub> (violet modification), prepared by reduction of TiCl<sub>4</sub> with flowing hydrogen at high temperature (29), generally shows hexagonal lamellae whose sizes, depending on the method of preparation, lie in the range from 1  $\mu$  to several hundred microns (see for instance the sample of Fig. 7). Sometimes the  $\alpha$ -TiCl<sub>3</sub> lamellae do not show any defined geometrical shape, and their dimensions may reach a millimeter (see for instance the sample of Fig. 8).

FIG. 7. Photomicrograph of  $\alpha$ -TiCl<sub>3</sub> (sample B).FIG. 8. Photomicrograph of  $\alpha$ -TiCl<sub>3</sub> (sample C).FIG. 9. Propylene polymerization rate at constant pressure and temperature a function of polymerization time ( $p_{C_3H_6} = 1,450$  mm. Hg,  $t = 70^\circ$ ).

	1	2
$\alpha$ -TiCl <sub>3</sub> (sample A), g./l.	0.80	1.00
[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ] mol./l.	$4.45 \times 10^{-2}$	$2.94 \times 10^{-2}$

In Fig. 9 the characteristic behavior of propylene polymerization rate plotted *vs.* polymerization time. The data were obtained by operating at constant pressure with a catalytic system containing  $\alpha$ -TiCl<sub>3</sub> crystals having initial sizes between 1 and 10  $\mu$  ( $\alpha$ -TiCl<sub>3</sub> sample A).

It may be noticed that during the initial polymerization period 'adjust'

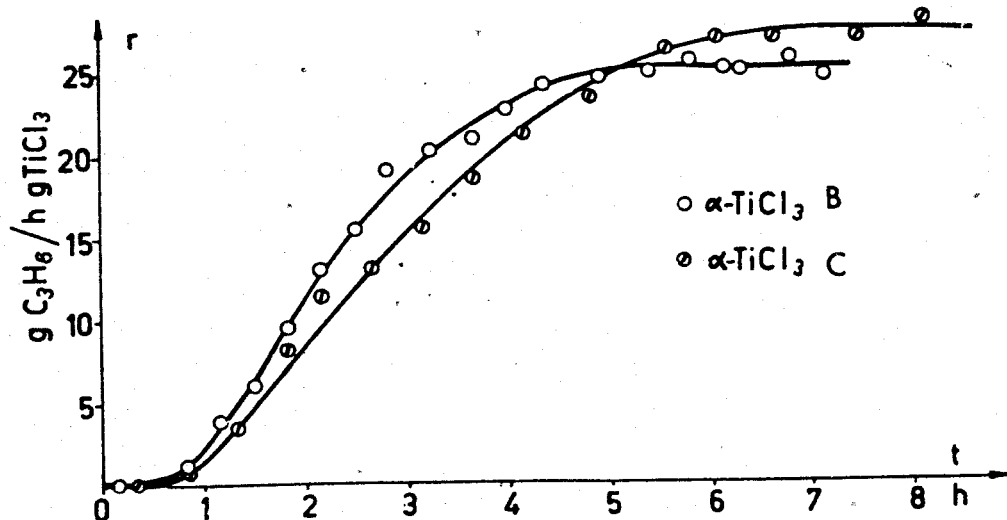


FIG. 10. Propylene polymerization rate at constant pressure and temperature ( $p_{\text{C}_3\text{H}_6} = 1,450$  mm. Hg,  $t = 70^\circ\text{C}$ ) obtained with two samples of unground  $\alpha\text{-TiCl}_3$  whose crystals have different sizes (see Figs. 7 and 8). ( $\alpha\text{-TiCl}_3$  : 1.64 g./l.,  $[\text{Al}(\text{C}_2\text{H}_5)_3]$  :  $2.94 \times 10^{-2}$  mol./l.).

ment period) the activity of the catalyst increases until it has reached a value which remains, afterwards, practically constant in the time.

This adjustment period has been explained on the assumption that crystals and aggregates of  $\alpha\text{-TiCl}_3$  are smashed and cleaved under the mechanical action of growing polymeric chains, so that we have a consequent increase up to a constant value, in the number of active centers which directly participate in the polymerization.

This assumption has been proved by the following experimental data:

1. The polymerization rate, under steady-state conditions, appeared to be almost independent of the initial size of the  $\alpha\text{-TiCl}_3$  crystals (Fig. 10).

2. By operating with ground  $\alpha\text{-TiCl}_3$  (sizes  $\leq 2 \mu$ ) the adjustment period was definitely affected. The initial period, characterized by an increasing rate which might otherwise last for 7–8 hrs., was greatly shortened and modified (see Fig. 11) (30, 31).

3. The rate that can be reached under steady-state conditions (for instance, by operating at  $70^\circ$ ) seems to be practically unaffected by a moderate amount of grinding (see Fig. 11). The effect of a moderate degree of grinding on the extent of  $\alpha\text{-TiCl}_3$  active surface leads to a final result similar to that resulting from the mechanical disaggregation caused by the action of the growing polymeric chains.

It may be assumed that in any case the final size of the  $\alpha\text{-TiCl}_3$  particles reaches approximately the same limiting value. On the other hand, it is most likely that the exceptionally small and active  $\alpha\text{-TiCl}_3$  particles, obtained during the grinding, are unstable and lose their activity on ageing. In fact, at the beginning of the reaction, when using ground  $\alpha\text{-TiCl}_3$ , the

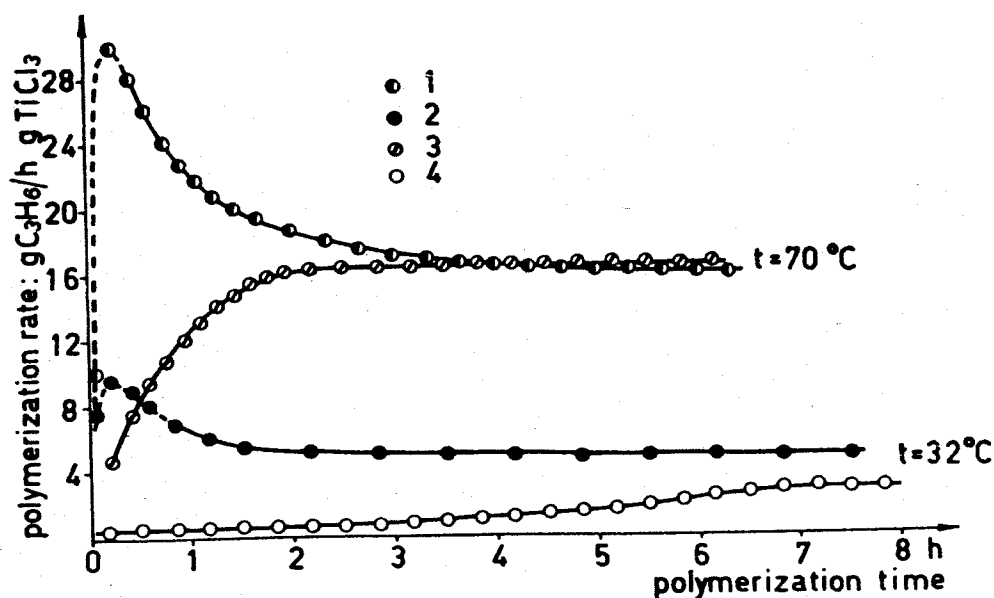


FIG. 11. Effect of previous physical treatments on a sample of  $\alpha$ -TiCl<sub>3</sub> on the propylene polymerization rate, at constant pressure and temperature ( $t = 70^\circ$ ,  $p_{C_3H_6} = 1,450$  mm. Hg). 1 and 2: ground  $\alpha$ -TiCl<sub>3</sub> (sample A) (sizes  $\leq 2 \mu$ ). 3 and 4: unground  $\alpha$ -TiCl<sub>3</sub> (sample A) (sizes within 1 to 10  $\mu$ ).

polymerization rate very quickly reaches a maximum and decreases afterwards, more or less slowly, until attaining the steady-state condition. The presence of such a maximum may be ascribed to very small  $\alpha$ -TiCl<sub>3</sub> particles which lose their activity during the polymerization, either by recrystallization, by reaction with Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, or by occlusion in the solid polymeric product. In particular, it may be observed that the maximum disappears when operating with Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl instead of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (32).

4. By operating with unground  $\alpha$ -TiCl<sub>3</sub> the time ( $t_{3/4}$ ) which is necessary to reach the  $\frac{3}{4}$  of the value of polymerization rate in steady-state conditions varies inversely with the polymerization rate measured under steady-state conditions (30, 31). In fact, by comparing the polymerization carried out at different temperatures and pressures, referred to the same amount of  $\alpha$ -TiCl<sub>3</sub>, we observe different values of  $t_{3/4}$  mainly depending upon the overall polymerization rate, and consequently upon the value reached by the rate under steady-state conditions (Fig. 12) (31).

5. The use, in the propylene polymerization, of unground  $\alpha$ -TiCl<sub>3</sub> that had been previously maintained, for many hours, in the presence of solutions of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> at temperatures lower than 80°, does not substantially modify the observed reaction rate and its variation during the adjustment period (31).

6. It has been observed by microscopic examinations that the  $\alpha$ -TiCl lamellae are very thin and brittle.

7. In some tests it has been observed that the polymerization rate a

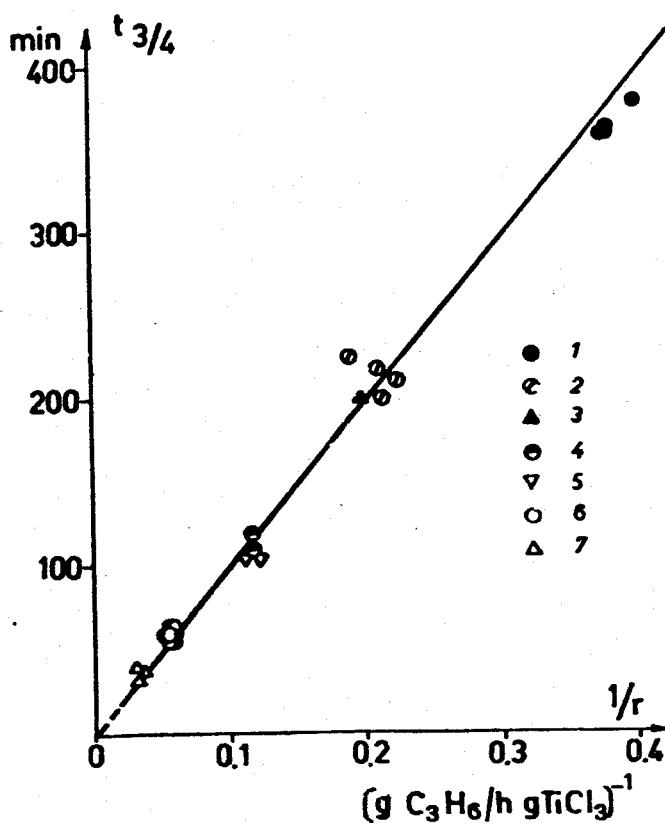


FIG. 12. Dependency of the  $t_{3/4}$  index of the adjustment period, on the reciprocal of the propylene polymerization rate in steady state conditions. Tests performed with unground  $\alpha$ -TiCl<sub>3</sub> (sample A).

	1	2	3	4	5	6	7
$t$ , °C	32	43	32	56	70	70	70
$p_{C_3H_6}$ , mm. Hg	1,680	1,640	2,380	1,570	750	1,450	2,450

zero time is not zero; it keeps the initial value for several minutes before starting to increase (see, for instance, the lowest curve of Fig. 11).

8. It has also been found that the polymer formed from the beginning of the reaction is already prevalingly isotactic. This means that, from the start of the reaction, there exist a certain number of active centers on the solid  $\alpha$ -TiCl<sub>3</sub> surface which immediately yield isotactic polymer; consequently, it can be excluded that, at least for the active centers present on the initial free surface of  $\alpha$ -titanium trichloride, there is an initial activation process, whose rate is slow enough to be observed even when operating at low temperature (30°).

The above statements are in good agreement with the fact that, after the reaction has been carried out in steady-state conditions and has been stopped by taking off the monomer, thereafter, when the initial value of monomer concentration has been re-established (Fig. 13), the reaction starts

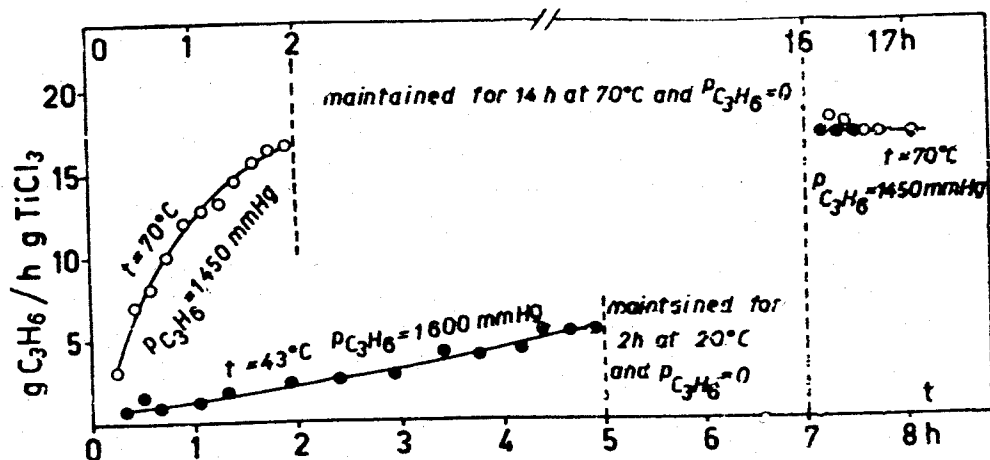


FIG. 13. Effect of the variations of the steady-state conditions on the propylene polymerization rate.

again at once and at the same steady-state rate. The lowest curve of Fig. 13 shows that the steady-state rate at a given temperature (below  $80^{\circ}$ ) is the same also if the steady-state conditions had been previously reached at lower temperature (30, 31).

### C. CATALYTIC BEHAVIOR OF $\alpha$ -TiCl<sub>3</sub> IN STEREOSPECIFIC PROPYLENE POLYMERIZATION

From the curve reported in Fig. 9, we may observe that the polymerization rate, obtained by operating at constant pressure, after the initial adjustment period, remains practically constant for many hours. This occurs only when operating with pure reagents and solvents, with not too finely ground  $\alpha$ -TiCl<sub>3</sub>, and under such conditions as to get limited polymerization rates per unit volume solvent (some g. of C<sub>3</sub>H<sub>6</sub>/hr. per liter of solvent) (30, 33).

This time-constant rate is proportional to the  $\alpha$ -TiCl<sub>3</sub> amount which proves that, at least formally, the over-all polymerization process is really a catalytic one, with regard to the  $\alpha$ -TiCl<sub>3</sub>. The catalytic behavior of  $\alpha$ -TiCl<sub>3</sub> is, in any case, connected with the existence on its surface of metal-organic complexes which act in the polymerization only if  $\alpha$ -TiCl<sub>3</sub> is present. This makes stereospecific polymerization processes (of coordinated anionic nature) very different from the better known polymerization processes, initiated with free radicals. In the latter process, the initiator is not a true catalyst, since it decomposes during the reaction, forming radicals which are bound to the dead polymer; on the contrary, in the case of stereospecific polymerization, each molecule of polymer, at the end of its growing period, can be removed from the active center on the solid surface of the catalyst which maintains its initial activity.

There is evidence that each active center which initiates a polymer chain (coordination complex between the titanium salt and a metal-alkyl



compound) retains unaltered its ability to form macromolecules, independent of the number of polymer molecules produced.

Many homogeneous catalytic processes, in particular of anionic nature, are known, in which the polymerization takes place by stepwise addition (polymerization of ethylene oxide (34) of ethylene at low pressure and temperature with  $AlR_3$  (7, 35), of styrene by Szwarc catalysts (36), for which the growth of the macromolecule can last for a very long time). This led some researchers to talk of a life of macromolecules and of living molecules (37).

This attribute is justified by the fact that the growth of the macromolecules does not show any termination; it stops when the monomer is removed, but is resumed immediately at the same rate when the monomer concentration is restored to its initial value. In some cases (e.g., the case of "living polymers" of Szwarc, obtained with anionic catalysts), it is exactly the same macromolecule which continues to grow, yielding polymers whose molecular weight increases with the polymerization time.

In the case under examination (heterogeneous catalysis in the presence of coordinated polymetallic complexes) the molecular weight of the polymer is generally almost independent of the polymerization time, whenever the polymerization lasts for more than about 10 min.

The macromolecules bound to the catalytic complex can be detached from the active center, but their detachment leaves unchanged the activity of the catalytic center which can initiate the formation of another macromolecule.

#### D. INFLUENCE OF THE OPERATING CONDITIONS ON THE POLYMERIZATION STEADY-STATE RATE.

1. *Experimental Apparatus and Operating Conditions.* The polymerization of propylene in the presence of a heterogeneous catalyst and a solvent occurred at a relatively low partial olefin pressure and was carried out in an apparatus continuously fed during the reaction with the olefin in the gaseous state at constant pressure (Fig. 14).

The amount of olefin consumed was determined by the decrease of pressure with time, measured on the feed vessel, kept at constant temperature by water circulation, where the olefin was maintained in the gaseous state.

It has been said that the polymerization rate observed under steady-state conditions, with a given sample of  $\alpha$ - $TiCl_3$  is practically independent of the initial sizes of the crystals. It is, moreover, convenient to point out that no all samples of  $\alpha$ - $TiCl_3$  prepared by the different methods we have examined lead in all cases to rates equal to each other. The most active samples of  $\alpha$ - $TiCl_3$  have an activity that does not exceed three times the value given by less active samples which we have here examined.

As the initial sizes of  $\alpha$ - $TiCl_3$  crystals seem to have very little influence

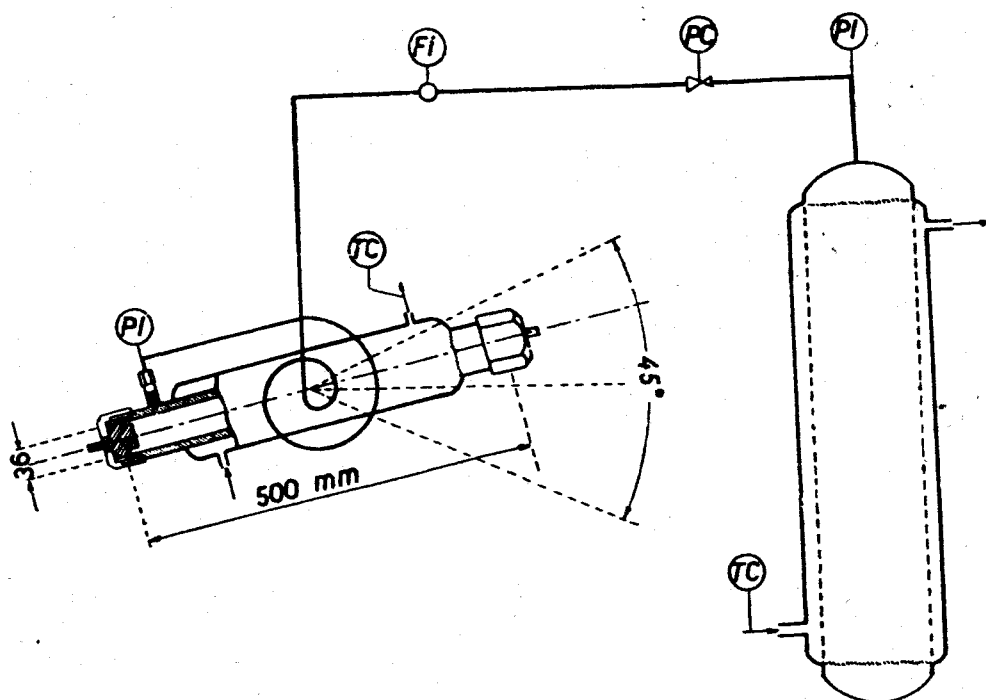


FIG. 14. Apparatus used for kinetic measurements of propylene polymerization (reaction vessel rocking 45 times per min. through a  $45^\circ$  angle). PI = pressure gage, PC = pressure control, FI = flow indicator, TC = temperature control.

on the steady-state rate, such differences could be ascribed to the degree of purity of  $\alpha$ -titanium trichloride.

The most frequent impurities of commercial  $\alpha$ -titanium trichloride are generally other chlorides ( $\text{TiCl}_4$ ,  $\text{TiCl}_2$ ), metallic titanium, titanium nitride and the products resulting from oxidation or hydrolysis of the titanium chlorides, the latter being unstable at air and moisture.

