CONSIGLIO NAZIONALE DELLE RICERCHE
COMITATO NAZIONALE PER LA CHIMICA

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Stereospecific polymerizations by means of coordinated anionic catalysis

Introductory Lecture

ESTRATTO DA:
« *Convegno internazionale sulla chimica dei composti di coordinazione* »
« *International Symposium on the chemistry of the coordination compounds* »
SUPPLEMENTO A « LA RICERCA SCIENTIFICA » - ANNO 28° - 1958
ROMA

Summary: The phenomena stereoisomerism in the linear polymers of olefines and diolefines and the nature of the stereospecific polymerization processes are shortly discussed. They allowed the first synthesis of isotactic and syndiotactic polymers and of the four pure stereoisomers of polybutadiene, that is: the polymers having 1,2-isotactic, 1,2-syndiotactic, 1,4-cis, and 1,4-trans enchainments.

The structure of catalytic complexes, that promove the stereospecific polymerization in the ionic coordinated catalysis, is pointed out. They are electron deficient complexes containing bridge-bonds between very electropositive transition metals, with valence less than the maximum, and very electropositive metals with very small ion diameter, to which electronegative carbon atoms are coordinated.

Some soluble complexes, based on Titanium and Aluminum, are described, that act as catalysts in homogeneous solution.

The best stereospecific catalysts for the synthesis of isotactic polymers are heterogeneous ones and their stereospecificity is connected with the presence of a crystalline substrate, formed by a layer lattice on which the active centers contain chemisorbed or epitattely bound metallorganic complexes (that may exist in enantiomorphous forms).

INTRODUCTION.

I accepted the invitation of my friend Prof. Caglioti to talk on complexes as catalysts because it is my opinion that chemists who work on complexes might be interested to know how a new field, fertile of important applications, has recently been opened up both to catalysis and to chemistry of coordination compounds.

It is not my intention to speak here in general about the use of complexes as catalysts: this is a very wide subject matter, with a large number of examples, many of which have been known for a very long time. It will be sufficient to mention the wide field of Friedel-Crafts catalysts, most of which in fact are formed by complexes. They have had various important practical applications also in the industrial field, for inst. in alkylation processes, in the polymerization of olefins to low polymers and in cationic type, not stereospecific processes, whereby unsaturated ethylenic monomers containing electron releasing substituents (such as e. g. isobutene and isobutyl vinyl ether) are polymerized to high molecular weight polymers.

I am going to deal here only with a new field, that of coordinated anionic catalysis, which has been introduced to practice only recently and which has led to the discovery of truly stereospecific polymerization processes yielding polymers of olefins and diolefins having a sterically regular structure.

The synthesis of these new polymers not only is of scientific interest, but also of the greatest practical interest because of their applications in the production of new plastics, new textile fibers, and new rubbers. [1].

Stereoisomerism in the linear polymers of olefins and diolefins.

I will consider briefly stereoisomeric phenomena in high, linear polymers because they are related with the nature of the catalytic complexes which generate them.

