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

G. NATTA AND I. PASQUON

*Istituto di Chimica Industriale del Politecnico, Milan, Italy*

# 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.

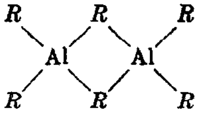
The stereospecific polymerization of $\alpha$-olefins takes place only in the presence of heterogeneous catalytic systems, including a crystalline substrate (formed by halides of transition metals, such as $TiCl_3$, $TiCl_2$, $VCl_3$, $CrCl_3$, $CoCl_2$, etc.) and a suitable metallorganic compound (*5*).

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.

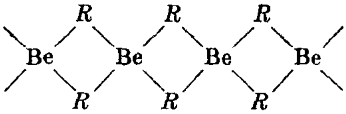
The above-mentioned metallorganic compounds must have the property of forming complexes with the halides of transitions metals. It is required, in order to get catalytic complexes, that the metal of metallorganic compounds be able to create a strong localized electric field; therefore, metals having a very small ionic diameter (below 1 A.) 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, $Al(C_2H_5)_3$, $AlCl(C_2H_5)_2$, $Al(iC_4H_9)_3$, $Be(C_2H_5)_2$]. 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



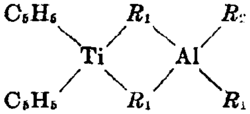
I



II

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:



III

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 α-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 α-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:* $\alpha$-$TiCl_3$-$M(C_2H_5)_n$
$t = 75°$, $p_{C_3H_6} = 2.4$ atm.)

| Metal of the metal alkyl compound | Ionic radii of the metal, A. | Polypropylene not extractable in boiling *n*-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, $CoCl_2$) 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 nonstereospecific 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).

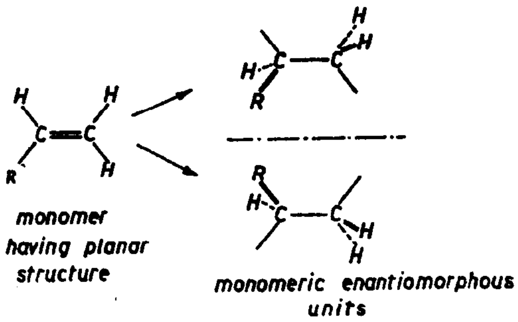


FIG. 1.

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 α-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 $(\mathrm{CH}R{=}\mathrm{CH}_2)_n$ 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,

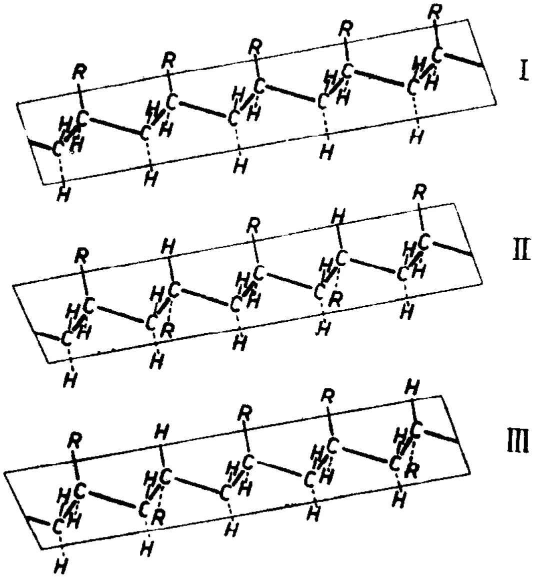


FIG. 2. Chains of stereoisomeric poly-$\alpha$-olefins supposing the main chain stretched on a plane. I. Isotactic. II. Syndiotactic. III. Atactic.

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.