Some of these impurities have opposite effects on the catalytic activity and stereospecificity, depending on their concentration.

As we shall show below, the stereospecificity of the catalytic system can be influenced by impurities contained in the  $\alpha$ -titanium trichloride.

The larger part of the results reported in this paper, have been obtained with an old sample of  $\alpha$ -titanium trichloride called  $\alpha$ - $\text{TiCl}_3$ —sample 1. This sample is neither one of the most active nor one of the most stereospecific products we have studied. The analytical tests carried out on this product, have given the following results:

Methanol insoluble residue: 1%

Ti:Cl ratio = 1:2.96 in g. atoms

Kinetic data have been obtained with unground  $\alpha$ -titanium trichloride operating at constant temperature and pressure of olefin, during the whole polymerization.

In some preliminary tests an examination was made of the influence of some physical factors on the reaction rate in the apparatus employed, such as mass and heat transfer depending on the degree of filling and stirring of the reaction vessel (33). It has been found that, for a given temperature, with the equipment used (see Fig. 14), there is a limiting rate, depending on the volume of the solvent, at which the mass and heat transfer phenomena become determining; operating, for instance, at 70°, in 250 cc. of solvent, the limiting rate is almost equal to 20 g. of polymerized  $C_3H_6$  per hour (33). All kinetic tests have been carried out at polymerization rates lower than this value.

The order in which the components of the catalytic system ( $\alpha$ -titanium trichloride and trialkylaluminum), the solvent (*n*-heptane), and the olefin are brought together has no practical influence on the polymerization rate.

The rate values are independent of the temperature at which the catalyst is prepared by the action of alkylaluminum solution on  $\alpha$ -titanium trichloride, provided that this temperature is not higher than 70° and the concentration of the alkylaluminum in solution is not too low (above  $0.5 \times 10^{-2}$  mol/l. *n*-heptane) (30, 33).

Most of the kinetic results reported in this study refer to concentrations of trialkylaluminum in solutions higher than  $1.4 \times 10^{-2}$  mol/l. of solvent.

On account of the sensitivity of the catalysts to traces of moisture or oxygen, it is generally not suitable to operate with lower concentrations of alkylaluminum, because the latter acts also as a protector of the solid catalyst. However, by operating with very pure solvents and reagents, the concentration of  $AlR_3$  can be reduced to lower values ( $10^{-3}$  –  $10^{-4}$  mol/l.)

*Triethylaluminum/ $\alpha$ -Titanium Trichloride Ratio.* Many tests have been carried out with different trialkylaluminum/titanium trichloride molar ratios (from 1 to 8.5) without any considerable difference in the kinetic results obtained with the considered  $\alpha$ - $TiCl_3$  sample (Fig. 15).

For ratios lower than 0.4, the data obtained are of uncertain interpretation, owing to the degree of purity of the solvents and reagents which have been used (33). For such low values of the ratio, the reaction rate again, time initially increases, goes through a maximum, and then decreases rapidly without attaining a stationary value. The decrease of the catalyst activity is due to a consumption of  $AlR_3$  and, in fact, the activity can be restored with the addition of small amount of  $AlR_3$ .

Overlooking the anomalies due to the lack of absolute purity of the reagents, one must assign a zero reaction order with respect to aluminum concentration, in the range of the above reported conditions.

The result is due to the fact that the alkylaluminum, in the concentrations considered above, is always in excess with respect to the number of active centers existing on the surface of the solid catalyst.

*[Triethylaluminum]/[ $C_3H_6$ ] Ratio.* Using a triethylaluminum concentration

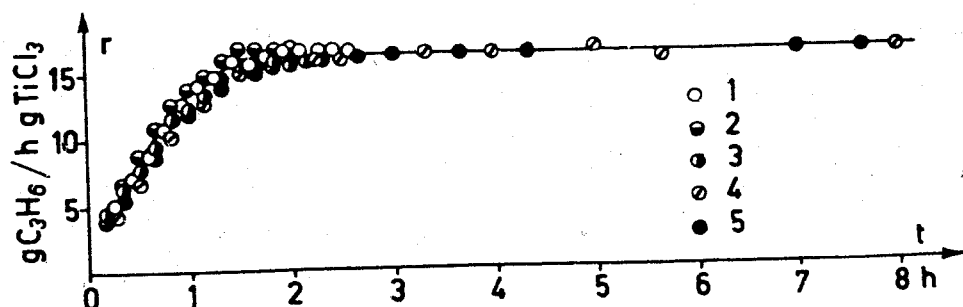


FIG. 15. Propylene polymerization rate at constant pressure and temperature ( $p_{C_3H_6} = 1,450$  mm. Hg,  $t = 70^\circ$ ), as function of polymerization time.

	1	2	3	4	5
$\alpha$ -TiCl <sub>3</sub> (sample A), g./L	3.80	4.36	3.80	0.80	1.64
[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ], mol./l.	$2.95 \times 10^{-2}$	$8.65 \times 10^{-2}$	$11.80 \times 10^{-2}$	$4.45 \times 10^{-2}$	$5.90 \times 10^{-2}$
Al/Ti, mol.	1.18	3.10	4.80	8.50	5.50
$\frac{[Al(C_2H_5)_3]}{[C_3H_6]}$	0.048	0.143	0.190	0.072	0.095

tion higher than about  $1.4 \times 10^{-2}$  mol/l. and a triethylaluminum/ $\alpha$ -titanium trichloride ratio higher than about 1, the value of this second ratio does not influence the kinetics of the over-all polymerization process. Therefore, in the range of variables tested: [triethylaluminum]/[C<sub>3</sub>H<sub>6</sub>] = 0.015 to 0.4, the formation of possible soluble alkylaluminum olefin complexes is not kinetically detectable (30, 33). This is confirmed by the independence of the olefin solubility in solutions of alkylaluminum in hydrocarbon on the alkylaluminum concentration (38).

*Amount of  $\alpha$ -TiCl<sub>3</sub>.* In Fig. 15 the polymerization rate, obtained at constant pressure of olefin with different amount of  $\alpha$ -TiCl<sub>3</sub>, is plotted vs. time. The steady-state rate is found to be proportional to the amount of  $\alpha$ -TiCl<sub>3</sub> present in the reaction system (Fig. 16), in agreement with the heterogeneous nature of the catalysis (30, 33).

*Propylene Partial Pressure.* The polymerization rate, under steady-state conditions (Figs. 17 and 18) is proportional to the partial pressure of propylene (30, 33).

*Polymerization Temperature. Apparent Activation Energy Based on the Steady-State Rate.\** The rates observed at different temperatures, referred

\* In our kinetic calculations, we refer to the directly observed partial pressure of propylene, rather than to its fugacity, because over the temperature and pressure range examined, we can assume that partial pressures and fugacities are practically proportional. In fact, from the literature data, the variation in propylene fugacity coefficient, in the range of our kinetic tests, is small (about 0.97 at  $30^\circ$  and 2700 mm Hg; about 0.99 at  $70^\circ$  and 450 mm. Hg of propylene partial pressure).

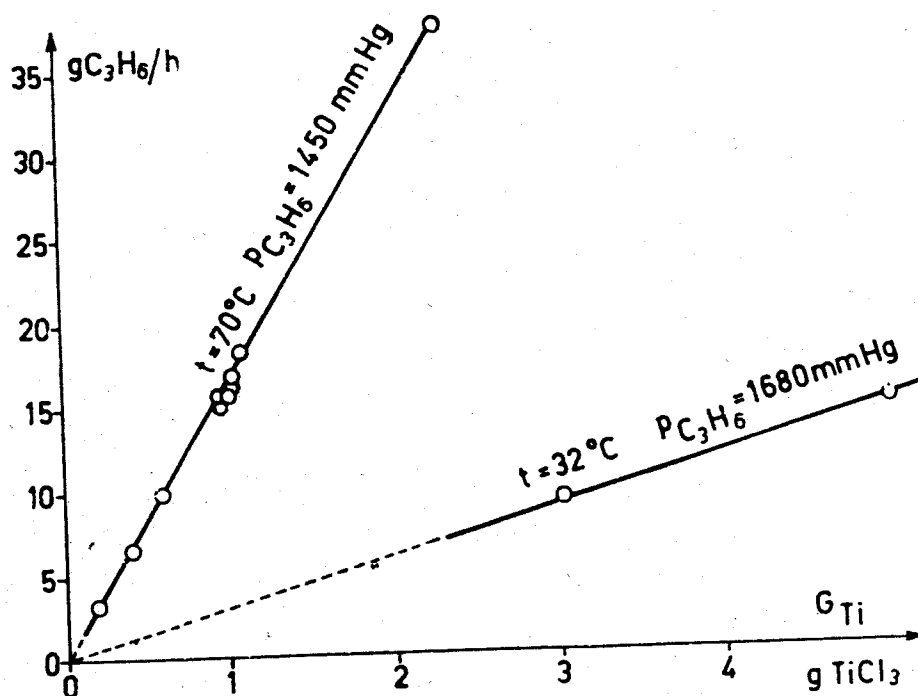


FIG. 16. Dependency of propylene polymerization rate in steady-state conditions on the amount of  $\alpha\text{-TiCl}_3$  (sample A) in the catalytic system.

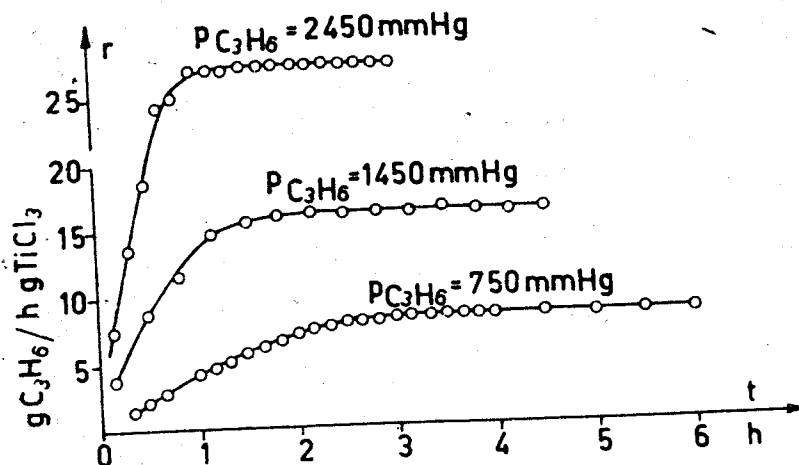


FIG. 17. Propylene polymerization rate at constant temperature ( $70^\circ$ ) and at different pressures as function of polymerization time ( $\alpha\text{-TiCl}_3$ : sample A:  $3.60 \text{ g./l.}$ ;  $[\text{Al}(\text{C}_2\text{H}_5)_3]$ :  $5.88 \times 10^{-2} \text{ mol./l.}$ ).

to a given amount of  $\alpha\text{-TiCl}_3$  and to a given partial pressure of propylene, are reported versus polymerization time in Fig. 19.

The diagram shown in Fig. 20, which gives the log of the polymerization rate under steady-state conditions, plotted *vs.* the reciprocal of the absolute temperature, was drawn from the above data. The activation energy calculated from the data reported in Fig. 20 is about  $10,000 \text{ cal./mol.}$

The activation energy referred to the concentration of the olefin in the liquid phase can be deduced from the one referred to the pressure in the gaseous phase, by adding the solution heat of the propylene in *n*-heptane

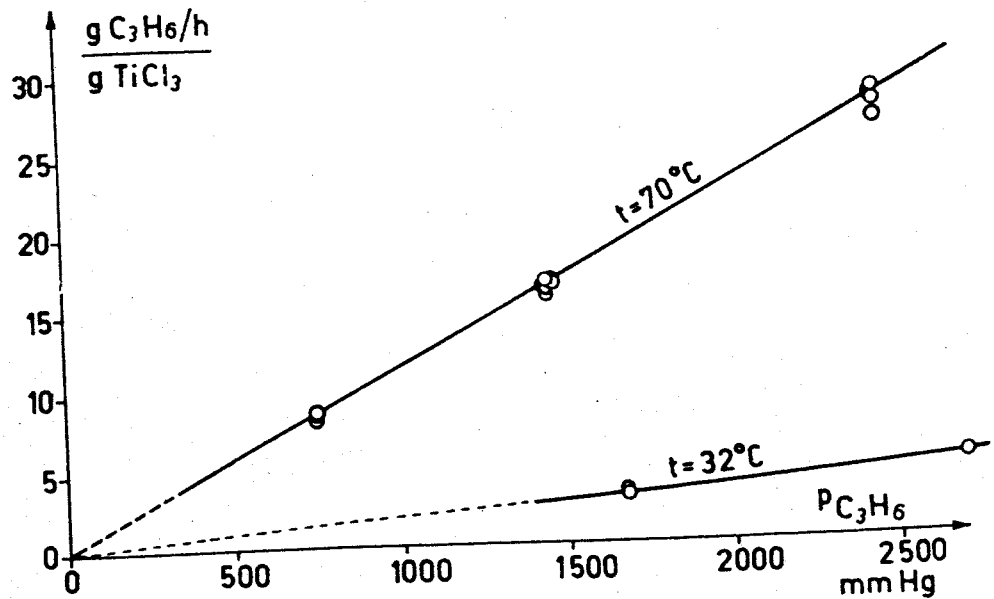


FIG. 18. Dependency of propylene polymerization rate in steady-state conditions on the propylene partial pressure ( $\alpha$ - $\text{TiCl}_3$ : sample A).

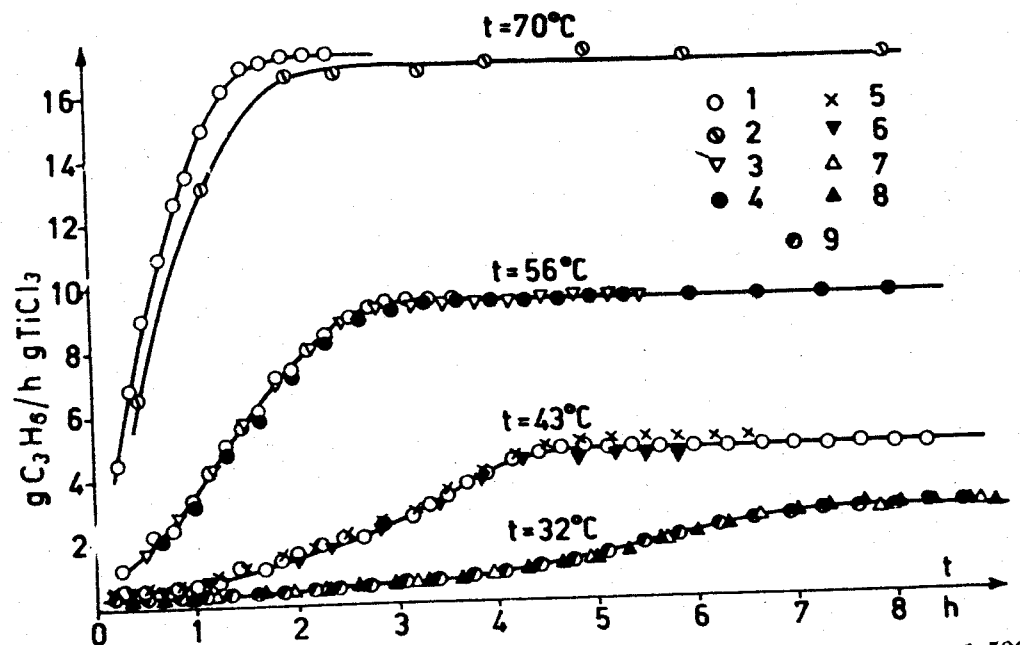


FIG. 19. Propylene polymerization rate at constant pressure ( $p_{\text{C}_3\text{H}_6} = 1,500$  mm. Hg) at different temperature, as function of polymerization time.

	$\alpha$ - $\text{TiCl}_3$ (Sample A), g./l.	$[\text{Al}(\text{C}_2\text{H}_5)_3]$ , mol. /l.	Al/Ti, mol.
1	3.80	$2.95 \times 10^{-2}$	1.18
2	0.80	$4.45 \times 10^{-2}$	8.50
3	7.60	$7.36 \times 10^{-2}$	1.50
4	1.60	$5.90 \times 10^{-2}$	5.60
5	7.60	$17.70 \times 10^{-2}$	3.60
6	10.80	$7.36 \times 10^{-2}$	1.05
7	20.20	$7.36 \times 10^{-2}$	0.52
8	12.16	$17.70 \times 10^{-2}$	2.20
9	12.10	$7.36 \times 10^{-2}$	0.94

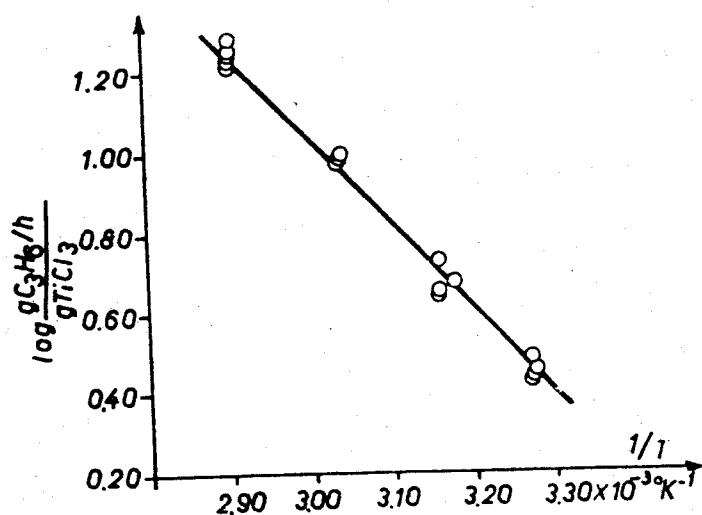


FIG. 20. Log of propylene polymerization rate in steady-state conditions as function of  $1/T$  ( $p_{C_3H_6} = 1,500$  mm. Hg,  $\alpha$ - $TiCl_3$ : sample A).

equal to about 4000 cal./mol. Consequently, the activation energy measured from the steady-state rate and referred to the olefin concentration in the liquid phase corresponds to 14,000 cal./mol. (30, 31).

If we consider the results reported so far, the polymerization rate of propylene under steady-state conditions, catalyzed by the catalytic system  $Al(C_2H_5)_3$ - $\alpha$ - $TiCl_3$ - $n$ -heptane, shows the following relation:

$$r = A e^{-10,000/RT} G_{Ti} p_{C_3H_6} \quad (1)$$

For the sample of  $\alpha$ - $TiCl_3$  to which the above data are referred

$$r = 2 \times 10^7 e^{-10,000/RT} G_{Ti} p_{C_3H_6} \quad (2)$$

where  $r$  = polymerization rate under steady-state conditions (g.  $C_3H_6/h$ )

$p_{C_3H_6}$  = partial pressure of propylene (atm.)

$G_{Ti}$  = g.  $\alpha$ - $TiCl_3$  in the catalytic system.

Equation (1) is applicable to other samples of  $\alpha$ - $TiCl_3$  by varying the value of  $A$ . For instance, the sample (B) shown in Fig. 7 shows a value  $A = 3.4 \times 10^7$ .

### III. Chain Transfer, Termination Processes, and Molecular Weight of the Polymers

The chain transfer and termination processes have been studied by the following methods:

Intrinsic viscosity measurements on the resulting polymer.

Analysis of end groups of polymeric chains by chemical, radiochemical and physical methods ( $IR$  examination).

By operating particularly at  $70^\circ$  it has been observed that every transfer and termination process of polymeric chains involves in the same way

(from a qualitative point of view) the growing macromolecules, independently of their steric structure. We must, however, notice that the molecular weight of the atactic polymers which are always present in small amount in the crude polymer, is generally much lower than that of the isotactic polymer. In fact, while the intrinsic viscosity of the isotactic polymer generally ranges from 2 to 5, we found correspondingly 0.5-1 for the atactic polymer.

We shall examine in detail the influence of the different factors controlling the intrinsic viscosity of the isotactic polymers during the polymerization.