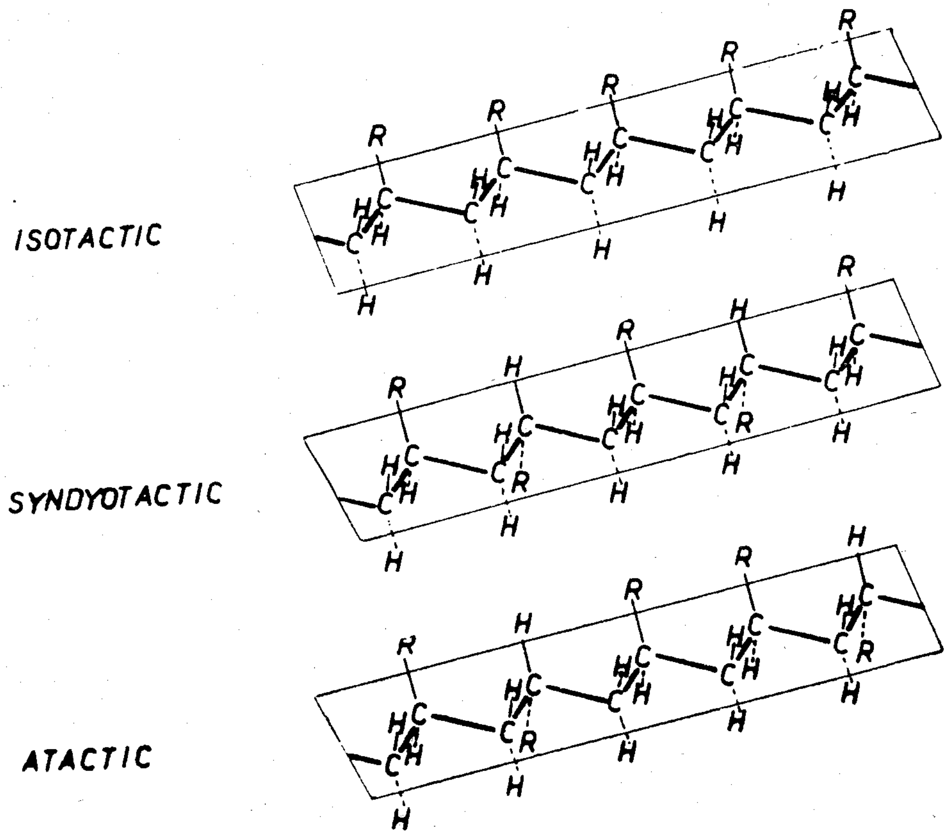


Fig. 1. – Chains of different stereoisomers of vinyl polymers supposed lying in a plane.

The stereospecific catalysts have made it possible to obtain, by polyaddition of vinyl monomers, long linear head-to-tail chains consisting of sequences of monomeric units having the same steric structure. These polymers, which we called « isotactic » polymers, [2] are able to crystallize, while those in which the monomeric units of different steric structure are arranged at random, (« atactic » polymers) generally cannot crystallize.

With certain monomers and special stereospecific catalysts we obtained also another type of crystalline polymers containing long regular head-to-tail sequences of monomeric units with alternatively opposite steric configuration, which we called « syndiotactic » polymers. The chains of these types of stereoisomeric vinyl polymers, supposed stretched in a plane, are represented in figure 1.