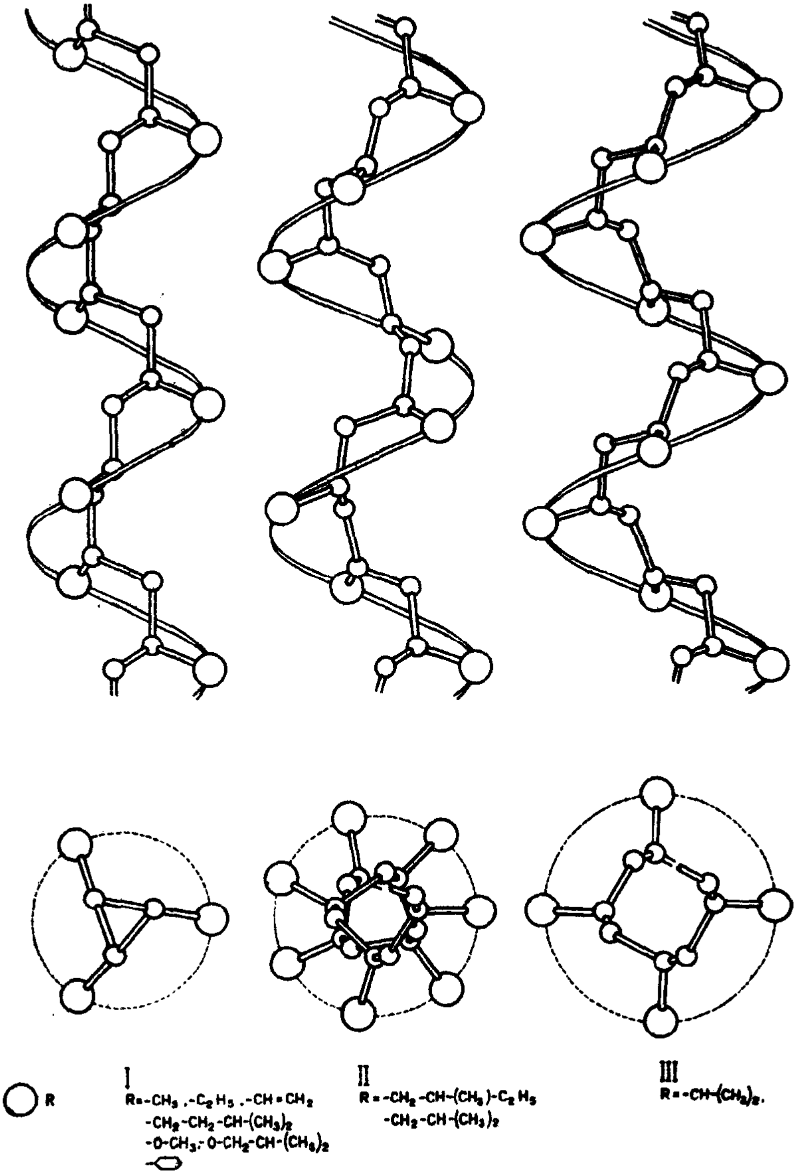
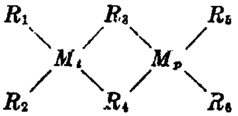


Fig. 3. Chains of isotactic polymers.

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.

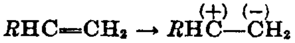
The catalytic complexes may possess a type of structure as follows:



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 α-olefins.