#### A. CATALYSTS USED AND THEIR STEREOSPECIFICITY

The steric composition of the polypropylenes depends on the degree of purity of  $\alpha$ -TiCl<sub>3</sub> used in the polymerization. It has been observed, for instance, that the so-called isotacticity index of polypropylene (polymer residue after extraction in boiling *n*-heptane) can attain values ranging from 75 to 90%, depending on the catalytic properties of the samples of  $\alpha$ -TiCl<sub>3</sub>. Also the average molecular weight depends on the purity of the  $\alpha$ -TiCl<sub>3</sub> samples used. For instance, the same sample of a type of  $\alpha$ -TiCl<sub>3</sub> which, in the raw state, during a 2-hr. polymerization test of propylene, gives polymers having an intrinsic viscosity equal to 1.5 after a series of washings with anhydrous hydrocarbons (before the polymerization tests) leads to polymers having intrinsic viscosities which increase with the number of washings, until they reach an asymptotic value of about 3.3. For that reason, the study of chain transfer and termination processes in propylene polymerization has been performed by using a standard type of  $\alpha$ -TiCl<sub>3</sub> (sample A) which is the same as that used in the previously performed kinetic tests, but treated as follows (31):

Grinding in a stainless steel bottle, containing spheres of stainless steel (the dimensions of  $\alpha$ -TiCl<sub>3</sub> after grinding are  $\leq 2 \mu$ ).

Washing with anhydrous *n*-heptane several times.

The  $\alpha$ -TiCl<sub>3</sub> treated in this way gives reproducible results for the kinetic behavior, the molecular weights, and the steric composition of the polymer.

The atactic amorphous portion (9-16% of the total) contained in the obtained polypropylene has been separated by treating the raw polymer with *n*-heptane at room temperature. When operating in such a way, we have not separated the stereoblock fraction (extractable in boiling *n*-heptane) from the isotactic (not extractable in boiling *n*-heptane) fraction of polymer. The results reported in this paper are generally referred to the crystalline fraction, named non-atactic, which contains also some stereoblock polymers (at the considered polymerization temperatures, the latter generally correspond only to 5-7% of the total) (9).



### B. INDEPENDENCE OF THE MOLECULAR WEIGHT AND STERIC COMPOSITION OF THE POLYMER OF REACTION TIME, FOR LONG REACTION TIMES

Many polymerization tests have been carried out under different conditions (temperature from 30 to 70° and propylene partial pressure from 450 to 1,450 mm. Hg). When operating under such conditions, we never observed any effect of polymerization time, on the molecular weight and steric composition of the polymer, either after a few minutes of polymerization (e.g., in the interval in which the reaction rate with ground  $\alpha$ -TiCl<sub>3</sub> shows a maximum) or after many hours (when a small decrease in the over-all polymerization rate occurs) (Table II). This means that, under the tested conditions, the growing time of each polymeric chain is not slow enough to be measured, on the basis of the above reported kinetic data. For this reason, by operating particularly at 70° and with a propylene partial pressure of about 1 atm. and assuming that all active centers which are present on the surface of  $\alpha$ -TiCl<sub>3</sub> have the same activity, the average

TABLE II  
*Polymerization of Propylene to Isotactic Polymer. Independence of the Molecular Weight and of the Steric Composition from the Polymerization Time*

$t, ^\circ\text{C}$	$P_{\text{C}_3\text{H}_6}$ , mm. Hg	$[\text{Al}(\text{C}_2\text{H}_5)_3]$ , mol./l.	$\alpha$ -TiCl <sub>3</sub> , (sample A), g./l.	Al/Ti, mol.	Polymeri- zation time, hr.	Non- atactic polymer, %	Intrinsic viscosity of the non-atactic polymer: $[\eta]$ , 100 cm. <sup>3</sup> g.
31	700	$2.94 \times 10^{-2}$	1.50	3	14	89	4.40
					31	88.5	4.34
31	1450	$2.94 \times 10^{-2}$	3.00	1.5	1	85	4.66
					4	86	4.65
31	1450	$2.94 \times 10^{-2}$	1.50	3	8	86	4.70
					17	84	4.90
51	1110	$1.47 \times 10^{-2}$	0.30	7.5	8	87	4.50
					24	87	4.45
70	450	$2.36 \times 10^{-2}$	1.20	3	10	90	3.56
					15	90	3.47
70	450	$2.94 \times 10^{-2}$	1.50	3	4	91	3.28
					7	91	3.14
70	450	$7.36 \times 10^{-2}$	11.30	1	$\frac{1}{3}$	91	2.18
					1	90	2.13
70	950	$2.94 \times 10^{-2}$	1.50	3	$\frac{1}{2}$	88.5	3.84
					2	88.5	3.78
					6	88	3.84
70	1450	$1.77 \times 10^{-2}$	0.91	3	4	88	4.16
					7	87	4.20

<sup>a</sup> The data are related to the polymers insoluble in *n*-heptane at room temperature and include the stereoblock polymers soluble in boiling *n*-heptane (5-7% of the whole polymer) and the isotactic polymer.

growing time of each macromolecule must not be longer than a few minutes (39, 40).

### C. CHAIN TRANSFER PROCESS DEPENDING ON ALKYLALUMINUM CONCENTRATION

We have separately studied the nature of end groups and the dependence of the molecular weight of the polymeric chains, on the alkylaluminum concentration in the catalytic system.

#### 1. Intrinsic Viscosities

The measurements of intrinsic viscosity  $[\eta]$  have been carried out at 135° in tetralin. Under these conditions, the relationship between  $[\eta]$  and viscosimetric molecular weight  $M$ , for isotactic polypropylene is (41):

$$[\eta] = KM^{0.74}$$

In fig. 21, the values of  $1/[\eta]^{1.974} = 1/[\eta]^{1.35}$  (this factor can be assumed as being proportional to the reciprocal of the degree of polymerization  $x_n$ ) of the considered polypropylene fraction, are plotted vs. the square root of alkylaluminum concentration.

The data plotted in Fig. 21, corresponding to constant quantities of  $\alpha$ -titanium trichloride, can be assumed to give straight lines and the straight lines obtained for several values of  $C_{Ti}$  can be assumed to be parallel.

The limiting line for  $C_{Ti} = 0$  has been calculated from the data plotted in Fig. 22. The dependence of the intrinsic viscosity of the polymer (and consequently of its molecular weight) on the alkylaluminum concentration

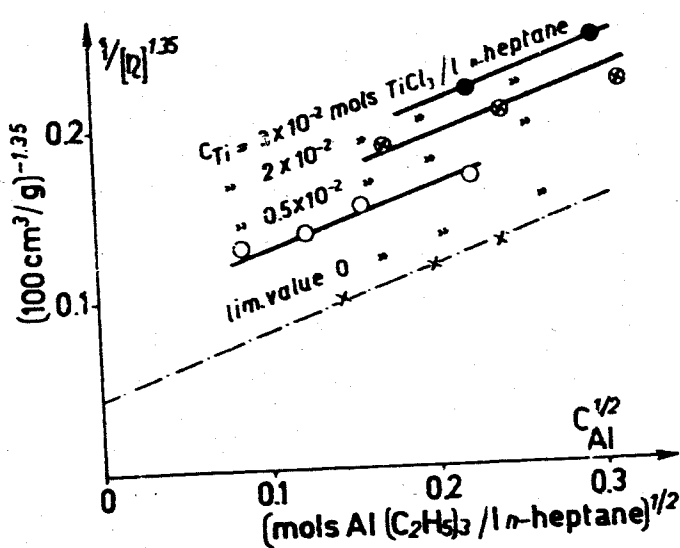


FIG. 21. Dependency of the reciprocal of the polymerization degree (proportional to  $1/[\eta]^{1.35}$ ) of the non-atactic polypropylene fraction, on the square root of the aluminum alkyl concentration ( $t = 70^\circ$ ,  $p_{C_2H_6} = 950$  mm. Hg, ground  $\alpha$ -TiCl<sub>3</sub>; sample A)

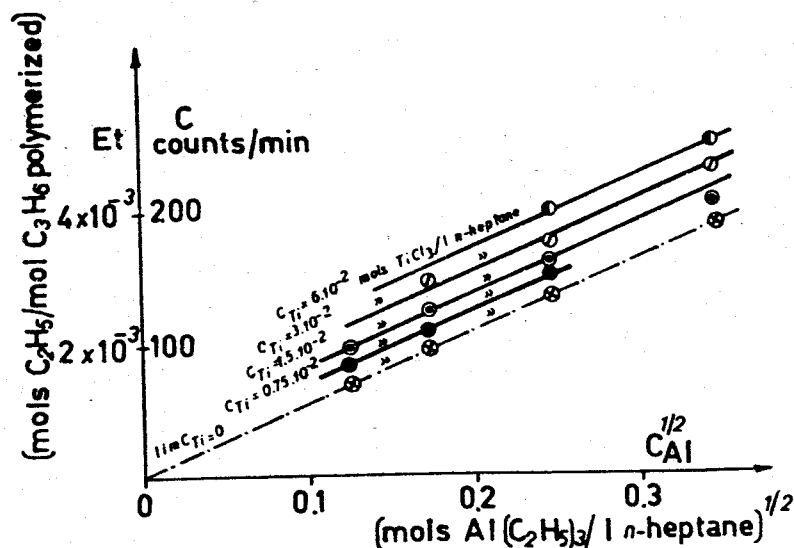


FIG. 22. Specific radioactivity (and corresponding values of  $-\text{C}_2\text{H}_5$  mol. per mol. of polymerized  $\text{C}_3\text{H}_6$ ) of the non-atactic polypropylene fraction, as function of the square root of the alkylaluminum concentration. (Tests performed with  $^{14}\text{C}$ -labeled  $\text{Al}(\text{C}_2\text{H}_5)_3$  at  $t = 70^\circ$ ,  $p_{\text{C}_3\text{H}_6} = 450$  mm. Hg, ground  $\alpha$ - $\text{TiCl}_3$ : sample A).

shows that this compound takes part (directly or indirectly) in a transfer or termination process of the growing polymeric chains.

## 2. Radiochemical Determination of End Groups

An attempt was made to determine whether the variations of the molecular weight with the alkylaluminum concentration are due to a chain transfer, with participation of the alkyl groups of alkylaluminum. Polymerization tests were performed, using  $^{14}\text{C}$ -labeled ethylaluminum and detecting the radioactivity of the polymer.

Careful preliminary tests were necessary to demonstrate the suitability of these methods for the present study. In particular, it was necessary to verify that the radioactivity detectable in the polymer may not be caused by contamination or other processes different from the ones taken into consideration. It was then found that it is possible to remove thoroughly from the polymer the last traces of unreacted ethylaluminum or of its soluble complexes with titanium compounds by washing with anhydrous hydrocarbon. No alkylation of the preformed polymer caused by triethylaluminum or its derivatives has been observed (42).

There is evidence that sometimes a permanent radioactive contamination of the polymer appears when one adds to a suspension of the polymer in  $n$ -heptane  $^{14}\text{C}$ -labeled triethylaluminum and certain samples of  $\alpha$ -titanium trichloride (particularly when the  $\alpha$ - $\text{TiCl}_3$  contains  $\text{TiCl}_4$  or other compounds of Ti(IV), as impurities).

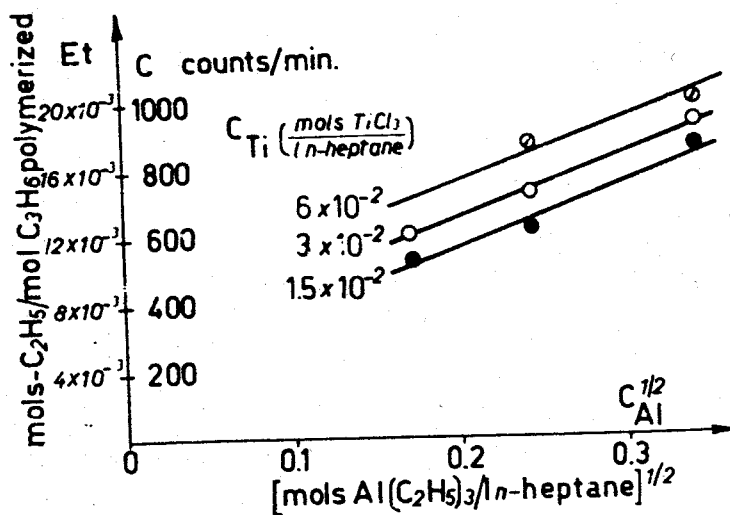


FIG. 23. Specific radioactivity (and corresponding values of  $-C_2H_5$  mol. per mol. of polymerized  $C_3H_6$ ) of the atactic polypropylene fraction, as function of the square root of the alkyl-aluminum concentration. (Tests performed with  $^{14}C$ -labeled  $Al(C_2H_5)_3$  at  $t = 70^\circ$ ,  $p_{C_3H_6} = 450$  mm. Hg, ground  $\alpha$ - $TiCl_3$ ; sample A).

This contamination remains after purification of the polymer from alkyl-aluminum by washing. Other samples (such as that shown in Fig. 7) are not contaminated. The amount of this contamination is in any case limited.

This point will be discussed in one of the next paragraphs.

All the reported data relating to radioactivity measurements have been corrected for radioactive contamination.

The use of  $^{14}C$ -labeled triethylaluminum allowed us to demonstrate that the quantity of  $-C_2H_5$  groups [deriving from  $Al(C_2H_5)_3$ ] which is bound to the non-atactic polymer at the end of the polymerization, when operating with a constant amount of titanium trichloride, is a linear function of the square root of the alkylaluminum concentration (Fig. 22), in the considered range of experimental conditions (42). Similar results have been obtained by analyzing the fraction of amorphous polymer (Fig. 23) (38).

### 3. Polymeric Isotactic Chains Bound to the Aluminum

Determinations of aluminum have been carried out on fractions of polymeric product containing isotactic chains deriving from the polymerization. These measurements were performed in an attempt to establish whether the chain transfer process, depending on the alkylaluminum concentration, leads to the formation of macromolecules which remain bound to the aluminum. The polymer has been therefore purified by physical methods from the unreacted ethylaluminum and from the heterogeneous catalyst.

The above determinations were carried out by taking into consideration

a fraction of the polymeric product containing isotactic chains that may be easily separated from the catalyst in the following way (43):

The unreacted alkylaluminum and the atactic polymer were removed from the vessel in which the polymerization was carried out, by means of decantation and repeated washings with anhydrous *n*-heptane at 50°; the separation of most of the polymer from the  $\alpha$ -TiCl<sub>3</sub> was then made by washing at 100° with anhydrous xylene.

The polymer contained in the xylene solution was further purified by repeated precipitations and washings of the polymer precipitated with anhydrous xylene at -70°.

The aluminum was determined spectrophotometrically using 8-hydroxyquinoline in a known quantity of polymer obtained from the xylene solution and previously purified. The absence of titanium from the polymeric product, isolated in this fashion, was checked by conventional analytical methods.

The results obtained are plotted in Table III. In the same table, for purposes of comparison, are recorded the amounts of ethyl groups derived from the Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, as found in certain fractions of the polymer by the radiochemical methods. The amount of aluminum bound in the polymer is higher in the test performed with higher triethylaluminum concentrations. A comparison with the tests performed with the same alkylaluminum concentrations, but with different amount of  $\alpha$ -TiCl<sub>3</sub>, shows, on the contrary, that the amount of aluminum bound to the polymer decreases remarkably

TABLE III

*End Groups in the Isotactic Polypropylene, Deriving from the Chain Transfer Processes Depending on the Catalyst Concentration (Catalytic System:  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-*n*-Heptane)*

Polymerization conditions				Al atoms, C <sub>3</sub> H <sub>6</sub> mol. in polymer fraction, soluble in xylene at 100°	-C <sub>2</sub> H <sub>5</sub> end groups/C <sub>3</sub> H <sub>6</sub> mol. in the polymer fraction insoluble in <i>n</i> -heptane at room temper- ature <sup>b</sup>	-C <sub>2</sub> H <sub>5</sub> end groups/C <sub>3</sub> H <sub>6</sub> mol. in the isotactic polymer fraction not extractable in boiling <i>n</i> -heptane <sup>c</sup>
$\alpha$ -TiCl <sub>3</sub> (sample A), g.	Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> , mol.	Solvent, 250 cm. <sup>3</sup>	<i>t</i> , °C.			
0.11	$9.9 \times 10^{-3}$	Heptane	70	$0.5 \times 10^{-3}$	$2.3 \times 10^{-3}$	$1.4 \times 10^{-3}$
0.15	$9.9 \times 10^{-3}$	Heptane	70	$0.6 \times 10^{-3}$	$2.3 \times 10^{-3}$	$1.4 \times 10^{-3}$
0.50	$9.9 \times 10^{-3}$	Heptane	70	$1.35 \times 10^{-3a}$	$2.7 \times 10^{-3}$	$1.7 \times 10^{-3}$
0.50	$39.6 \times 10^{-3}$	Heptane	70	$2.7 \times 10^{-3}$	$4.9 \times 10^{-3}$	$3.0 \times 10^{-3}$
0.50	$9.9 \times 10^{-3}$	Xylene	100	$2.2 \times 10^{-3}$	—	—

<sup>a</sup> Average of the values (which lay in the range 1.3-1.4) obtained in four polymerization tests.

<sup>b</sup> This fraction contains the isotactic and stereoblock polymers.

<sup>c</sup> These data were calculated from the preceding ones, taking into account the percentage and the molecular weight of the stereoblock polymers contained in the fraction extractable in boiling *n*-heptane.

decreasing the amount of  $\alpha$ -TiCl<sub>3</sub>. Probably some soluble titanium compounds act catalytically in the transfer of alkyls from the aluminum to the polymeric chains.

#### 4. Mechanism of the Chain Transfer Process Depending on the Triethylaluminum Concentration

The results reported in the preceding paragraphs indicate that the triethylaluminum molecules present in solution take part in a chemical process which affects the molecular weight of the polymers. In polymerization tests carried out in a relatively short time, the amount of reacted ethylaluminum is very small; this is proved also by the fact that the results obtained in these tests are not dependent on the reaction time. Furthermore, it has already been found that in the considered range, the over-all reaction rates do not seem to be affected by the concentration of ethylaluminum.

It may be pointed out, therefore, that the ethylaluminum takes part in a chain transfer process. An almost linear dependence of  $1/[\eta]^{1.35}$  and of the number of  $-C_2H_5$  groups found in the polymer was found on the square root of the ethylaluminum concentration. The number of aluminum atoms chemically bound to the unpurified polymer decreases with the ethylaluminum concentration in the catalytic system.

These results make us believe that the rate of the chain transfer process under examination is given by the relation:

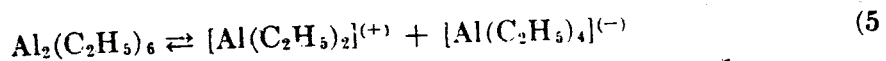
$$r_3 = k_3 C^* C_{Al}^{\frac{1}{2}} \quad (3)$$

where  $C_{Al}$  = molecular concentration of triethylaluminum  
 $C^*$  = number of active centers

This dependence on the square root of the ethylaluminum concentration may be interpreted by assuming that the triethylaluminum acts in dissociated form in the chain transfer process. It is in agreement with the well-known dimeric structure of triethylaluminum which is dissociated as follows:

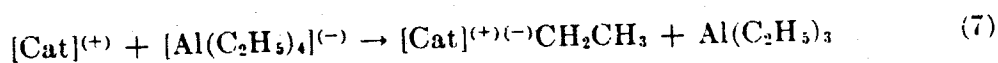
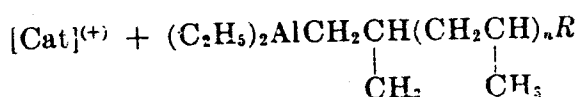
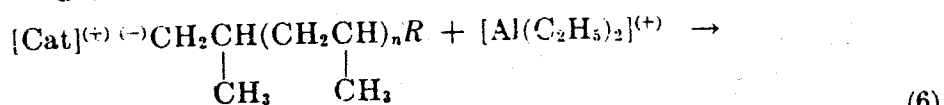


It has been also related by Bonitz (44) that besides the homopolar dissociation,  $Al_2(C_2H_5)_6$  may be partially dissociated in a heteropolar way:



To explain the results obtained in our researches, we could take into consideration a chain transfer mechanism, such as the following one (a

least in initial stage):



It is possible that in the later stages of polymerization there may occur transfer processes involving more than one ethyl group per aluminum atom.

In this way, the catalyst will be regenerated while the monomer alkyl-aluminum takes part in the equilibrium of association with other alkyls in solution.

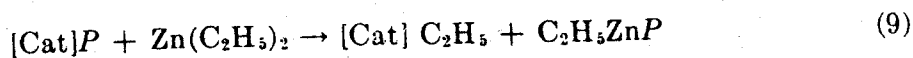
Another interpretation that may be taken into consideration, kinetically equivalent to the former one, is a total substitution of the polymeric alkyl-aluminum compound which is bound to a catalytically active complex containing the transition metal, as follows:



where  $P$  = polymeric chain

$Y$  = alkyl group (e.g., ethyl or polymeric chain—one of the two  $Y$  can be substituted by a chlorine atom).

It has been observed that other metallorganic compounds (e.g.,  $\text{Zn}(\text{C}_2\text{H}_5)_2$ , which is not associated as  $\text{Al}(\text{C}_2\text{H}_5)_3$ ) can be involved in chain transfer processes (45). In this case presumably alkyl groups are exchanged as follows:



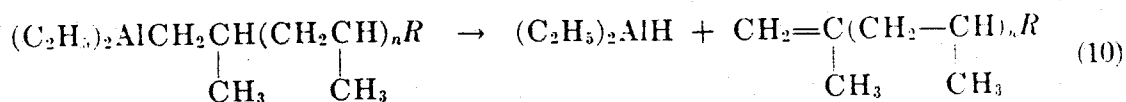
The rate of this chain transfer process is of first-order with regard to the  $\text{Zn}(\text{C}_2\text{H}_5)_2$  concentration (38).

The kinetics of the above reported chain transfer reactions seem to be also catalytically affected by the titanium compound present in the reaction system. In fact we have observed (Table III) that both the numbers of ethyl groups and aluminum atoms bound to the polymeric chains decrease with decreasing amount of titanium compound in the catalytic system.

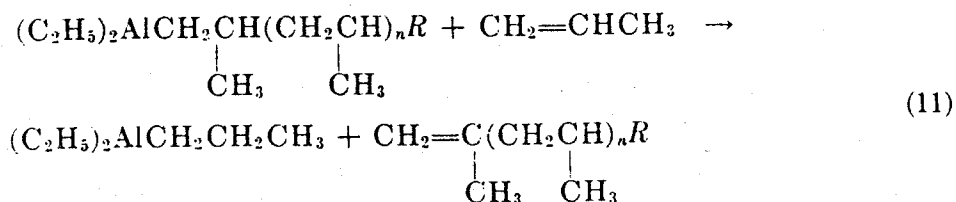
The above-recorded chain transfer processes and the processes of exchange between alkylaluminum in solution and alkylaluminum bound to the catalytic complex could also be effected by soluble polymeric alkylaluminum of the type  $(\text{C}_2\text{H}_5)\text{AlP}_2$  or  $(\text{C}_2\text{H}_5)_2\text{AlP}$  (where  $P$  = polymeric chain). This

will involve more than one ethyl group per atom of aluminum brought into the polymeric chains.

In any case, such chain transfer processes lead to a continuous increase of the molecular weight of the alkylaluminum compounds during the polymerization. It is, however, possible that alkylaluminum molecules having a low molecular weight are regenerated by a mechanism similar to those reported in the study of the kinetic behavior of ethylene polymerization, in the presence of trialkylaluminum (35) or through a dissociation to a hydride:



or through a transfer reaction with the monomer:



In the case of ethylene polymerization with  $\text{AlR}_3$  alone, however, the transfer reaction with the monomer which is thermodynamically displaced towards the right, depends on the temperature (35) and, practically, does not occur any more at low temperature ( $< 80^\circ$ ) if specific catalysts are not involved. Also in the propylene polymerization the corresponding reaction is strongly dependent on the temperature.

#### D. CHAIN TRANSFER PROCESS DEPENDING ON THE AMOUNT OF TITANIUM COMPOUND

As described in the previous paragraph, we investigated the influence of increasing amounts of titanium compounds on the molecular weight, and other characteristics of the polymer.

##### 1. *Intrinsic Viscosities*

In Fig. 24 the values of  $1/[\eta]^{1.35}$  for the non-atactic polypropylene obtained at  $70^\circ$  and 950 mm. Hg of partial pressure of propylene are plotted vs. the square root of the amount of titanium trichloride introduced in the unit volume of the catalytic system for different values of the trialkylaluminum concentration in solution (39, 40).

##### 2. *Radiochemical Determination of End Groups*

The radioactivity (and consequently the amount of  $-\text{C}_2\text{H}_5$  groups) observed in the considered polypropylene fraction obtained in polymerization tests carried out with constant concentrations of labeled triethylaluminum



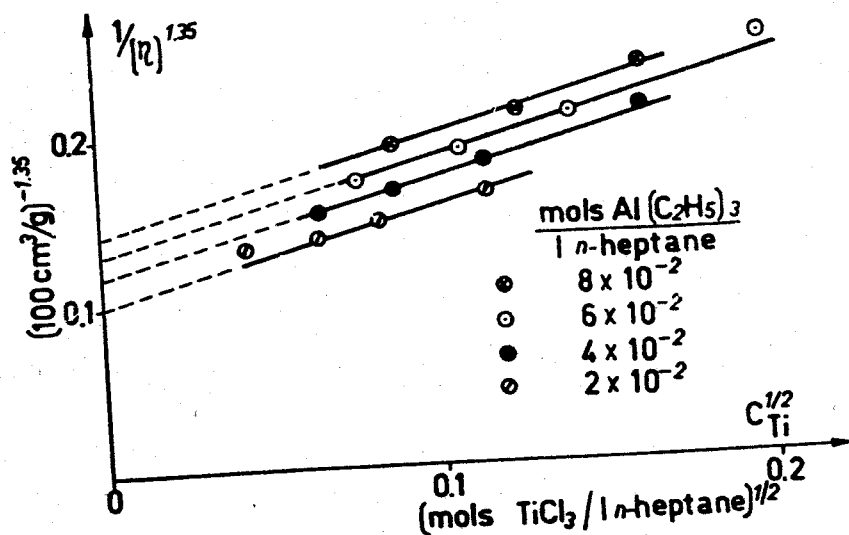


FIG. 24. Dependency of the reciprocal of the polymerization degree (proportional to  $1/[\eta]^{1.35}$ ) of the non-atactic polypropylene fraction on the square root of the amount of  $\alpha$ - $\text{TiCl}_3$  in the catalytic system ( $t = 70^\circ$ ,  $p_{\text{C}_2\text{H}_6} = 950$  mm. Hg, ground  $\alpha$ - $\text{TiCl}_3$ : sample A).

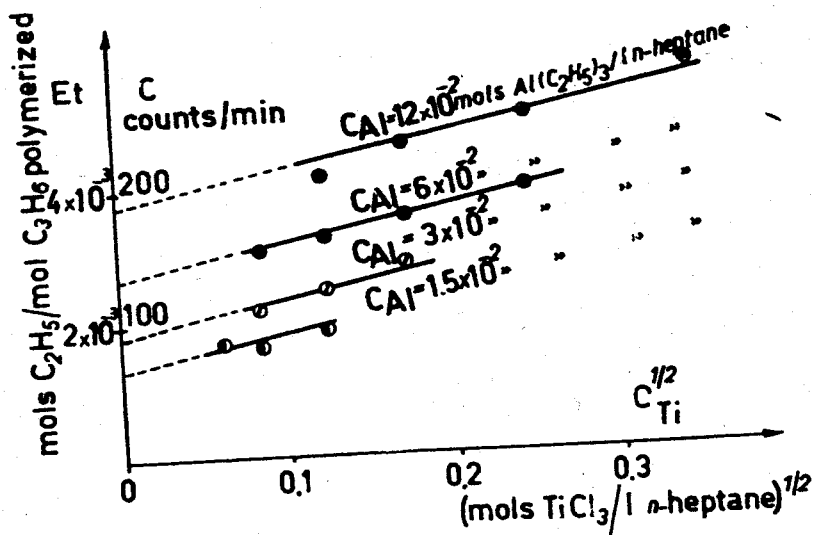


FIG. 25. Specific radioactivity (and corresponding values of  $-\text{C}_2\text{H}_5$  mol. per mol. of polymerized  $\text{C}_3\text{H}_6$ ) of the non-atactic polypropylene fraction, as function of the square root of the  $\alpha$ - $\text{TiCl}_3$  amount in the catalytic system. (Tests performed with  $^{14}\text{C}$ -labeled  $\text{Al}(\text{C}_2\text{H}_5)_3$  at  $t = 70^\circ$ ,  $p_{\text{C}_2\text{H}_6} = 450$  mm. Hg, ground  $\alpha$ - $\text{TiCl}_3$ : sample A)

and with different amounts of titanium trichloride is approximately linear function of the square root of the amount of titanium trichlorid introduced in unit volume of the catalytic system (Fig. 25) (42). Similar results have been obtained by analyzing the amorphous fractions of polypropylene (Fig. 26) (38).

### 3. Dependence of the Considered Chain Transfer Process on the Pressure

The use of radioactive triethylaluminum enabled us to prove that the rate of the considered chain transfer process depends also on the propylene

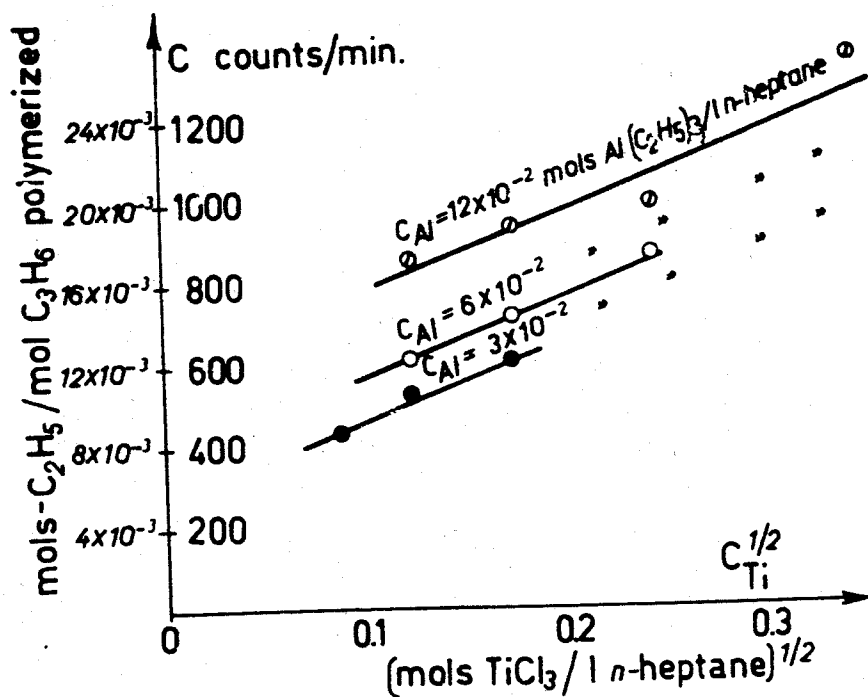


FIG. 26. Specific radioactivity (and corresponding values of  $-C_2H_5$  mol. per mol. of polymerized  $C_3H_6$ ) of the atactic polypropylene fraction, as function of the square root of the  $\alpha-TiCl_3$  amount in the catalytic system. (Tests performed with  $^{14}C$ -labeled  $Al(C_2H_5)_3$  at  $t = 70^\circ$ ,  $p_{C_3H_6} = 450$  mm. Hg, ground  $\alpha-TiCl_3$ : sample A.)

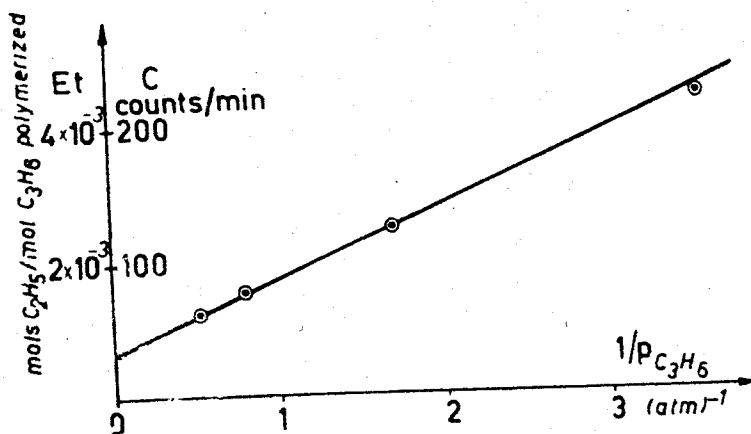


FIG. 27. Specific radioactivity (and corresponding values of  $-C_2H_5$  mol. per mol. of polymerized  $C_3H_6$ ) of the non-atactic polypropylene fraction, plotted vs.  $1/p_{C_3H_6}$  ( $t = 70^\circ$ , ground  $\alpha-TiCl_3$ : sample A:  $1.5 \times 10^{-2}$  mol./l.,  $^{14}C$ -labeled  $Al(C_2H_5)_3$ :  $3 \times 10^{-2}$  mol./l.).

partial pressure. From the diagrams plotted in Figs. 22, 25, 27, and 28 it appears, in fact, that the number of ethyl groups contained in the polymer (referred to the polymerized molecules of propylene) is given by the relationship:

$$Et = k' C_{Al}^{\frac{1}{2}} / p_{C_3H_6} + k'' C_{Ti}^{\frac{1}{2}} \quad (12)$$

This equation may be applied only in the range of experimental condi-

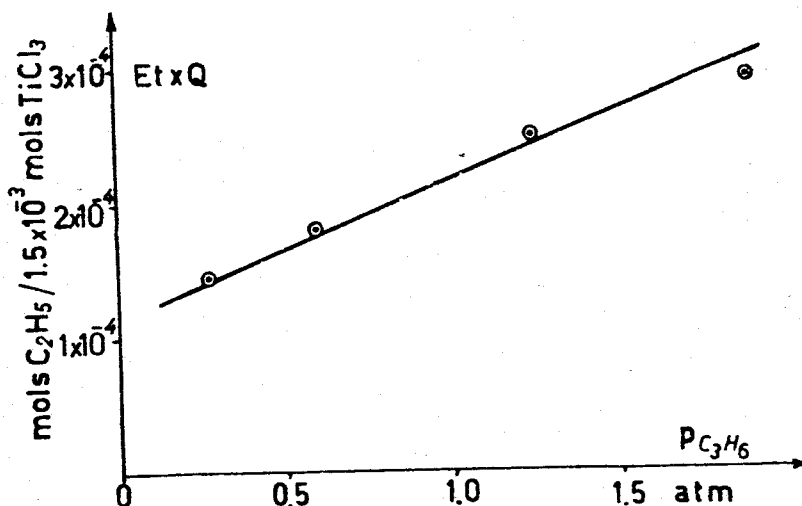


FIG. 28. Total number of  $-\text{C}_2\text{H}_5$  end groups found in the non-atactic polypropylene fraction, as function of  $p_{\text{C}_3\text{H}_6}$  ( $t = 70^\circ\text{C}$ , ground  $\alpha\text{-TiCl}_3$ ; sample A:  $1.5 \times 10^{-3}$  mol.,  $^{14}\text{C}$ -labeled  $\text{Al}(\text{C}_2\text{H}_5)_3$ :  $3 \times 10^{-3}$  mol., solvent:  $100 \text{ cm}^3$  *n*-heptane, polymerization time:  $1\frac{1}{2}$  hr.).

tions considered. In particular, it is not applicable to the limit conditions

$$C_{\text{Al}} = 0, \quad \text{or} \quad C_{\text{Ti}} = 0$$

The above relation may be transformed as follows:

$$Et = \frac{k_3 C_{\text{Al}}^{\frac{1}{2}} C^* + k_4 C_{\text{Ti}}^{\frac{1}{2}} p_{\text{C}_3\text{H}_6} C^*}{k_p p_{\text{C}_3\text{H}_6} C^*} \quad (13)$$

If we assume *a priori*, as will be proved in a further paragraph, that each simple chain transfer process whose rate depends on the catalyst concentration is followed by the insertion in the polymeric chains of  $-\text{C}_2\text{H}_5$  groups (deriving from triethylaluminum), the rate of the chain transfer process, depending on the amount of Ti, then would be

$$r_4 = k_4 C_{\text{Ti}}^{\frac{1}{2}} p_{\text{C}_3\text{H}_6} C^*$$

It is also in agreement with the data obtained from the determination of intrinsic viscosities of the polymers (46). In Fig 29 the reciprocals of the intrinsic viscosities (raised to 1.35) of the polymers obtained by operating at different pressures and with the same Al/Ti ratio, are plotted vs. the square root of the alkylaluminum concentration in the catalytic system. For a given Al/Ti ratio, the lines which correspond to different pressures are almost parallel between themselves; according to the fact that  $1/[\eta]^{1.35}$  can be represented by the relationship

$$1/[\eta]^{1.35} = 1/[\eta]_0^{1.35} + \Phi(\Sigma r_i / k_p p_{\text{C}_3\text{H}_6} C^*) \quad (14)$$

where  $\Sigma r_i$  = sum of the rates of chain transfer processes, depending on the catalyst concentration

$k_p p_{C_3H_6} C^*$  = over-all polymerization rate

$[\eta]_0$  = limit value of the polymer intrinsic viscosity obtained extrapolating the data up to the catalyst concentration equal to zero.

It follows that the function  $\Phi$  is not strongly influenced by the pressure; i.e.,  $\Sigma r_i$  should also be a function of the partial pressure of propylene.

#### 4. Interpretation of the Chain Transfer Process Depending on the Amount of Titanium Compound Introduced into the Catalytic System

It follows from the above reported results that an agent whose concentration depends upon the amount of titanium compound introduced into the reagent system takes part directly or indirectly in a chain transfer process.

It must be remembered that several compounds or soluble complexes of titanium which, alone, and also in the presence of  $AlR_3$ , do not polymerize the propylene, can effect the polymerization rate of the catalytic systems containing  $\alpha-TiCl_3$  and the molecular weight of the polymers obtained (10, 11).

The analogy between this last process and the one whose rate depends on the triethylaluminum concentration (like, for instance, its influence on the

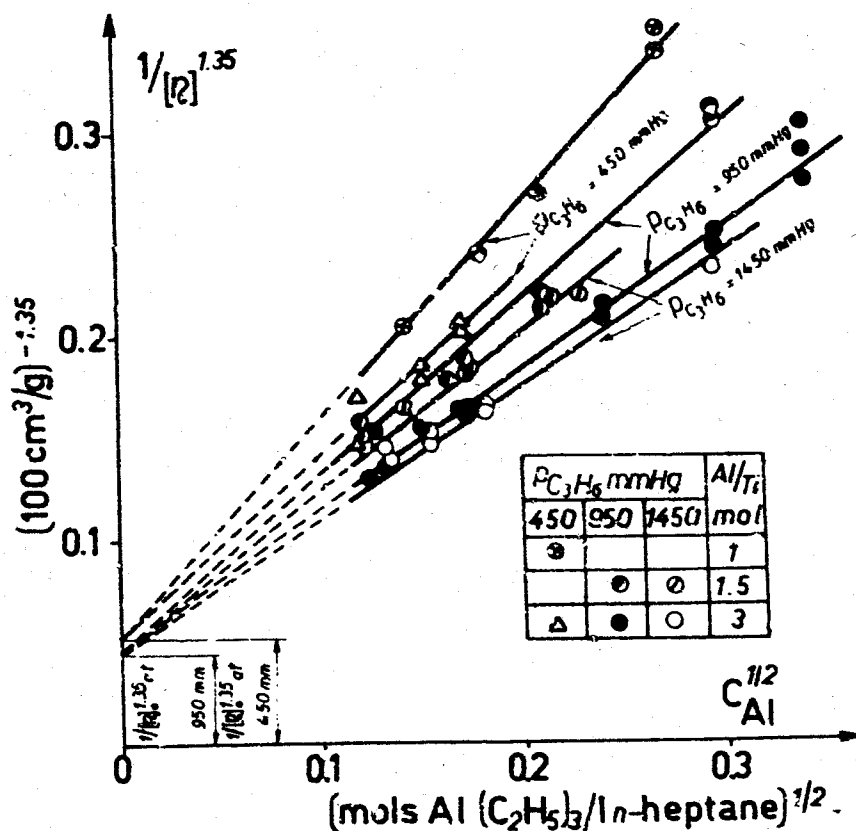
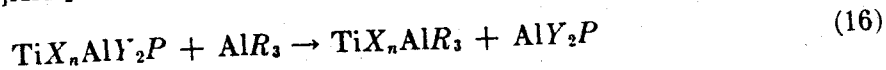


FIG. 29. Dependency of the reciprocal of the polymerization degree (proportional to  $1/[\eta]^{1.35}$ ) of the non-atactic polypropylene fraction on the square root of  $[Al(C_2H_5)_3]$ . Comparison between tests performed for few pressure values ( $t = 70^\circ$ , ground  $\alpha-TiCl_3$ ; sample A).

number of aluminum atoms and of  $-\text{C}_2\text{H}_5$  groups bound to the polymeric chains) enables us to state that in both cases an exchange occurs between alkyl groups deriving from alkylaluminum compounds and growing polymeric chains or between metallorganic compounds containing, respectively, alkyl groups and polymeric chains.