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



$$RHC{=}CH_2 \rightarrow RH\overset{(+)}{C}{-}\overset{(-)}{C}H_2$$

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

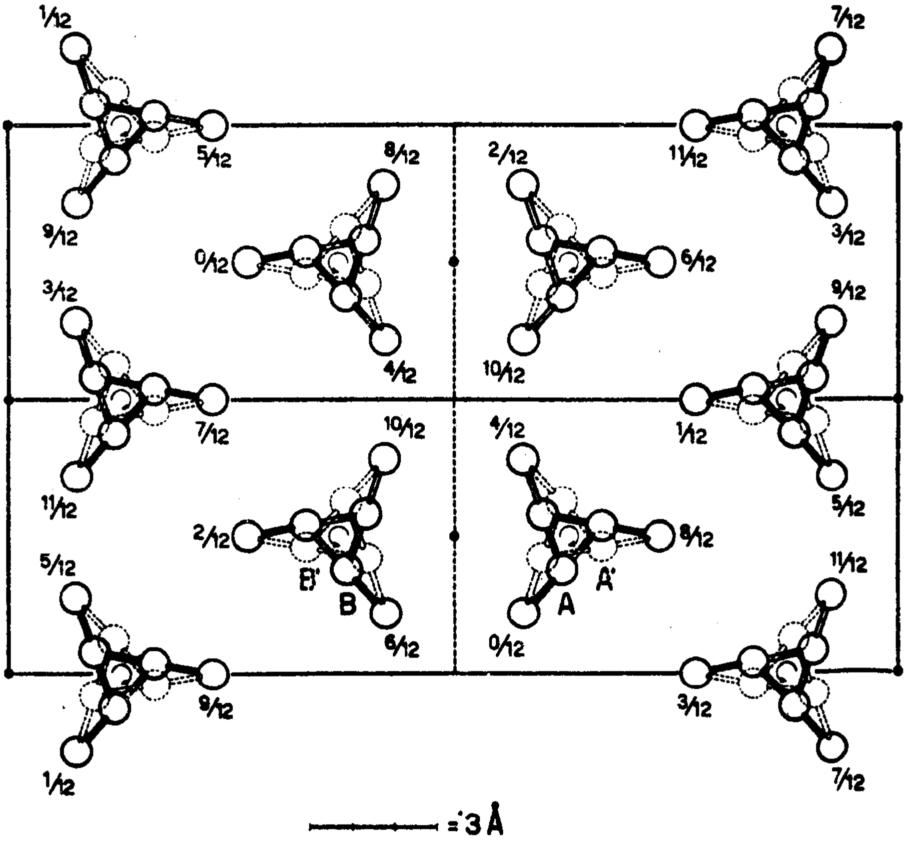


FIG. 4. Projection of the crystalline polypropylene lattice, on a plane perpendicular to the axis of the polymeric chains.

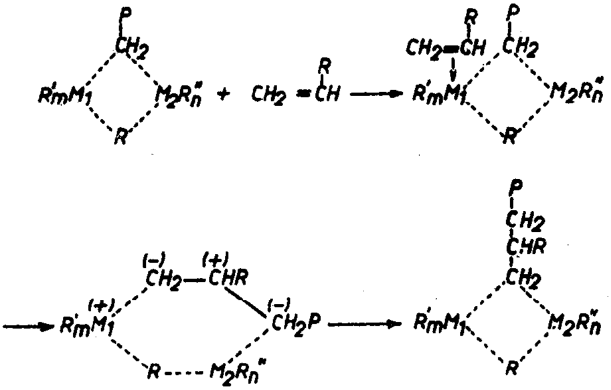


FIG. 5. Hypothesis of addition of a monomer molecule on the bond between the catalytic complex and the growing chain, in the anionic coordinated polymerization.

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:

$$[\overset{(+)}{\mathrm{Cat}}]\text{—}\overset{(-)}{\mathrm{C}}\mathrm{H_2}P + \mathrm{CH_2{=}CH}R \rightarrow [\overset{(+)}{\mathrm{Cat}}]\text{—}\overset{(-)}{\mathrm{C}}\mathrm{H_2CH}R\mathrm{CH_2}P$$