It may be that these compounds act catalytically on the chain transfer processes which depend on the alkylaluminum concentration. We can also consider that non-catalytic complexes containing alkylaluminum, exchange their metallorganic component with the catalytic complexes bound to the active centers of the crystalline substrate.



where  $[\text{Ti}_n\text{Cl}_m]$  means the active center (of the crystalline substrate) to which a metallorganic compound of the aluminum is bound, and  $\text{TiX}_n\text{AlR}_3$  means a generic complex of titanium which acts catalytically as an intermediate compound in the exchange of organoaluminum groups among complexes in solution and solid catalyst.

The dependence of the rate of the considered chain transfer process on the olefin pressure may be justified if we assume that such a process requires an activation state of the solid catalyst. Such an activation state would correspond to the activated intermediate complex which is formed during the polymerization process at the particular stage in which a monomeric unit bounds itself to the catalytic complex. As a result, the rate of the transfer process would depend on the rate of the chain-growing process, since the two processes (growing and chain transfer) would be considered as parallel and deriving from the same activated complex.

The chain transfer process whose rate depends only upon the alkylaluminum concentration (or upon the zinc-diethyl concentration) is, on the contrary, independent of the partial pressure of the olefin and may occur even if the polymerization stops for lack of monomer.

#### E. CHAIN TRANSFER PROCESS DEPENDING ON THE PROPYLENE PARTIAL PRESSURE

A study of the intrinsic viscosities of the polymers and of the chain-end groups enabled us to establish that there are processes affecting the molecular weight which are independent of the catalyst concentration. They are now discussed on the basis of experimental data obtained by different tests

##### 1. *Intrinsic Viscosities*

Taking into consideration the results so far observed (see also Fig. 30) it may be assumed that the reciprocal of the degree of polymerization  $\bar{P}_n$

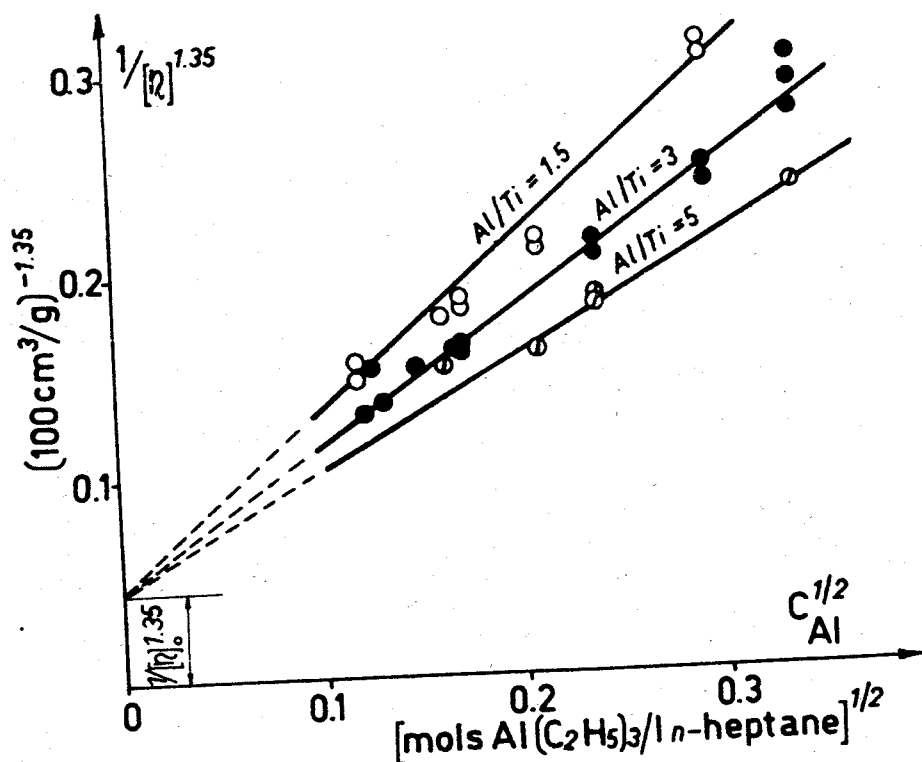


FIG. 30. Dependency of the reciprocal of the polymerization degree (proportional to  $1/[\eta]^{1.35}$ ) of the non-atactic polypropylene fraction on the square root of  $[\text{Al}(\text{C}_2\text{H}_5)_3]$ . (Tests performed for few values of Al/Ti ratio,  $t = 70^\circ$ ,  $p_{\text{C}_3\text{H}_6} = 950$  mm. Hg, ground  $\alpha\text{-TiCl}_3$ ; sample A).

propylene is given by the expression

$$\frac{1}{x_n} = \frac{1}{x_{n_0}} + \frac{k_3 C_{\text{Al}}^{1/2} C^* + k_4 C_{\text{Ti}}^{1/2} p_{\text{C}_3\text{H}_6} C^*}{k_p p_{\text{C}_3\text{H}_6} C^*} \quad (17)$$

For the term  $1/x_{n_0}$  it may be assumed:

$$1/x_{n_0} = \Sigma r_{t_0} / k_p p_{\text{C}_3\text{H}_6} C^* \quad (18)$$

where  $\Sigma r_{t_0}$  = sum of the rates of chain transfer and termination processes independent of the catalyst concentration. Tests performed at different pressures (see Fig. 29) have proved that  $1/[\eta]_0$ , and consequently  $1/x_{n_0}$  in the considered range of pressure, is only slightly affected by the partial pressure of olefin. This means that the term  $\Sigma r_{t_0}$  is a function of the pressure. We assumed that  $\Sigma r_{t_0}$  consists of two terms, one being of first order with regard to the pressure and the other one independent.

$$\frac{1}{x_{n_0}} = \frac{k_1 C^*}{k_p p_{\text{C}_3\text{H}_6} C^*} + \frac{k_2 p_{\text{C}_3\text{H}_6} C^*}{k_p p_{\text{C}_3\text{H}_6} C^*} \quad (19)$$

The term  $k_2 p_{\text{C}_3\text{H}_6} C^*$  represents the rate of a process of first order with regard to the partial pressure of the monomer, and  $k_1 C^*$  the rate of a process

independent of the olefin pressure. The first of these two processes can be equivalent to a chain transfer with the monomer.

Under the polymerization conditions previously described, (temperature below  $80^\circ$ ) the term  $k_1$  seems to be very small with respect to  $k_2 p_{C_3H_6}$ ; in fact, at low pressure (450 mm. Hg) the value of  $1/[\eta]_0^{1.35}$  may appear somewhat higher than the corresponding value obtained at 950 mm. Hg or higher pressures (see Fig.29). The values of  $1/[\eta]_0^{1.35}$  obtained, respectively, at 950 mm. Hg and 1,450 mm. Hg of propylene partial pressure are almost coincident (40, 46).

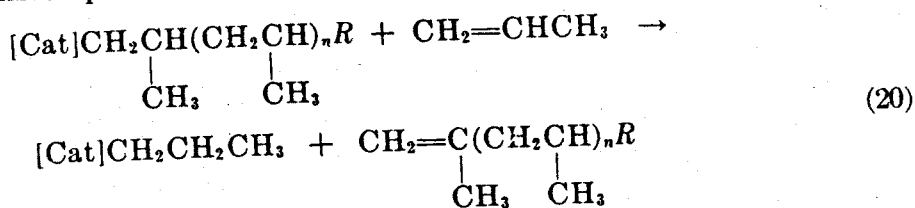
The numerical value of  $1/x_{n_0}$ , in the considered field, is then mainly determined by the term  $k_2/k_p$ , e.g., depending on the chain transfer with the monomer.

## 2. Infrared Spectra Analysis

The infrared spectra of the obtained polymers have shown that they contain vinylidenic end groups (22). Quantitative data for the amorphous fraction of polypropylene are reported in Table IV (38).

## 3. Mechanism of the Chain Transfer Process with the Monomer and of the Spontaneous Termination Process

From the results reported in the preceding paragraphs, the mechanism of the chain transfer process with the monomer may be as follows:



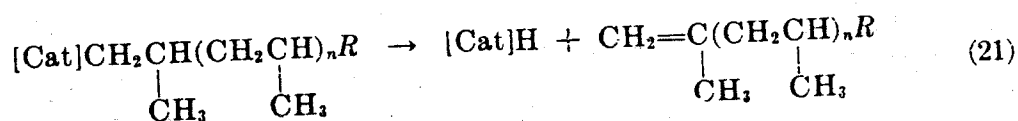
It may be that another process (whose rate is independent of the monomer and catalyst concentrations and can be detected at the considered

TABLE IV  
End Groups in the Small Atactic Fraction (Extractable in Boiling Ether) Obtained by Polymerization of Propylene with the Catalytic System:  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-*n*-Heptane

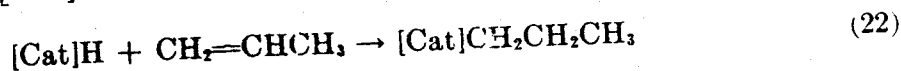
Polymerization conditions				-(CH <sub>2</sub> ) C=CH <sub>2</sub> end groups/C <sub>3</sub> H <sub>6</sub> mol. in atactic polymer*	-C <sub>2</sub> H <sub>5</sub> end groups/C <sub>3</sub> H <sub>6</sub> mol. in atactic polymer	Ratio -C <sub>2</sub> H <sub>5</sub> -(CH <sub>2</sub> ) C=CH
$\alpha$ -TiCl <sub>3</sub> , sample A, mol./l.	[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ] mol./l.	$p_{C_3H_6}$ , mm. Hg	$t$ , °C.			
$1.5 \times 10^{-2}$	$3 \times 10^{-2}$	450	70	$2.5 \times 10^{-3}$	$10.3 \times 10^{-3}$	4.15
$1.5 \times 10^{-2}$	$3 \times 10^{-2}$	950	70	$2.3 \times 10^{-3}$	$4.7 \times 10^{-3}$	2.05
$1.8 \times 10^{-2}$	$3 \times 10^{-2}$	1,450	70	$2.6 \times 10^{-3}$	$5.5 \times 10^{-3}$	2.10

\* IR measurements were carried out by Dr. M. Peraldo.

temperature '70°' only at low partial pressure of propylene) affects the molecular weight of the polymeric chains. This process could be a process of spontaneous dissociation which leads to the formation of an active hydride:

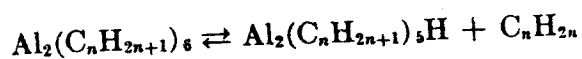


The complex  $[\text{Cat}]\text{H}$  could initiate a new polymeric chain as follows:



and therefore the spontaneous dissociation of the polymeric chain should not be considered *a priori* a real termination of the reaction chain.

At high temperature there exists an equilibrium between



nevertheless, it is most likely that the addition reaction of the monomer to the hydride, requires a greater energy of activation than the one corresponding to the addition of a monomeric unit to a growing chain, so that we may admit that complexes containing hydride cannot be alkylated immediately by the olefin. Hence, we may consider the reaction (22) as the first stage not only of a new polymeric chain but also of a new chain of reactions. In this case, the spontaneous dissociation could be considered as a real termination process of the chain reaction.

Indeed, reaction (20) can be considered as a real chain transfer with the monomer. In fact, by making a comparison between the reactions (20) and (6) and (7), it can be observed that, after these reactions, the catalytic complexes  $[\text{Cat}]\text{CH}_2\text{CH}_2\text{CH}_3$  and  $[\text{Cat}]\text{CH}_2\text{CH}_3$  are respectively formed and both these complexes can add monomeric units in the polymerization process. The reactions (6) and (7) are equivalent to a real chain transfer because the over-all polymerization rate appears to be independent of the triethylaluminum concentration. Considering the chemical analogies of the catalytic complexes, resulting from the reactions (20) and (7), it may also be assumed that the transfer reaction whose rate is of first order with regard to the monomer may be considered a real chain transfer (from a kinetic point of view).

#### F. INFLUENCE OF THE TEMPERATURE ON THE SINGLE-CHAIN TRANSFER AND TERMINATION PROCESSES

As the temperature decreases from 70 to 30°, either for limited or high concentrations of catalyst, it may be observed that the molecular weight of the obtained polymer, somewhat increases (Fig. 31). The fact that the value of the slope of the lines obtained by plotting  $1/[\eta]_0^{1.35}$  vs.  $C_{\text{Al}}^{\dagger}$  slightl



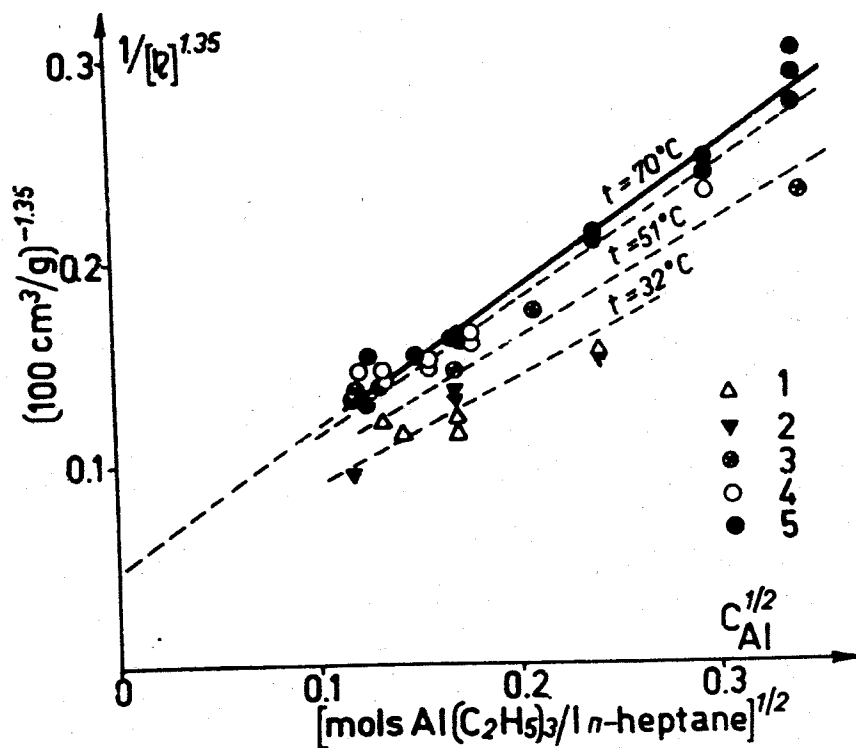


FIG. 31. Effect of temperature upon the polymerization degree of the non-atactic polypropylene fraction (ground  $\alpha$ -TiCl<sub>3</sub>; sample A).

	$t$ , °C	$p_{C_3H_6}$ , mm. Hg	[C <sub>3</sub> H <sub>6</sub> ], mol./l.	Al/Ti, mol.
1	31	1,450	1.18	3
2	31	700	0.57	3
3	51	1,110	0.63	3
4	70	1,450	0.62	3
5	70	950	0.41	3

varies with the temperature shows that the activation energy of the chain transfer processes, depending on the catalyst concentrations, are little different from the activation energy of the chain propagation process.

In order to define the value of the activation energy of the chain transfer process with the monomer, it would be necessary to know quite exactly the values of  $1/[\eta]_0^{1.35}$  at different temperatures. From the data plotted in Fig. 31, it may be observed, therefore, that also the activation energy of this process is just slightly greater than the activation energy of the chain propagation process.

#### G. COMPARISON BETWEEN INTRINSIC VISCOSITY AND SPECIFIC RADIOACTIVITY OF THE POLYMER OBTAINED IN THE PRESENCE OF <sup>14</sup>C-LABELED TRIALKYLALUMINUM

In this paragraph we intend to confirm the hypothesis that each process of chain transfer, depending on the concentration of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and

on the amount of  $\alpha$ -titanium trichloride present in the catalytic system, is followed by the introduction into the polymeric chain, of group,  $-\text{C}_2\text{H}_5$  deriving from the ethylaluminum.

According to the results acquired through the study of the intrinsic viscosities of the polymer, we have assumed that the reciprocal of the number average degree of polymerization is represented by the relationship:

$$\frac{1}{x_n} = \frac{k_1 C^* + k_2 p_{\text{C}_3\text{H}_6} C^* + k_3 C_{\text{Al}}^{\frac{1}{2}} C^* + k_4 C_{\text{Ti}}^{\frac{1}{2}} p_{\text{C}_3\text{H}_6} C^*}{k_p p_{\text{C}_3\text{H}_6} C^*} \quad (23)$$

The terms of the numerator indicate the rates of chain transfer and termination processes depending, respectively, on the concentration of the growing chains, on the partial pressure of olefin, on the concentration of alkylaluminum, and on the amount of titanium compounds.

Let us consider now the equation

$$Et = \frac{\bar{k}_3 C_{\text{Al}}^{\frac{1}{2}} C^* + \bar{k}_4 C_{\text{Ti}}^{\frac{1}{2}} p_{\text{C}_3\text{H}_6} C^*}{k_p p_{\text{C}_3\text{H}_6} C^*} \quad (24)$$

which gives the amount of ethyl groups found in the polymer after polymerization. The terms on the numerator show the rate of the processes which lead to the introduction of ethyl groups in the polymer.

The relation (24) can be substituted in Equation (23) if  $k_3$  and  $k_4$

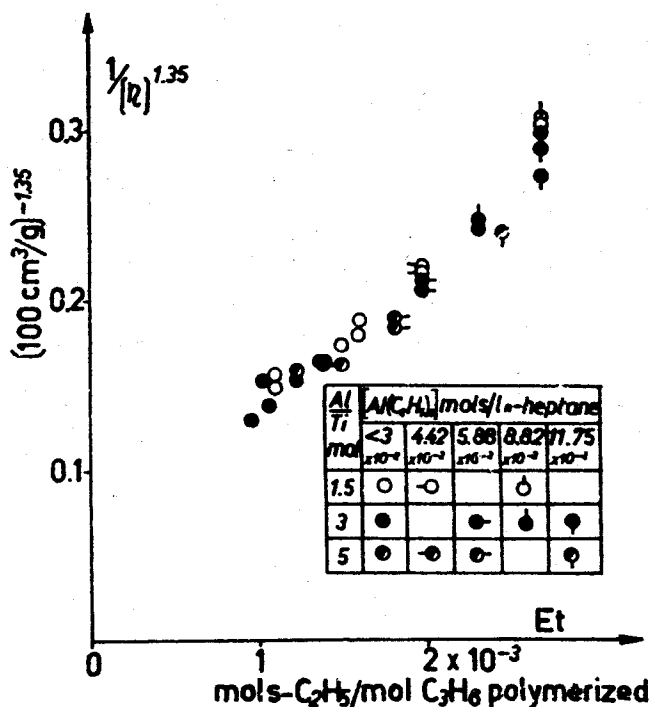


FIG. 32. Relation between the reciprocal of the intrinsic viscosity raised to 1.35 (proportional to the reciprocal of polymerization degree) of the non-atactic polypropylene fraction and the number of mol. of  $-\text{C}_2\text{H}_5$  groups found in the polymer. (Tests performed with  $^{14}\text{C}$ -labeled  $\text{Al}(\text{C}_2\text{H}_5)_3$  at  $70^\circ$  and 950 mm. Hg  $p_{\text{C}_3\text{H}_6}$ , ground  $\alpha$ - $\text{TiCl}_3$ ; sample A.)

have, respectively, the same numerical value as  $\bar{k}_3$  and  $\bar{k}_4$ . In this case, we shall find

$$1/x_n = 1/x_{n_0} + Et \quad (25)$$

The reciprocal of the intrinsic viscosities of the polymer would be a unique and linear function of the amount of ethyl groups (deriving from ethylaluminum found in the polymer).

This appears to be confirmed (except for some small irregularities, for high concentrations of ethylaluminum) by the data plotted in Fig. 32, where the values of  $1/[\eta]^{1.35}$  for polypropylene, obtained by operating with several titanium trichloride and trialkylaluminum concentrations are plotted *vs.* the amount of ethyl groups found in the polymer.

#### H. RELATIVE IMPORTANCE OF THE DIFFERENT CHAIN TRANSFER PROCESSES

In an attempt to calculate approximately the relative importance of the different chain transfer processes, we can put (41)

$$[\eta] = K'x_n^{0.74} \quad (26)$$

and taking into account Equations (26) and (23), we obtain

$$\frac{K}{[\eta]^{1.35}} = \frac{1}{x_n} = \frac{k_1 + k_2p_{C_3H_6} + k_3C_{A1}^{\frac{1}{2}} + k_4C_{Ti}^{\frac{1}{2}}p_{C_3H_6}}{k_p p_{C_3H_6}} \quad (27)$$

where  $K = K'^{1.35}$  and

$$\frac{K}{[\eta]_0^{1.35}} = \frac{1}{x_{n_0}} = \frac{k_1 + k_2p_{C_3H_6}}{k_p p_{C_3H_6}} \quad (28)$$

Let us consider the ratio

$$\frac{1/[\eta]^{1.35} - 1/[\eta]_0^{1.35}}{1/[\eta]_0^{1.35}} = \frac{r_3 + r_4}{r_1 + r_2} = \frac{k_3C_{A1}^{\frac{1}{2}} + k_4C_{Ti}^{\frac{1}{2}}p_{C_3H_6}}{k_1 + k_2p_{C_3H_6}} \quad (29)$$

The numerator includes the rates of the chain transfer processes which depend on the catalyst concentration; the denominator includes the rates of the processes which do not depend on the catalyst concentration.

Operating at low temperature ( $< 80^\circ$ ),  $k_1$  can be neglected with respect to  $k_2p_{C_3H_6}$ . Therefore, the relationship (29) is equal to the ratio between the number of polymeric chains interrupted by the chain transfer processes, depending on the catalyst concentration, and the number of polymeric chains interrupted by the chain transfer with monomer.

The values of

$$\frac{1/[\eta]^{1.35} - 1/[\eta]_0^{1.35}}{1/[\eta]_0^{1.35}}$$

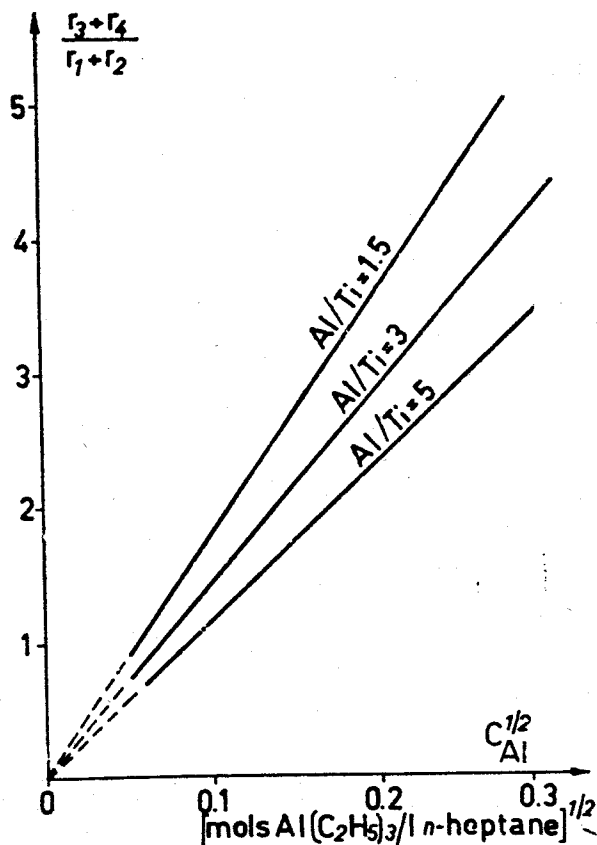


FIG. 33. Values of the ratio between the rate of the chain-transfer processes depending on the catalyst concentration and the rate of the chain-transfer process with the monomer (plus the rate of the spontaneous termination process) ( $t = 70^\circ$ ,  $p_{C_3H_6} = 950$  mm. Hg, ground  $\alpha$ -TiCl<sub>3</sub>; sample A). The values were calculated assuming for the isotactic polymeric fraction  $x_n = K_1[\eta]^{1.35} = K_2C_{Al}^{1.2}$ .

have been computed from the diagrams of Fig. 30, concerning polymerization experiments carried out at  $70^\circ$  and 950 mm. Hg partial pressure of propylene. The data so obtained are summarized in Fig. 33. We observe that the calculated values are strongly dependent on the value of  $1/[\eta]_0^{1.35}$ . On the other hand, the latter value cannot be exactly determined with the reported data (see, for instance, Fig. 30). Therefore, the data plotted in Fig. 33 are largely approximate.

The importance of the chain transfer process depending on the concentration of alkylaluminum, when compared with the one depending on the amount of  $\alpha$ -titanium trichloride present in the catalytic system, may be easily deduced from the diagrams plotted in figures 22 and 25. From such diagrams it follows for the catalytic system considered:

$$k_3/k_4 = 1.27 \quad (30)$$

#### I. RELATION BETWEEN INTRINSIC VISCOSITY AND NUMBER AVERAGE POLYMERIZATION DEGREE FOR POLYPROPYLENE

If the amount of polymeric chains containing an end group  $-C_2H_5$  and the fraction of such chains compared with the total number of them are

known, it should be possible to calculate the number average degree  $x_n$  of polymerization and compare this latter with the intrinsic viscosity.

If the value of  $x_n$  is calculated in such a way it will necessarily differ from the viscosimetric molecular weight (since the polypropylene is a polydispersed polymer) as may be calculated by already known relations (41).

Combining Equations (23), (24), and (26), we obtain

$$\frac{1}{[\eta]^{1.35}} = \frac{1}{[\eta]_0^{1.35}} + KEt \quad (31)$$

Drawing a straight line through the experimental points plotted in Fig. 32, we approximately obtain

$$x_n = 95[\eta]^{1.35} \quad (32)$$

where  $[\eta]$ , measured at 135° in tetralin, is expressed in 100 cm.<sup>3</sup> g.

This relation gives likely approximate values for the limited range of polymers obtained under the conditions previously examined, namely,  $t = 70^\circ$ ,  $p_{C_3H_6} = 950$  mm. Hg;  $C_{Ti}$  and  $C_{Al} = 1$  to  $15 \cdot 10^{-2}$  mol. l. *n*-heptane.

The number average degree of polymerization of non-atactic polypropylene, as evaluated from this relation, is much lower than the viscosimetric molecular weight resulting from the suggested relationship because the above-considered fraction of polypropylene contains isotactic and stereoblock macromolecules which have low molecular weight. On the other hand, that fraction is strongly dispersed (47) and, as it is usual in these cases, the number average molecular weight is lower than the viscosimetric one.

Moreover, we confirmed the results previously ascertained through radiochemical measurements. In fact, the comparison between such data and those obtained by *IR* measurements on the atactic polymer fraction (Table IV) shows that the ratio between the number of polymeric chains with a  $-C_2H_5$  end group (corresponding to a chain transfer process depending on the catalyst concentration) and the number of polymeric chains with a vinylidene end group of polymeric chains (corresponding to the chain transfer process with the monomer) is closely in accordance with the data reported in Fig. 33.

#### J. REMARKS ON THE CATALYTIC NATURE OF THE COORDINATED ANIONIC CATALYSIS

From the above summarized data, it follows that, during the polymerization, in the presence of triethylaluminum, there is a consumption of Al atoms and ethyl groups bound to the aluminum, because the triethylaluminum is involved in chain transfer processes without being regenerated. Therefore, the polymerization process is now thoroughly catalytic only with

respect to titanium trichloride. It must be noticed, however, that not all chain transfer processes lead to a consumption of alkylaluminum. If we take into consideration the chain transfer processes with the monomer, we can consider the coordinated anionic catalysis as thoroughly catalytic in the strictest sense. In practice, an excess of alkylaluminum is necessary if the polymerization is to be of long duration. In fact, the catalyst obtained by treating  $\alpha$ -titanium trichloride with trialkylaluminum and successively washed so as to eliminate the excess of chemisorbed alkylaluminum, makes only a very small amount of polymer (unless a further amount of alkylaluminum is added). It is most likely that the polymerization stops because of the presence of impurities (traces of  $O_2$ , moisture) which act as poisons of the catalyst when alkylaluminum is absent.

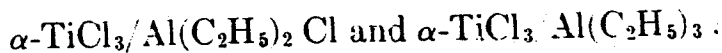
#### IV. Steric Composition of Polymers

The amount of amorphous polymer, which is generally produced in small percentage (9–16%) contemporaneously with the non-atactic polymer, is independent of reaction time (see Table II). It is on the contrary closely connected with the nature of the catalytic system employed and changes, for instance, when the triethylaluminum is substituted by other metal alkyls (beryllium alkyls, propylaluminum, isobutylaluminum, etc.) (5, 28). It also depends on the purity of the  $\alpha$ -titanium trichloride, in particular increasing in the presence of other crystalline modifications of titanium trichloride [i.e.  $\beta$ - $TiCl_3$  (27)] and of titanium compounds obtained by reduction of titanium tetrachloride at low temperature with aluminum alkyls.

In the Tables V–IX we reported the percentages of the fraction of *n*-heptane insoluble polymer at room temperature and the respective intrinsic viscosities. The data concern the polymers obtained from polymerization tests carried out with triethylaluminum concentrations varying from  $1.18 \times 10^{-2}$  to  $14.75 \times 10^{-2}$  mol./l., with ratios Al/Ti between 1 and 10, with propylene concentrations included between 0.19 and 0.63 mol./l. at temperatures of 31°, 51° and 70°C.

In a recent work (48), the influence of the variation of some factors, concerning the polymerization, on the steric composition of the polymer has been studied subjecting the obtained raw polymer to subsequent extractions with the following series of solvents employed at their boiling point: ether, *n*-heptane and *n*-octane.

We have examined polymers obtained in polymerization tests carried out at 70°C, with the following catalytic systems:



We have observed that with the decrease of the propylene partial pressure at which the polymerization is carried out, from 1600 mm. Hg to 250 mm. Hg, the percentage of each fraction of polymer extracted with the

TABLE V

Polymerization of Propylene to Isotactic Polymer with  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-*n*-Heptane Catalytic System. Tests Performed at 70°, 950 mm. Hg p<sub>C<sub>3</sub>H<sub>6</sub></sub>, [C<sub>3</sub>H<sub>6</sub>] = 0.41 mol./l.

[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ], mol./l.	$\alpha$ -TiCl <sub>3</sub> , (sample A), g./l.	$\frac{\text{Al}}{\text{Ti}}$ mol.	Polymeri- zation time, hr.	Non-atactic polymer, <sup>a</sup> %	Intrinsic viscosity of non-atactic polymer <sup>a</sup> : [ $\eta$ ] 100 cm <sup>3</sup> ./g.
1.47 × 10 <sup>-2</sup>	0.75	3	2	89	4.52
1.47 × 10 <sup>-2</sup>	1.50	1.5	2	89	3.92
1.47 × 10 <sup>-2</sup>	1.50	1.5	2	88.5	4.06
1.62 × 10 <sup>-2</sup>	0.83	3	2	88.5	4.00
1.77 × 10 <sup>-2</sup>	0.91	3	9	88.5	4.30
2.36 × 10 <sup>-2</sup>	1.20	3	2	89	4.00
2.22 × 10 <sup>-2</sup>	0.34	10	10	89	4.16
2.65 × 10 <sup>-2</sup>	2.72	1.5	½	89	3.60
2.80 × 10 <sup>-2</sup>	0.87	5	7	89	3.92
2.94 × 10 <sup>-2</sup>	3.00	1.5	2	89	3.43
2.94 × 10 <sup>-2</sup>	3.00	1.5	2	89	3.51
2.94 × 10 <sup>-2</sup>	1.50	3	½	88.5	3.84
2.94 × 10 <sup>-2</sup>	1.50	3	2	88.5	3.78
2.94 × 10 <sup>-2</sup>	1.50	3	6	88	3.84
2.94 × 10 <sup>-2</sup>	0.45	10	4	89	4.08
4.42 × 10 <sup>-2</sup>	4.52	1.5	2	89	3.07
4.42 × 10 <sup>-2</sup>	4.52	1.5	2	89.5	3.12
4.42 × 10 <sup>-2</sup>	1.36	5	2	90	3.84
5.88 × 10 <sup>-2</sup>	3.02	3	2	90	3.12
5.88 × 10 <sup>-2</sup>	3.02	3	2	90.5	3.18
5.88 × 10 <sup>-2</sup>	1.82	5	2	88.5	3.47
5.88 × 10 <sup>-2</sup>	1.82	5	2	89	3.51
8.82 × 10 <sup>-2</sup>	9.05	1.5	1	90	2.38
8.82 × 10 <sup>-2</sup>	9.05	1.5	1	89.5	2.42
8.82 × 10 <sup>-2</sup>	4.52	3	1	90	2.76
8.82 × 10 <sup>-2</sup>	4.52	3	1	90.5	2.86
10.30 × 10 <sup>-2</sup>	1.58	10	2	90	3.28
11.75 × 10 <sup>-2</sup>	6.05	3	2	90.5	2.44
11.75 × 10 <sup>-2</sup>	6.05	3	2	90	2.50
11.75 × 10 <sup>-2</sup>	6.05	3	2	90	2.60
11.75 × 10 <sup>-2</sup>	3.62	5	2	90.5	2.86
11.75 × 10 <sup>-2</sup>	1.82	10	2	90.5	3.08
14.75 × 10 <sup>-2</sup>	2.27	10	2	90	2.84
14.75 × 10 <sup>-2</sup>	2.27	10	2	90.5	3.03
14.75 × 10 <sup>-2</sup>	2.27	10	2	91	3.18

<sup>a</sup> The data are related to the polymers insoluble in *n*-heptane at room temperature and include also the stereoblock polymers soluble in boiling *n*-heptane (5-7% of the whole polymer).

TABLE VI

Polymerization of Propylene to Isotactic Polymer with the  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-*n*-Heptane Catalytic System. Tests Performed at  $t = 51^\circ$ , 1,110 mm. Hg  $p_{C_3H_6}$ ,  
[C<sub>3</sub>H<sub>6</sub>] = 0.63 mol./l. *n*-Heptane

[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ], mol./l	$\alpha$ -TiCl <sub>3</sub> (sample A), g/l.	$\frac{Al}{Ti}$ mol.	Polymeri- zation time, hr.	Non-atactic polymer, <sup>a</sup> %	Intrinsic viscosity of non-atactic polymer <sup>a</sup> : [ $\eta$ ], 100 cm. <sup>3</sup> /g.
$1.47 \times 10^{-2}$	1.13	2	8	83	4.20
$1.47 \times 10^{-2}$	0.75	3	9	85	4.38
$1.47 \times 10^{-2}$	0.75	3	9	86	4.35
$1.47 \times 10^{-2}$	0.30	7.5	8	87	4.50
$1.47 \times 10^{-2}$	0.30	7.5	24	87	4.45
$2.36 \times 10^{-2}$	0.60	6	9	85	4.00
$2.94 \times 10^{-2}$	1.50	3	5	87	4.16
$4.42 \times 10^{-2}$	2.26	3	1½	88.5	3.60
$11.75 \times 10^{-2}$	6.05	3	2½	89	2.92

<sup>a</sup> The data are related to the polymers insoluble in *n*-heptane at room temperature and include also the stereoblock polymers soluble in boiling *n*-heptane (5-7% of the whole polymer).

TABLE VII

Polymerization of Propylene to Isotactic Polymers with the  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-*n*-Heptane Catalytic System. Tests Performed at  $t = 70^\circ$ , 450 mm. Hg  $p_{C_3H_6}$ ,  
[C<sub>3</sub>H<sub>6</sub>] = 0.19 mol./l.

[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ], mol./l.	$\alpha$ -TiCl <sub>3</sub> (sample A), g./l.	$\frac{Al}{Ti}$ mol.	Polymeri- zation time, hr.	Non-atactic polymer, <sup>a</sup> %	Intrinsic viscosity of non-atactic polymer <sup>a</sup> : [ $\eta$ ], 100 cm. <sup>3</sup> /g.
$1.18 \times 10^{-2}$	0.62	3	30	89	4.10
$1.18 \times 10^{-2}$	0.62	3	30	89	3.70
$1.77 \times 10^{-2}$	1.82	1.5	11	90	3.52
$2.06 \times 10^{-2}$	3.18	1	11	90.5	3.22
$2.36 \times 10^{-2}$	1.20	3	10	90	3.56
$2.36 \times 10^{-2}$	1.20	3	15	90	3.47
$2.94 \times 10^{-2}$	3.00	1.5	2½	90	3.14
$2.94 \times 10^{-2}$	3.00	1.5	2½	90	3.22
$2.94 \times 10^{-2}$	1.50	3	4	91	3.28
$2.94 \times 10^{-2}$	1.50	3	7	91	3.14
$3.24 \times 10^{-2}$	5.00	1	¾	90	2.86
$4.42 \times 10^{-2}$	6.80	1	5	91	2.63
$4.42 \times 10^{-2}$	4.54	1.5	3	90.5	2.74
$7.36 \times 10^{-2}$	11.30	1	1½	91	2.18
$7.36 \times 10^{-2}$	11.30	1	1	90	2.13

<sup>a</sup> The data are related to the polymers insoluble in *n*-heptane at room temperature and include also the stereoblock polymers soluble in boiling *n*-heptane (5-7% of the whole polymer).



TABLE VIII

*Polymerization of Propylene to Isotactic Polymer with the  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> *n*-Heptane Catalytic System. Tests Performed at  $t = 70^\circ$ , 1450 mm. Hg  
 $p_{C_3H_6}$ , [C<sub>3</sub>H<sub>6</sub>] = 0.62 mol./l.*

[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ], mol./l.	$\alpha$ -TiCl <sub>3</sub> (sample A) g./l.	$\frac{Al}{Ti}$ , mol.	Polymeri- zation time, hr.	Non-atactic polymer <sup>a</sup> , %	Intrinsic viscosity of non-atactic polymer <sup>a</sup> : $[\eta]$ 100 cm. <sup>3</sup> /g.
$1.47 \times 10^{-2}$	0.75	3	8	87	4.16
$1.77 \times 10^{-2}$	0.91	3	4	88	4.16
$1.77 \times 10^{-2}$	0.91	3	7	87	4.20
$2.06 \times 10^{-2}$	2.10	1.5	2	87	3.87
$2.36 \times 10^{-2}$	1.20	3	2	87	4.04
$2.36 \times 10^{-2}$	1.20	3	2	87	4.12
$2.94 \times 10^{-2}$	3.00	1.5	1	86	3.57
$2.94 \times 10^{-2}$	1.50	3	6	89	3.83
$2.94 \times 10^{-2}$	1.50	3	6	89	3.88
$4.42 \times 10^{-2}$	4.52	1.5	1½	90	3.12
$5.30 \times 10^{-2}$	5.45	1.5	2	88	3.03
$8.84 \times 10^{-2}$	4.54	3	¾	88	2.92

<sup>a</sup> The data are related to the polymers insoluble in *n*-heptane at room temperature and include also the stereoblock polymers soluble in boiling *n*-heptane (5-7% of the whole polymer).

TABLE IX

*Polymerization of Propylene to Isotactic Polymer with the  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> *n*-Heptane Catalytic System. Tests Performed at  $t = 31^\circ$ ,  
700 mm. Hg.  $p_{C_3H_6}$ , [C<sub>3</sub>H<sub>6</sub>] = 0.57 mol./l.*

[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ], mol./l.	$\alpha$ -TiCl <sub>3</sub> (sample A), g./l.	$\frac{Al}{Ti}$ , mol.	Polymeri- zation time, hr.	Non-atactic polymer, <sup>a</sup> %	Intrinsic viscosity of non-atactic polymer <sup>a</sup> : $[\eta]$ 100 cm. <sup>3</sup> /g.
$1.17 \times 10^{-2}$	0.75	3	40	89.5	5.85
$2.94 \times 10^{-2}$	1.50	3	14	89	4.40
$2.94 \times 10^{-2}$	1.50	3	31	88.5	4.34
$5.88 \times 10^{-2}$	3.00	3	2	89.5	4.00

<sup>a</sup> The data are related to the polymers insoluble in *n*-heptane at room temperature and include also the stereoblock polymers soluble in boiling *n*-heptane (5-7% of the whole polymer).

above-mentioned solvents increases. This phenomenon can be easily observed working at the lowest pressures; it was not observed in previous works in which generally we worked at partial pressures of propylene superior to 1 atm.

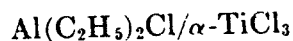
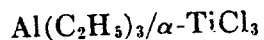
We have also observed an increase of the percentage of polymer extractable in *n*-octane when varying the concentration of the triethylaluminum from  $1.5 \times 10^{-2}$  to  $12 \times 10^{-2}$  mol./l.

These results made us conclude that the inversions of steric configuration of the monomeric units which happen during the growing of the atactic or stereoblock polymeric chains is determined by several different processes. The rate of one of these is independent of the pressure of the olefin, and therefore, being the growing rate of the polymeric chain of first order with regard to the olefin pressure, the frequency of the inversions along the chain increases when the olefin pressure decreases. The inversion phenomena during the growing of the polymeric chains are also connected with the chain transfer phenomena, whose rates depend on the concentration of the components of the catalytic system.