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

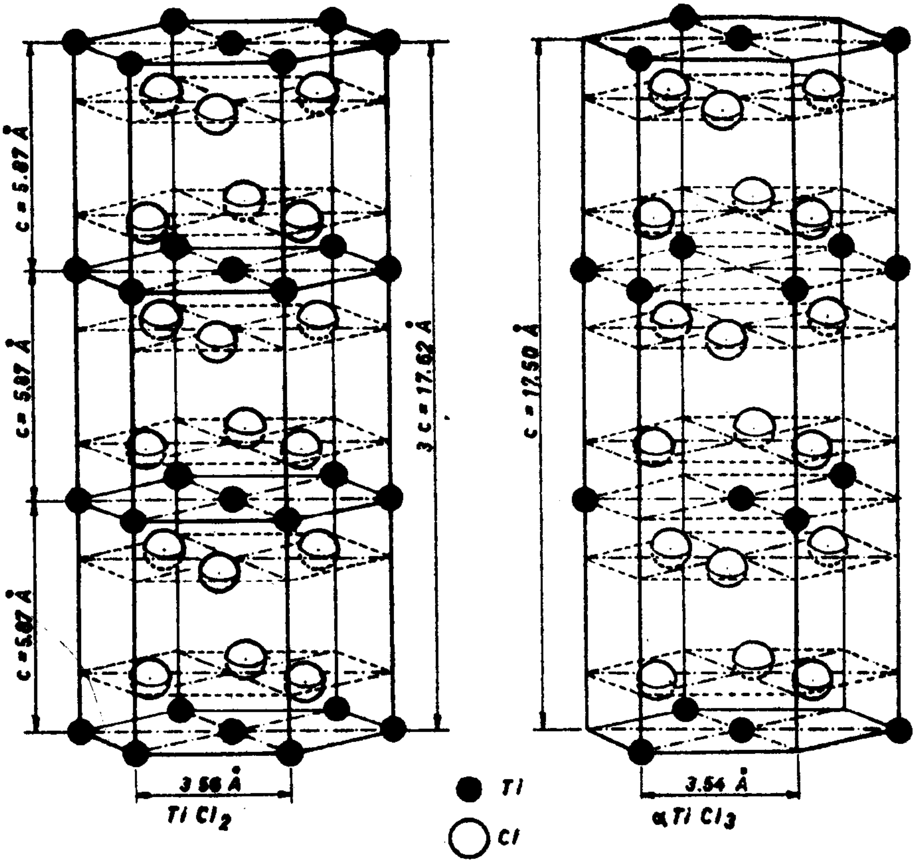


FIG. 6. α-$TiCl_3$ and $TiCl_2$ crystalline lattices.

lattice (α-$TiCl_3$, $TiCl_2$, $VCl_3$, etc.) (Fig. 6) (*23, 24*) are all suitable for the preparation of stereospecific catalysts (*9, 5, 25, 26*).

In the case of $TiCl_3$ the less crystalline forms obtained at low temperature by precipitation from solution of $TiCl_4$ and alkylaluminum are less stereospecific than the well-crystallized forms obtained at high temperature (*5*). $TiCl_3$ crystallizes in three forms at least (*27*), and the greatest stereospecificity is given by the α-form.

For this reason the catalytic systems, which we have mostly employed for studies of stereospecific polymerization of α-olefins, are those made using α-$TiCl_3$.

## 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 α-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 α-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., $\alpha$-$TiCl_3$, $\beta$-$TiCl_3$), 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:

$Al(C_2H_5)_3$-$\alpha$-$TiCl_3$-$n$-heptane or $Al(C_2H_5)_2Cl$-$\alpha$-$TiCl_3$-$n$-heptane.

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 α-TiCl₃ CRYSTALS ON THE POLYMERIZATION RATE. ADJUSTMENT PERIOD

The $\alpha$-$TiCl_3$ (violet modification), prepared by reduction of $TiCl_4$ 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 μ to several hundred microns (see for instance the sample of Fig. 7). Sometimes the $\alpha$-$TiCl_3$ lamellae do not show any defined geometric shape, and their dimensions may reach a millimeter (see for instance the sample of Fig. 8).

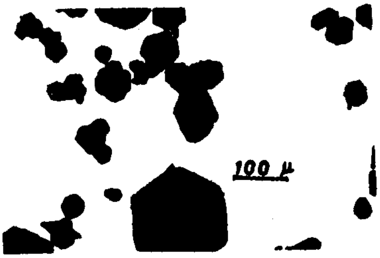


FIG. 7. Photomicrograph of α-$TiCl_3$ (sample *B*).

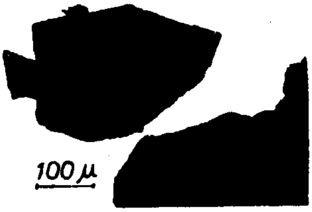


FIG. 8. Photomicrograph of α-$TiCl_3$ (sample *C*).

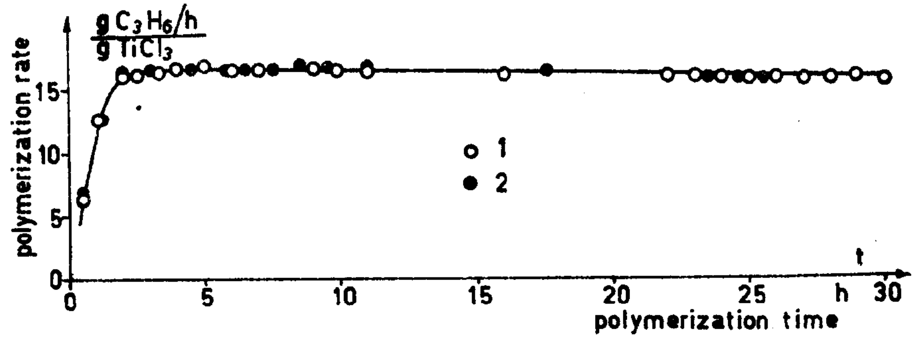


FIG. 9. Propylene polymerization rate at constant pressure and temperature as function of polymerization time ($p_{C_3H_6}$ = 1,450 mm. Hg, $t$ = 70°).

| | 1 | 2 |
|---|---|---|
| α-$TiCl_3$ (sample *A*),g./l. | 0.80 | 1.00 |
| $[Al(C_2H_5)_3]$mol./l. | $4.45 \times 10^{-3}$ | $2.94 \times 10^{-3}$ |

In Fig. 9 the characteristic behavior of propylene polymerization rate is plotted *vs.* polymerization time. The data were obtained by operating at constant pressure with a catalytic system containing α-$TiCl_3$ crystals having initial sizes between 1 and 10 μ (α-$TiCl_3$ sample A).

It may be noticed that during the initial polymerization period (adjust-

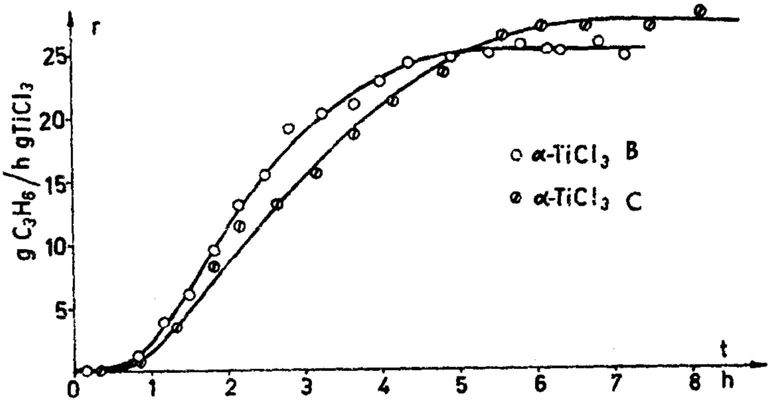


FIG. 10. Propylene polymerization rate at constant pressure and temperature ($p_{C_3H_6}$ = 1,450 mm. Hg, $t$ = 70°C) obtained with two samples of unground $\alpha$-$TiCl_3$ whose crystals have different sizes (see Figs. 7 and 8). ($\alpha$-$TiCl_3$ : 1.64 g./l., $[Al(C_2H_5)_3]$: $2.94 \times 10^{-3}$ 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 $\alpha$-$TiCl_3$ 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 $\alpha$-$TiCl_3$ crystals (Fig. 10).
2. By operating with ground $\alpha$-$TiCl_3$ (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°) 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 $\alpha$-$TiCl_3$ 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 $\alpha$-$TiCl_3$ particles reaches approximately the same limiting value. On the other hand, it is most likely that the exceptionally small and active $\alpha$-$TiCl_3$ particles, obtained during the grinding, are unstable and lose their activity on ageing. In fact, at the beginning of the reaction, when using ground $\alpha$-$TiCl_3$, the