### V. Determination of the Number of Active Centers

The coordinated anionic catalysis is one of the few examples of heterogeneous catalysis in which it is possible to estimate the actual number of active centers, present on the catalyst surface, which directly take part in the chemical catalytic process.

In the stereospecific polymerization of propylene, such active centers, which are formed by treating  $\alpha$ -TiCl<sub>3</sub> with alkylaluminum, have been determined by using <sup>14</sup>C-labeled alkylaluminum. The two systems studied were



In both cases the determination of active centers has been performed by means of absorption tests of <sup>14</sup>C-labeled alkylaluminum on samples of ground  $\alpha$ -titanium trichloride. In the first case, two  $\alpha$ -TiCl<sub>3</sub> samples were used, one of them (sample A) having low catalytic activity, the other one (sample B) high activity. In the second case, only the sample A was used, and the determination of active centers was also made by a kinetic method, still using labeled alkylaluminum.

#### A. ADSORPTION OF <sup>14</sup>C-LABELED ALKYLALUMINUMS ON $\alpha$ -TITANIUM TRICHLORIDE

The following determinations have been performed:

Direct determination of <sup>14</sup>C-labeled ethyl groups bound on the surface of titanium trichloride samples, treated either with triethylaluminum or diethylaluminum monochloride solutions, at different temperatures.

Determination of active centers by the number of <sup>14</sup>C-labeled  $-\text{C}_2\text{H}_5$

groups found in a polymer, obtained using, as catalyst,  $\alpha$ -titanium trichloride pretreated with labeled alkylaluminums.

Before carrying out such determinations in an attempt to estimate the number of active centers correctly, it has been necessary to define the magnitude of the eventual radioactive contaminations of the polymers, caused by phenomena extraneous to the polymerization process.

### 1. *Measurements of Casual Radioactive Contaminations*

It has been pointed out that the product obtained by treating certain samples of ground  $\alpha$ -titanium trichloride (particularly those which contain traces of  $\text{TiCl}_4$  or other  $\text{Ti(IV)}$  compounds) with radioactive alkylaluminum, shows a certain degree of radioactivity also after submitting it to the action of an acid or an alcohol in an attempt to decompose the metal-carbon bonds. Such radioactivity is due to a contaminant, the nature of which depends on the degree of purity and the amount of crude  $\alpha$ -titanium trichloride employed. It generally decreases, eventually attaining very low values if the crude  $\alpha$ -titanium trichloride is repeatedly washed with anhydrous benzene before its use.

We have observed that the radioactive contamination is practically independent of the temperature (49). We believe that this radioactive contamination is due to the presence of traces of radioactive polyethylene resulting from ethylene polymerization. Ethylene can result, in fact, from the disproportionation of  $\text{C}_2\text{H}_5$  radicals released by decomposition of ethyl titanium compounds, which derive from the reaction between ethylaluminum and traces of titanium tetrachloride or other tetravalent titanium compounds that are sometimes present as impurities in the  $\alpha$ -titanium trichloride.

This assumption is confirmed by the fact that adding titanium tetrachloride to  $\alpha$ -titanium trichloride catalysts a greater contamination in the reaction products with labeled ethylaluminum is obtained (42).

When other samples of  $\alpha$ -titanium trichloride are used, for instance, unground  $\alpha$ -titanium trichloride (sample B, see Fig. 7), having a high catalytic activity, we do not observe radioactive contamination. Other types of contamination due, for instance, to the incomplete removal of alkylaluminum from the polymer or to secondary reactions of its alkylation, are not present in the reported tests.

### 2. *Adsorption Tests with $^{14}\text{C}$ -Labeled Triethylaluminum and Diethylaluminum Monochloride on $\alpha$ -Titanium Trichloride*

The following method was applied in an attempt to evaluate the amount of ethyl groups fixed on the  $\alpha$ -titanium trichloride surface by treating it with ethylaluminum solutions:

Treatment of a given amount of titanium trichloride, at a given temperature, with a solution of radioactive ethylaluminum.

Filtering and washing of the solid phase at a given temperature, under nitrogen, with carefully purified anhydrous benzene (or other hydrocarbon solvent) until any radioactivity disappears from the washing solvent.

Subsequent addition to the solid phase of an amount of inactive alkylaluminum in solution and decomposition of all alkyl-metal bonds with 10%  $\text{H}_2\text{SO}_4$ .

Purification of the gas released at high temperature, by washing at  $-78^\circ$  in order to separate the solvent and other hydrocarbons having an high molecular weight, which are entrained by the gas.

Combustion of the gas released.

Absorption of the  $\text{CO}_2$  on  $\text{Ba}(\text{OH})_2$ .

Determination of the  $^{14}\text{C}/^{12}\text{C}$  ratio in the  $\text{BaCO}_3$ .

The radioactivity measurements of  $\text{BaCO}_3$  allowed us to calculate, according to the law of the isotope dilution, the amount of ethyl groups, fixed on the  $\alpha$ -titanium trichloride surface.

The results obtained in such tests, in the interval  $-18$ – $+100^\circ$ , for the considered system  $\alpha$ -titanium trichloride-triethylaluminum and at  $70^\circ$  for the considered system  $\alpha$ -titanium trichloride-diethylaluminum monochloride, are tabulated in Table X (49).

In all tests, the initial treatment of  $\alpha$ -titanium trichloride, with the ethylaluminum solution, was carried out under conditions suitable for the practically complete saturation of the  $\alpha$ -titanium trichloride surface at the temperature considered by the metallorganic compound.

The above conditions were found by varying, in preliminary tests, the concentration of the alkylaluminum solution and the contact time.

From the results obtained, one may conclude that:

Metallorganic complexes containing ethyl groups are present on the  $\alpha$ -titanium trichloride surface.

Within the temperature range  $+20$  to  $-18^\circ\text{C}$ , after raising the equilibrium conditions, the amount of ethyl groups strongly fixed on the  $\alpha$ -titanium trichloride surface, seems to be almost independent of the temperature.

For the considered sample of  $\alpha\text{-TiCl}_3$ , above  $20^\circ$  approximately, the amount of the fixed ethyl groups decreased with increasing temperature and depends on the temperature at which, after treatment with alkylaluminum solution, the washings of the  $\alpha$ -titanium trichloride are carried out.

At the lowest temperatures considered ( $-18^\circ$ ), it has been observed that the adsorption process is relatively slow.

The adsorption process is partially reversible. However, we can suppose that almost a portion of the ethyl groups (probably bound to a metallor-

TABLE X

Number of Conventional Active Centers in a Sample of Ground  $\alpha$ -TiCl<sub>3</sub>,  
Determined by Adsorption Tests of <sup>14</sup>C-Labeled Alkylaluminum  
Compounds, Followed by Polymerization of Propylene.  
( $\alpha$ -TiCl<sub>3</sub>-Ground: Sample A: 0.5 g.; Alkylaluminum  
Compound: 0.5 cm.<sup>3</sup>; Solvent: 30 cm.<sup>3</sup>).

Alkylaluminum compound	Adsorption temperature, °C	Adsorption time, hr.	Solvent	Temperature washing with anhydrous solvent, °C	-C <sub>2</sub> H <sub>5</sub> mol. adsorbed per mol. of $\alpha$ -TiCl <sub>3</sub>	
					Total alkyl groups remaining on $\alpha$ -TiCl <sub>3</sub> surface after washing	Number of alkyl groups corresponding to active centers (preadsorbed alkyl groups found in the polymer)
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-18	½	n-heptane	-18	17.0 × 10 <sup>-3</sup>	nd.
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	-18	3	"	-18	45.0 × 10 <sup>-3</sup>	9.3 × 10 <sup>-3</sup>
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	20	½	benzene	20	48.2 × 10 <sup>-3</sup>	10.1 × 10 <sup>-3</sup>
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	46	½	"	46	17.7 × 10 <sup>-3</sup>	10.5 × 10 <sup>-3</sup>
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	70	½	"	20	10.5 × 10 <sup>-3</sup>	10.8 × 10 <sup>-3</sup>
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	70	½	"	70	6.2 × 10 <sup>-3</sup>	6.7 × 10 <sup>-3</sup>
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	100	½	toluene	100	3.0 × 10 <sup>-3</sup>	3.0 × 10 <sup>-3</sup>
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl	70	½	n-heptane	20	3.0 × 10 <sup>-3</sup>	3.1 × 10 <sup>-3</sup>
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> <sup>a</sup>	70	½	n-heptane	20	5.0 × 10 <sup>-3</sup>	<0.2 × 10 <sup>-3</sup>

<sup>a</sup> This test was performed with unground  $\alpha$ -TiCl<sub>3</sub>: sample B (See fig. 7).

ganic complex) is strongly fixed to the crystalline substrate ( $\alpha$ -titanium trichloride); actually repeated washings with anhydrous solvent are not sufficient to give a complete desorption of the alkyl compounds.

The amount of ethyl groups bound to the  $\alpha$ -titanium trichloride surface, treated with diethylaluminum monochloride, is somewhat smaller than the one observed by the treatment with triethylaluminum (49).

It has been observed by many authors that the catalytic activity of several crystals is related to some particular faces of the crystal (50).

In the case of  $\alpha$ -titanium trichloride, microscopic examination reveals that the widest faces are those (001). Owing to the sandwich structure of the  $\alpha$ -titanium trichloride, such faces are constituted by Cl atoms only.

There is some evidence that the faces on which titanium atoms may exist, e.g., lateral faces (thus, not the 001 faces supposed free from fault), show a greater catalytic activity. From adsorption measurements of radioactive triethylaluminum on an  $\alpha$ -titanium trichloride sample having well developed crystals (sample B, see Fig. 7), one may observe that the total amount of alkylaluminum which can be adsorbed (Table X, last line) is remarkably greater than the one sufficient to form a monomolecular layer on the lateral faces of the crystals (38). It is most likely that the alkyl-

aluminum adsorbed on that  $\alpha$ -titanium trichloride sample is mostly adsorbed along the 001 faces of the crystals. In the following paragraph it will be, however, demonstrated that, as for the sample here considered, the whole amount of alkylaluminum adsorbed does not correspond to the active centers (see Table X, last line).

### 3. Evaluation of the Active Centers

$\alpha$ -Titanium trichloride, on whose surface a given amount of ethyl groups was previously bound, was employed in the propylene (or ethylene) polymerization, generally after a further addition of non-radioactive alkylaluminum. The ethyl groups were bound on  $\alpha$ -titanium trichloride surface by treating titanium trichloride with a radioactive alkylaluminum compound, followed or not by repeated washings with anhydrous *n*-heptane.

Further addition of alkylaluminum is not, in any case, indispensable for the formation of the catalyst, given the fact that an olefin polymerization occurs also without it although for a short time.

In tests carried out with further addition of non-radioactive alkylaluminum, we obtained 0.5 to 2 g. of isotactic polypropylene per 0.5 g. of  $\alpha$ -titanium trichloride, according to the polymerization time.

The polymer obtained in these tests was found to be always radioactive. It is most likely that the radioactive carbon found in the polymer comes from the ethyl groups initially contained in the catalytic complexes bound to the active centers of the  $\alpha$ -titanium trichloride surface. The results obtained in such measurements are summarized in Table X (49).

It has been assumed that all radioactive carbon found in the polymer is contained in it as  $-\text{C}_2\text{H}_5$  groups.

In the interval 70–100°, by using the sample A of  $\alpha$ -titanium trichloride, all ethyl groups, initially bound to the  $\alpha$ -titanium trichloride surface, were later found in the obtained polymer.

Within the range  $-18$  to  $50^\circ$  the amount of ethyl groups found in the polymer is smaller than the total amount, initially bound to the  $\alpha$ -titanium trichloride surface. In other tests, carried out with other samples of  $\alpha$ -titanium trichloride, the same behavior was also observed when operating at  $70^\circ$  (see Table X, last line).

If the temperature of washing of the  $\alpha\text{-TiCl}_3$ , after being treated with radioactive ethylaluminum, is kept below about  $50^\circ$ , the number of ethyl groups found in the polymer remains practically independent of the temperature at which the adsorption of the triethylaluminum was made and of the amount and kind of polymer (polypropylene or polyethylene) obtained in each experiment.

If the washing-temperature is higher (e.g.,  $70^\circ$ ), the number of ethyl groups found in the polymer is lower.

TABLE XI

*Propylene Polymerization with the  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-*n*-Heptane Catalytic System. Comparison between Two Samples of  $\alpha$ -TiCl<sub>3</sub>*

Sample A: Ti/Cl = 2.96 (Initial Sizes of the Crystals  $\leq 2 \mu$ . Sample B: Ti/Cl = 3.00 (Initial Sizes of the Crystals: within 1 to 200  $\mu$ —See Fig. 7).

$\alpha$ -TiCl <sub>3</sub> sample	A	B	B/A ratio
Catalytic activity at 70°C expressed as: g. C <sub>3</sub> H <sub>6</sub> polymerized in steady-state conditions/hr. g. TiCl <sub>3</sub> atm. $p_{C_3H_6}$	8	13	1.63
Conventional active centers (number of —C <sub>2</sub> H <sub>5</sub> groups initially fixed on the active centers) mol./mol. of ground $\alpha$ -TiCl <sub>3</sub>	$1 \times 10^{-2}$	$1.7 \times 10^{-2}$	1.7

The number of ethyl groups, and, therefore, the number of the corresponding active centers found in the catalytic system diethylaluminum monochloride- $\alpha$ -titanium trichloride, is smaller than the one found in the system triethylaluminum- $\alpha$ -titanium trichloride. It is interesting to notice that for the two samples of  $\alpha$ -TiCl<sub>3</sub> (A and B), the activity ratio in the propylene polymerization is almost equal to the ratio (determined from ethyl groups) between the number of active centers (Table XI) (38).

#### 4. Discussion of the Results

The results summarized in the previous sections show that, for the considered sample of  $\alpha$ -TiCl<sub>3</sub>, there are two types of adsorption of the triethylaluminum on  $\alpha$ -titanium trichloride, one of them is connected with active centers which are directly active in the stereospecific polymerization of propylene.

Moreover, it has been possible to confirm that the formation of isotactic macromolecules occurs through a process of polymerization of the monomeric units on a metal-carbon bond. The actual structure of the complex containing ethyl groups bound to the  $\alpha$ -titanium trichloride surface is not completely known. For this reason, it is not possible to say whether the number of ethyl groups found in the polymer may be considered equal to the number of active centers, which are expected to exist on the  $\alpha$ -titanium trichloride surface, where the growing process of macromolecules occurs. The number of ethyl groups found in the polymer may be a multiple of the molecules of the chemisorbed complex, and therefore a multiple of the actual active centers, considered as sites of the  $\alpha$ -titanium trichloride surface, on which that complex is chemisorbed. This factor will be the larger the larger

the number of ethyl groups present in the complex adsorbed on  $\alpha$ -titanium trichloride.

For the above reasons, we have named the active centers so determined "conventional active centers."

It was observed that, during the treatment with radioactive alkylaluminum of some samples of  $\alpha$ -titanium trichloride containing small amounts of Ti(IV) compounds, traces of ethylene may be released which may polymerize to give traces of polymer that could be considered as the cause of radioactive contamination. The polymerization of ethylene would occur on active centers that, at least partly, may be also active for propylene polymerization. For that reason, one can suppose that, after having prepared the catalyst, more or less long polyethylenic chains, instead of the  $-\text{C}_2\text{H}_5$  groups only, are fixed on some active centers.

However, we think that, such an occurrence does not substantially alter the value determined for the  $-\text{C}_2\text{H}_5$  groups, which correspond to the active centers. In fact, the radioactive contamination, expressed in terms of numbers of carbon atoms, is only a small fraction of the carbon atoms corresponding to the active centers. In some tests, moreover, it has been possible to observe that the product which may be considered the cause of the radioactive contamination is not soluble in boiling ether and is, only partly soluble in heptane; it contains, therefore, long chains of ethylene groups. This assumption was confirmed by some adsorption tests of triethylaluminum carried out at  $70^\circ$  on  $\alpha$ -titanium trichloride (sample A) (Table X). In these tests the number of ethyl groups fixed on  $\alpha$ -titanium trichloride, measured from gas evolution, by decomposing the catalyst, was found to be practically equal to the corresponding number of ethyl groups found in the polymer after polymerization, corrected for the radioactive contamination. One must consider also that the determination of the radioactivity of the evolved gas was carried out after cooling the gas at  $-78^\circ$ , so as to separate the hydrocarbons higher than ethylene (49).

#### B. DETERMINATION OF THE NUMBER OF ACTIVE CENTERS BY A KINETIC METHOD

In the above paragraph the number of conventional active centers, initially present on the surface of the catalyst, have been evaluated.

It has already been noticed that the number of active centers, which the monomer can directly reach, on the surface of the catalyst, may vary after the start of the polymerization, until it assumes to a constant value.

The previously described method for the determination of the number of active centers gives, therefore, a value that may not correspond to the number of active centers found in steady-state conditions.



In the present section, there will be summarized the measurement employed for the determination of the whole number of centers which participate in the polymerization until it reaches the steady-state condition

### 1. Introduction

The method employed to calculate the total number of active centers relies upon the determination of the variation occurring in the ratio between ethyl groups (deriving from the alkylaluminum) which are present in the polymer and the whole amount of polymerized propylene, on increasing time of polymerization.

Such a ratio can be directly determined on the polymer free of catalyst, provided that the polymerization of propylene is carried out in the presence of  $^{14}\text{C}$ -labeled alkylaluminum.

The processes leading to the entry of ethyl groups into the polymer chains are: *Formation of the catalyst*, followed by the start of the polymerization, the formation of carbon-metal bonds, present in the catalyst,

*Chain transfer* between the ethyl groups contained in the metallic compounds (ethylaluminum in particular) and the growing polymeric chains. Since the catalyst is formed by the reaction of alkylaluminum with  $\alpha$ -titanium trichloride, each active center is of the type  $[\text{Cat}]\text{C}_2\text{H}_5$ , and the first polymeric chain originated by each active center has a terminal  $-\text{C}_2\text{H}_5$  group. During the polymerization, many different chain transfer processes are involved, some of them not involving a transfer of ethyl groups. Therefore, only a portion of the chains ends with a  $-\text{C}_2\text{H}_5$  group.

We shall indicate by  $(r_3 + r_4)$  the sum of the entry rates of ethyl groups into the polymeric chains, during the polymerization, and by  $C^*$  the concentration of conventional active centers (in mols), involved in the polymerization within the interval of time 0,  $t$ .

Since at the end of the reaction the catalyst is decomposed and the polymeric chains, which were growing at the moment when the polymerization was interrupted, were separated from the catalyst, the whole amount of ethyl groups that may be found in the polymer is as a result (we assume that at the beginning of the reaction, one  $-\text{C}_2\text{H}_5$  groups correspond to each active center):

$$C^* + \int_0^t (r_3 + r_4) dt$$

and, with respect to the amount of polymer obtained at the time

$$E_t = \frac{C^* + \int_0^t (r_3 + r_4) dt}{Q_t}$$

where  $E_t = -C_2H_5$  mol./mol. of polymerized propylene at the time  $t$   
 $Q_t =$  mols of propylene polymerized at the time  $t$   
 By assuming  $r_3 + r_4$  independent of the time and

$$Q_t = \int_0^t r_p dt = r_p t,$$

then (34) becomes

$$E_t = \frac{C^* + (r_3 + r_4)t}{r_p t} \quad (35)$$

Such a relationship should allow the determination of  $C^*$ , provided that a regular variation of ethyl is detectable experimentally, on varying the polymerization time. This will occur only when  $(r_3 + r_4)$  is small enough to make possible the evaluation of  $C^*$ .  $(r_3 + r_4)$  can be deduced from experimental data. In fact, for large enough polymerization times, we get

$$E_t = E_{t_\infty} = \frac{r_3 + r_4}{r_p} = \text{constant} \quad (36)$$

where  $E_{t_\infty}$  = the asymptotic value to which  $E_t$  tends with the increasing of polymerization time.

Thus, it follows

$$C^* = (E_t - E_{t_\infty})Q_t \quad (37)$$

It is necessary to notice that Equation (37) can give reliable results only if  $(r_3 + r_4)/r_p$  remains practically invariable during the whole polymerization, so that its value can be calculated after large polymerization times.