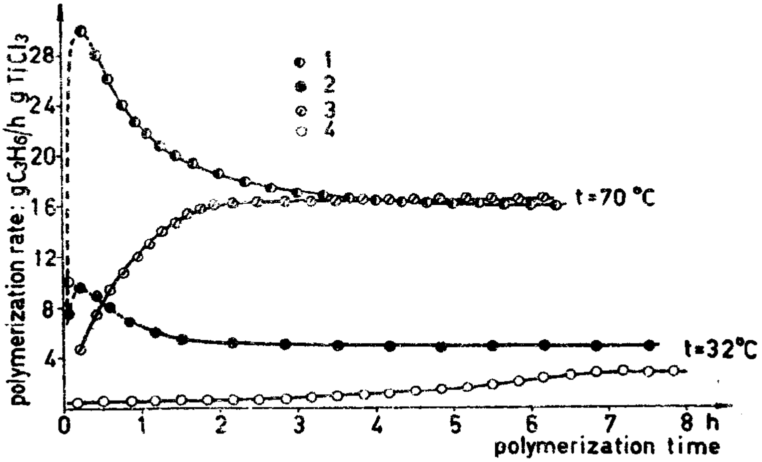


FIG. 11. Effect of previous physical treatments on a sample of α-$TiCl_3$ on the propylene polymerization rate, at constant pressure and temperature ($t$ = 70° $p_{C_3H_6}$ = 1,450 mm. Hg). 1 and 2: ground α$TiCl_3$ (sample $A$) (sizes ≤2 μ). 3 and 4: unground α$TiCl_3$ (sample A) (sizes within 1 to 10 μ).

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 α-$TiCl_3$ particles which lose their activity during the polymerization, either by recrystallization, by reaction with $Al(C_2H_5)_3$, or by occlusion in the solid polymeric product. In particular, it may be observed that the maximum disappears when operating with $Al(C_2H_5)_2Cl$ instead of $Al(C_2H_5)_3$ (*32*).

4. By operating with unground α-$TiCl_3$ the time ($t_{3/4}$) which is necessary to reach the ¾ 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 α-$TiCl_3$, 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 α-$TiCl_3$ that had been previously maintained, for many hours, in the presence of solutions of $Al(C_2H_5)_3$ 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 α-$TiCl_3$ lamellae are very thin and brittle.

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

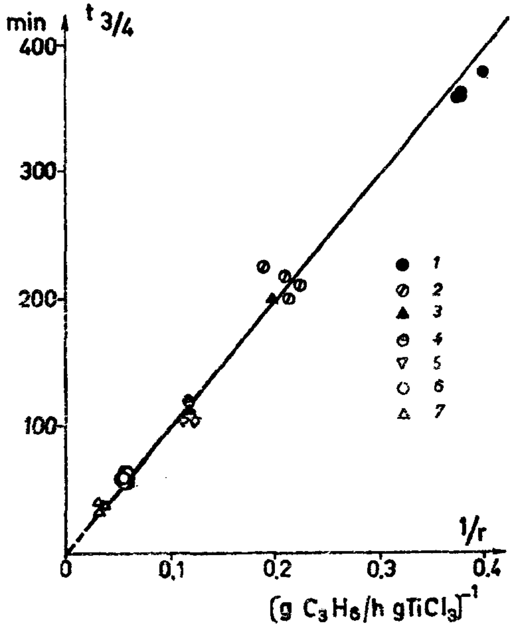


FIG. 12. Dependency of the $t_{3/4}$ index of the adjustment period, on the reciprocal of the propylene polymerization rate in steady state conditions. Tests performed with unground α-$TiCl_3$ (sample *A*).

| | 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 | 2,680 | 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 prevailingly isotactic. This means that, from the start of the reaction, there exist a certain number of active centers on the solid α-$TiCl_3$ 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 α-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