Furthermore, this method enabled us to evaluate separately the number of the conventional active centers from which, respectively, each of two particular fractions of polymer, having different steric composition, is originated: an amorphous one, ether soluble, and another one (ether extraction residue) containing stereoblock and isotactic chains.

## 2. Total Number of Active Centers

In Fig. 34 has been plotted the specific radioactivity (corrected for the radioactive contamination) and the corresponding number of  $-C_2H_5$  groups found in the polymer against the polymerized propylene mols.

The evaluated number of active centers  $C^*$  does not depend in practice on the polymerization time. In fact, the curve of Fig. 34, drawn by assuming  $C^* = 0.6 \times 10^{-2}$  mol. of  $-C_2H_5$  per mol. of  $\alpha$ -titanium trichloride and

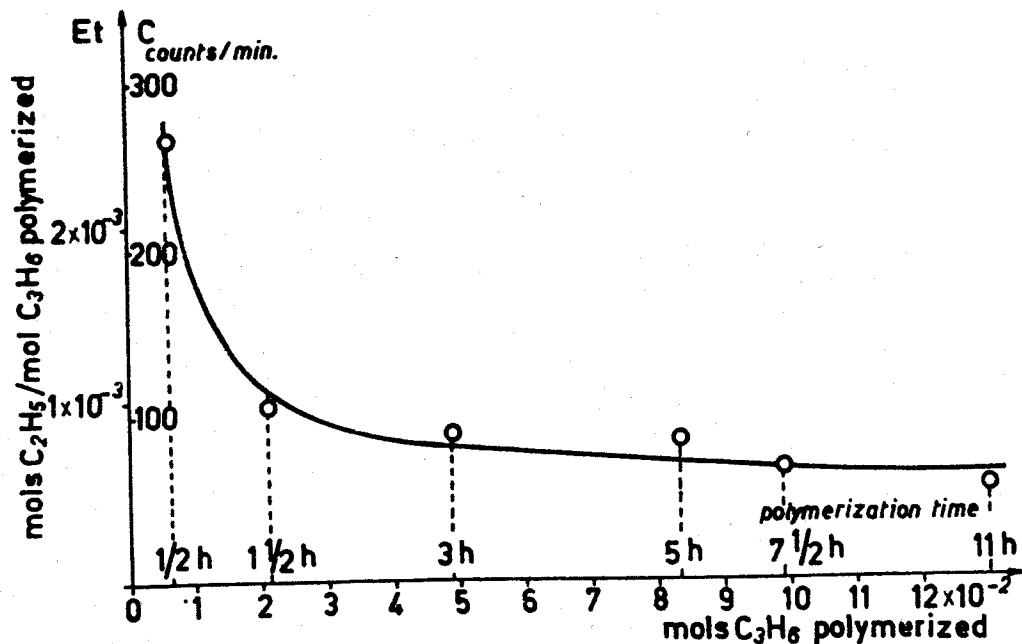


FIG. 34. Specific radioactivity of the polymer (and corresponding values of  $-\text{C}_2\text{H}_5$  mol. per mol. of polymerized  $\text{C}_3\text{H}_6$ ) plotted vs. the amount of polymer obtained at different polymerization times ( $t = 70^\circ$ ,  $p_{\text{C}_3\text{H}_6} = 450$  mm. Hg,  $^{14}\text{C}$ -labeled  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ :  $4.88 \times 10^{-2}$  mol./l., ground  $\alpha\text{-TiCl}_3$ : sample A:  $1.95 \times 10^{-2}$  mol./l.).

$E_{t_\infty} = 0.5 \times 10^{-3}$   $\text{C}_2\text{H}_5$  mol. per mol. of polymerized  $-\text{C}_2\text{H}_5$ , agrees with the values deduced from the experimental tests quite well (32).

Therefore, with the catalyst under consideration, ground  $\alpha$ -titanium trichloride- $\text{AlCl}(\text{C}_2\text{H}_5)_2$ , the totality of active centers is involved in the catalytic process, once the polymerization starts. We may deduce from the time constancy of the polymerization rate from the very beginning of the reaction that, in this case, the number of active centers is invariable and that the calculated value corresponds to the number of conventional active centers involved in the polymerization, in steady-state conditions.

### 3. Active Centers Generating Non-Atactic Polymers

The same methods employed with raw polymers were used for fractions of isotactic polypropylene (ether extraction residue), containing also some stereoblock polymers (32).

The results obtained are plotted in Fig. 35.

In this case, the value  $0.4 \times 10^{-2}$  mol. of  $\text{C}_2\text{H}_5$  mol. of  $\alpha$ -titanium trichloride was found for  $C^*$ . Such active centers, although they represent only  $\frac{2}{3}$  of the whole amount of centers present in the polymerization, generate nearly 93% of the whole amount of polymer. Such a result may be interpreted by the assumption that the growth rate of the amorphous polymeric chains (having a molecular weight which is lower than that of the isotactic chains) is about  $\frac{1}{6}$  of the growth rate of isotactic chains.

These data must be considered as being largely approximate.

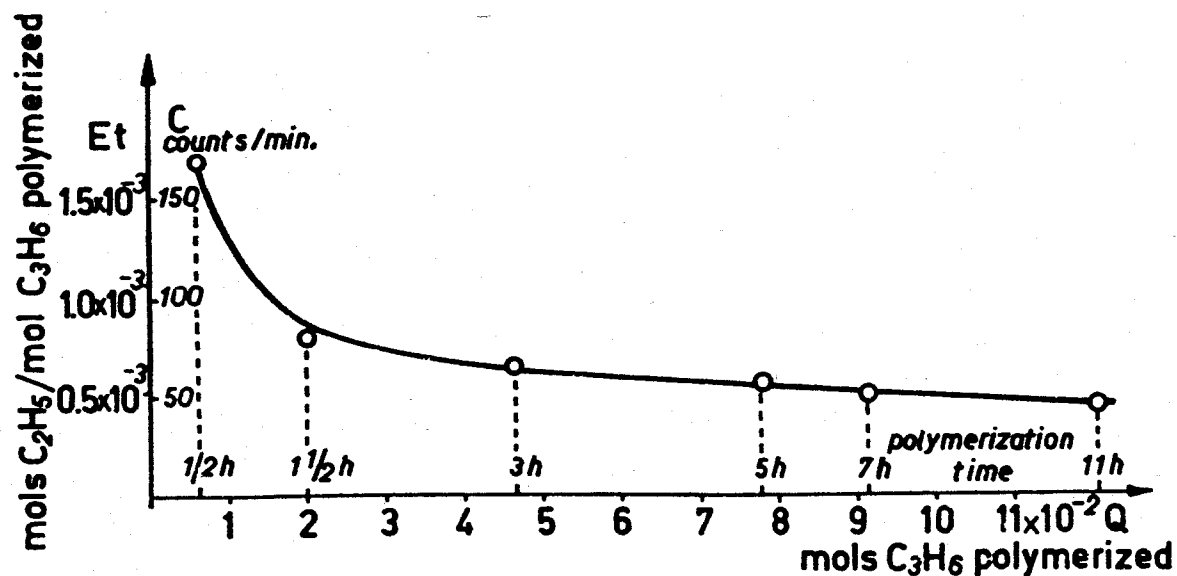


FIG. 35. Specific radioactivity of the non-atactic polymeric fraction (and corresponding values of  $-\text{C}_2\text{H}_5$  mol. per mol. of polymerized  $\text{C}_3\text{H}_6$ ) plotted vs. the amount of polymers obtained at different polymerization times. (Tests performed in the conditions reported in Fig. 34.)

#### 4. Discussion of the Results

By comparing the above reported data with the ones of Table X, it becomes evident that the amount of  $-\text{C}_2\text{H}_5$  groups corresponding to the active centers, which were determined by the kinetic method for the system  $\alpha$ -titanium trichloride-diethyl monochloride aluminum, are of the same order of magnitude as those determined by adsorption, although the former results are somewhat higher (0.6 instead of 0.3%  $\text{C}_2\text{H}_5$  mol./ $\text{TiCl}_3$  mol.).

Such a discrepancy of values may be ascribed to many reasons:

1. The data obtained through adsorption measurements may be defective because, by this method, only the ethyl groups, which are present on the surface of  $\alpha$ -titanium trichloride since the start of the polymerization, have been determined.

2. The reported data were corrected for radioactive contamination; such contamination was measured before polymerization, in conditions that could not be strictly related to the ones occurring during the polymerization.

## VI. Mean Lifetime of the Growing Polymeric Chains

### A. DETERMINATION OF THE MEAN LIFETIME FROM THE NUMBER OF ACTIVE CENTERS

The data summarized in the previous paragraphs (namely, over-all polymerization rate, average polymerization degree for isotactic polymer, and number of active centers) enabled us to evaluate the mean lifetime of the

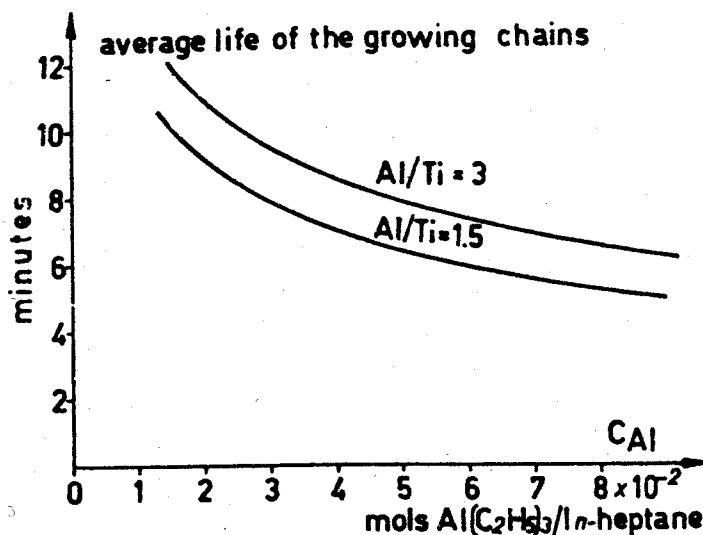


FIG. 36. Approximate values of the mean lifetime of the chains of polypropylene growing on the active centers of a catalytic system:  $\alpha$ -TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>-*n*-heptane at 70° and 950 mm. Hg  $p_{C_3H_6}$ . (The calculations were performed assuming the number of conventional active centers:  $C = 1$  mol. per 100 mol. of ground  $\alpha$ -TiCl<sub>3</sub>; sample A and  $x_n = 95[\eta]^{1.35}$ .)

growing macromolecules of polypropylene, in the  $\alpha$ -titanium trichloride-triethylaluminum catalytic system.

The assumption was made that the growth life is related to the time during which the polymeric chain remains bound to the active center.

The determination of the mean lifetime of the growing macromolecules was made under the following conditions:  $t = 70^\circ$ ,  $p_{C_3H_6} = 950$  mm. Hg. We have considered that polymeric fraction for which the relationship between intrinsic viscosity and average numerical polymerization degree is known (see Sec. III, I).

The number of isotactic chains growing at the same time, was assumed as being equal to the number of conventional active centers:  $1 \times 10^{-2}$  mol./mol. of  $\alpha$ -TiCl<sub>3</sub>. The results obtained are plotted in Fig. 36.

The value so calculated is approximate and conventional and could not be otherwise because of the data assumed for its determination. On the other hand, the life of a single macromolecule may differ remarkably from the average value, since the catalytic system under consideration gives rise to largely polydispersed polymers. Furthermore, the growth rate of a single macromolecule may be far away from the average value; actually, we believe that the more crystalline fractions which generally correspond to higher molecular weight, have a higher growth rate.

#### B. VARIATION OF THE MOLECULAR WEIGHT DURING THE POLYMERIZATION

In a polymerization process the number average degree of polymerization ( $x_n$ ) at a given instant, is given by the relationship

$$x_n = \frac{\text{monomer polymerized at time } t}{\text{macromolecules present in the system at time } t} \quad (38)$$

Hence,

$$x_n = \int_0^t r_p dt / \left( C_i^* + \int_0^t \Sigma r_t dt \right) \quad (39)$$

where  $r_p$  = polymerization rate

$\Sigma r_t$  = sum of the rates of chains transfer and termination processes

$C_i^*$  = number of growing chains at time  $t$

If  $r_p$ ,  $\Sigma r_t$ , and  $C_i^*$  are independent of the time,

$$1/x_n = C_i^*/r_p t + \Sigma r_t/r_p \quad (40)$$

By substituting the intrinsic viscosity and considering that  $[\eta] = Kx^\alpha$ ,

$$1/([\eta]/K)^{1/\alpha} = C_i^*/r_p t + \Sigma r_t/r_p \quad (41)$$

A variation of  $[\eta]$  against polymerization time is observed when the ratio  $C_i^*/\Sigma r_t$  is not too small. In Figs. 37 and 38 are plotted the values of the intrinsic viscosity and its reciprocal raised to 1.35 for the isotactic polymer fraction, obtained with two catalytic systems:  $\alpha$ -TiCl<sub>3</sub>/Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>.

These data enable us to determine the mean lifetime ( $L$ ) of the growing macromolecules (38), with the result that

$$L = C_i^* x_n / r_p \quad (42)$$

It follows from the relationship (41) assuming  $\beta = 1/\alpha$ ,

$$\frac{d(1/[\eta])^\beta}{d(1/t)} = \frac{C_i^*}{r_p K^\beta} \quad (43)$$

and consequently

$$L = \frac{d(1/[\eta])^\beta}{d(1/t)} [\eta]^\beta \quad (44)$$

From Figs. 37 or 38 we obtain for the asymptotic value of  $[\eta]$ , respectively,  $L_A = 16$  min. and  $L_D = 10$  min. for the two considered catalytic systems. We have assumed  $\beta = 1.35$ .

These values are smaller than the ones which may be found from the data tabulated in the above section, but as previously noticed, this discrepancy might be justified by the fact that the value assumed for the conventional active centers, which give rise to isotactic chains, is undoubtedly higher than the real ones. We have also observed that the polymerization rate obtained in the considered conditions is higher than the one calculated with the relationship (2). It really occurs at the beginning of the

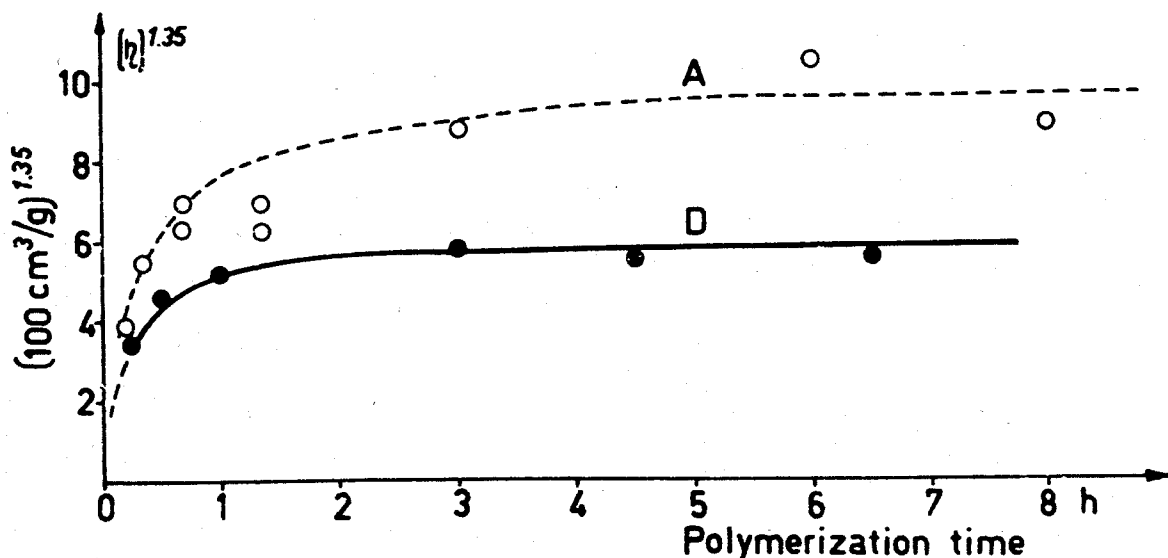


FIG. 37. Intrinsic viscosity raised to 1.35 (proportional to polymerization degree) of the non-atactic polypropylene fraction, plotted vs. the polymerization time. (The tests were performed with 4 g./l. of two samples (A and D) of ground  $\alpha$ -TiCl<sub>3</sub>,  $2.35 \times 10^{-2}$  mol. Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>/l.,  $t = 15^\circ$ ,  $p_{C_2H_6} = 200$  mm. Hg.)

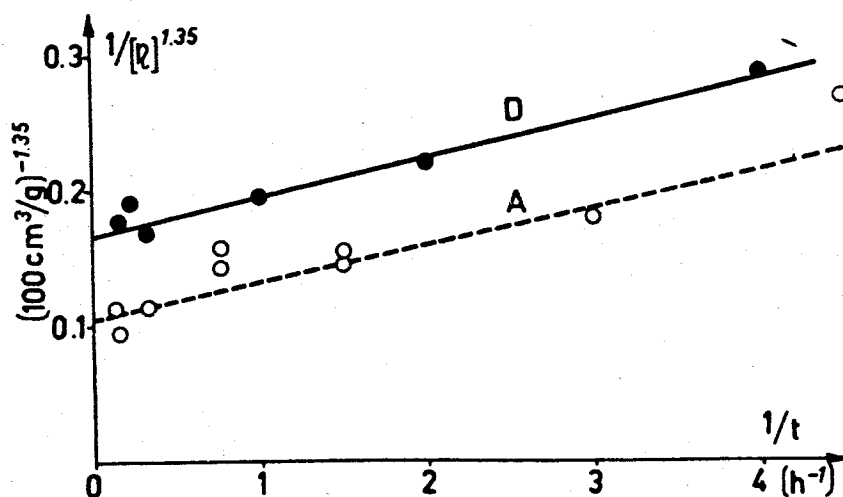


FIG. 38. Reciprocal of the intrinsic viscosity (raised to 1.35) plotted vs. the reciprocal of the polymerization time. (The experimental points are those reported in Fig. 37.)

polymerization process by employing ground  $\alpha$ -TiCl<sub>3</sub> (see, for instance, Fig. 11).

On the other hand, the slope of the lines plotted in Fig. 38, from the value of which the mean life of the chains is calculated, may be greatly effected even by small errors in the determination of the intrinsic viscosity of polymers obtained by shorter time tests. The resulting data are mostly concerned by eventual errors.

Finally, we believe that the growth rate of the longest and sterically purest polymeric chains is higher than that for the shortest chains.

### C. BLOCK COPOLYMERS (HETEROBLOCK POLYMERS)\*

From the data summarized in the above sections, it follows that

The mean lifetime of polypropylene chains growing on each active center can reach several minutes.

The catalytic complexes can "be alive" for a long time in the absence of monomer.

The active centers of the catalytic system  $\alpha\text{-TiCl}_3/\text{Al}(\text{C}_2\text{H}_5)_3$  may polymerize either propylene or ethylene.

Such findings allow us to foresee the possibility of synthesizing block copolymers formed alternately by sequences of monomeric units having different natures.

To attempt this polymerization, experiments have been performed by feeding a catalytic system, kept at  $15^\circ$ , alternately during a few minutes: with propylene at low pressure ( $<1$  atm.), with nitrogen in order to strip the propylene, with ethylene at low pressure ( $<1$  atm.), with nitrogen, and so on.

The presence of block copolymers has been established by submitting the polymer obtained to extractions with various solvents, by examination of each fraction by X-rays, by measurements of its melting point, and by resilience measurements (52, 10).

## VII. Conclusions

The data here related on the kinetics of the propylene polymerization and of the transfer processes and the studies of the catalysts carried out with  $^{14}\text{C}$ -labelled alkylaluminums, derive from a series of researches mostly carried out some time ago, when the knowledge of the mechanism of the considered catalytic processes was still rather limited. Nevertheless, it helped remarkably to know these new processes of anionic coordinated polymerization: their true catalytic nature (which regard to  $\alpha\text{-TiCl}_3$ ) differentiates them from the more usual polymerization processes (radicalic) which, actually, are not catalytic. They substantially contributed to demonstrate that the anionic coordinated polymerization is a step-wise addition process in which each monomeric unit inserts itself into a metal carbon bond of the catalytic complex.

We think that the reported studies, in spite of their preliminary character, can contribute not only to open new fields of investigation in the branch of macromolecular researches and to know the nature of a particular kind of catalytic complexes, but also to deepen the knowledges in the field of the heterogeneous catalysis.

We wish to thank Miss Mirella Bersani for translating this work.

\* The denomination "heteroblock polymers" was suggested in order to differentiate these polymers from the stereoblock ones which contain only one type of monomer (51).



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