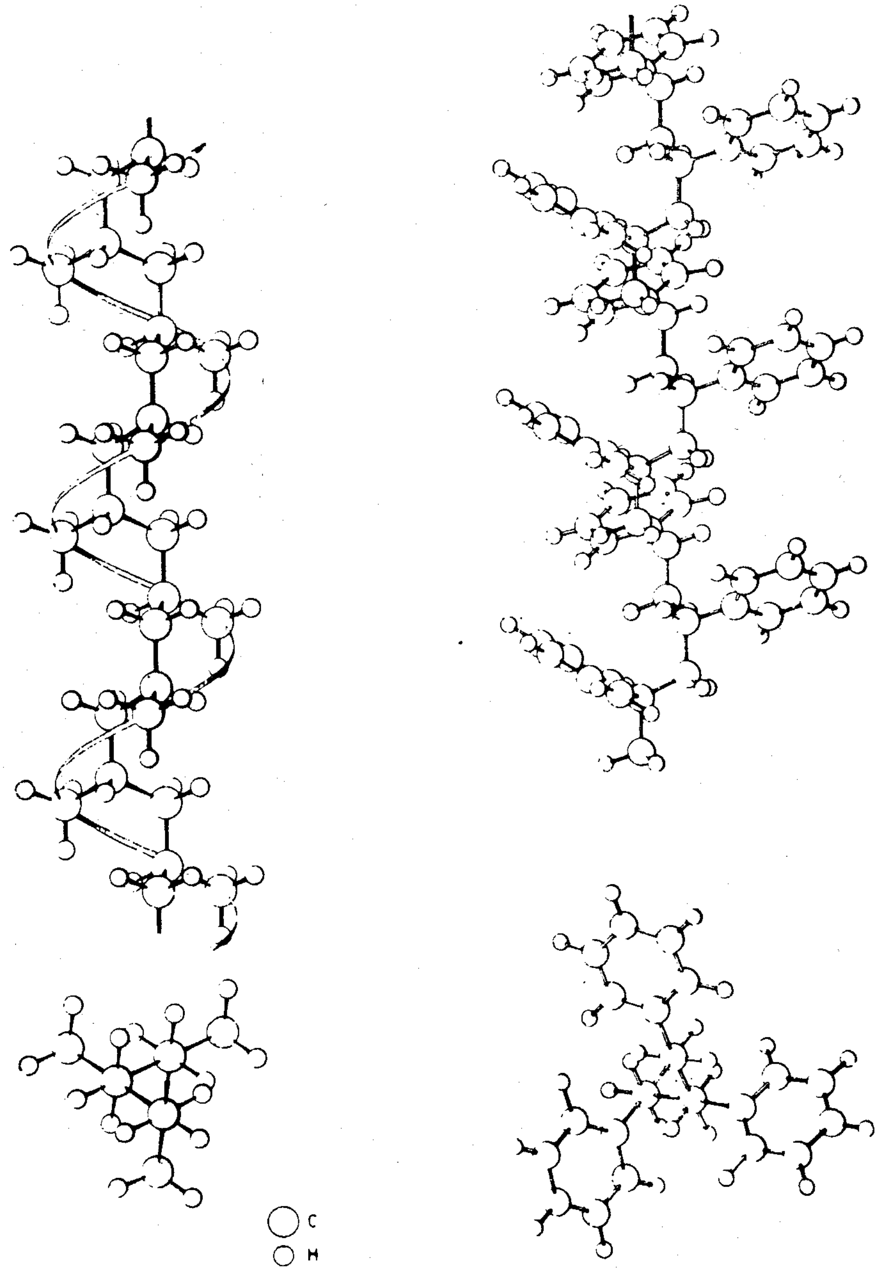


Fig. 2. – Chain structure in isotactic polypropylene and polystyrene as determined by X-Rays.

In figure 2 the forms which the chains of isotactic polypropylene and polystyrene assume in crystals are shown [3].

In the case of diolefins the new stereospecific polymerization processes have made it possible to obtain not only crystalline polymers cor-

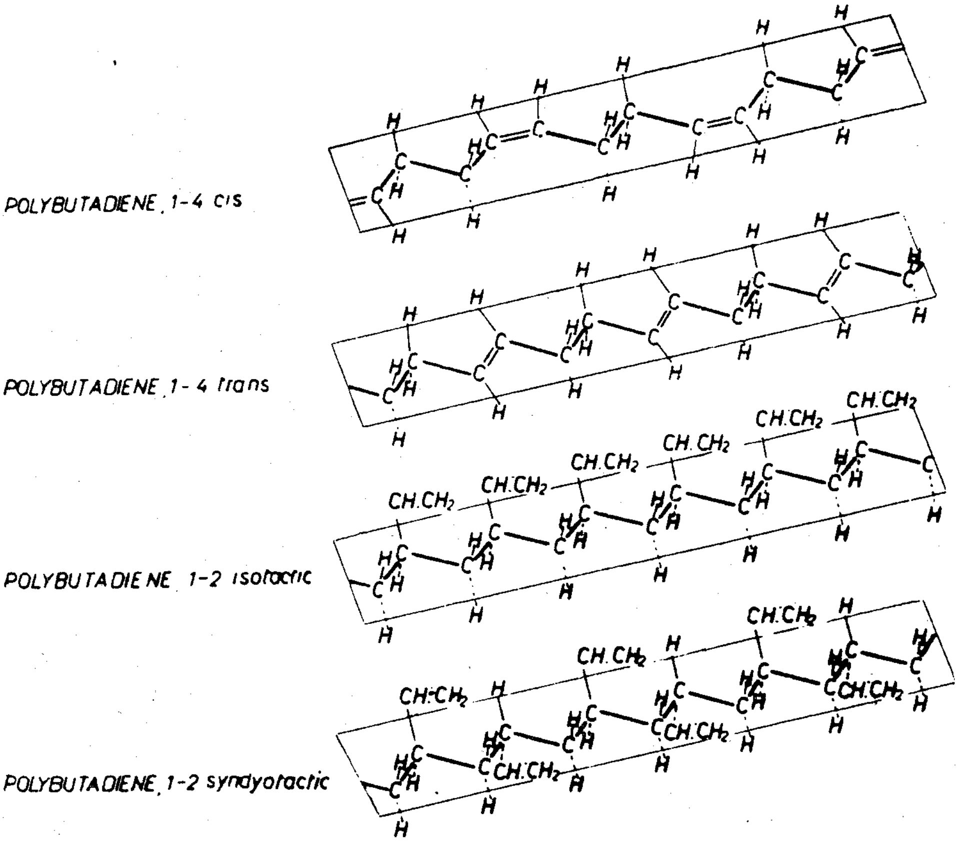


FIG. 3. – Chains of different pure stereoisomers of polybutadiene supposed lying in a plane.

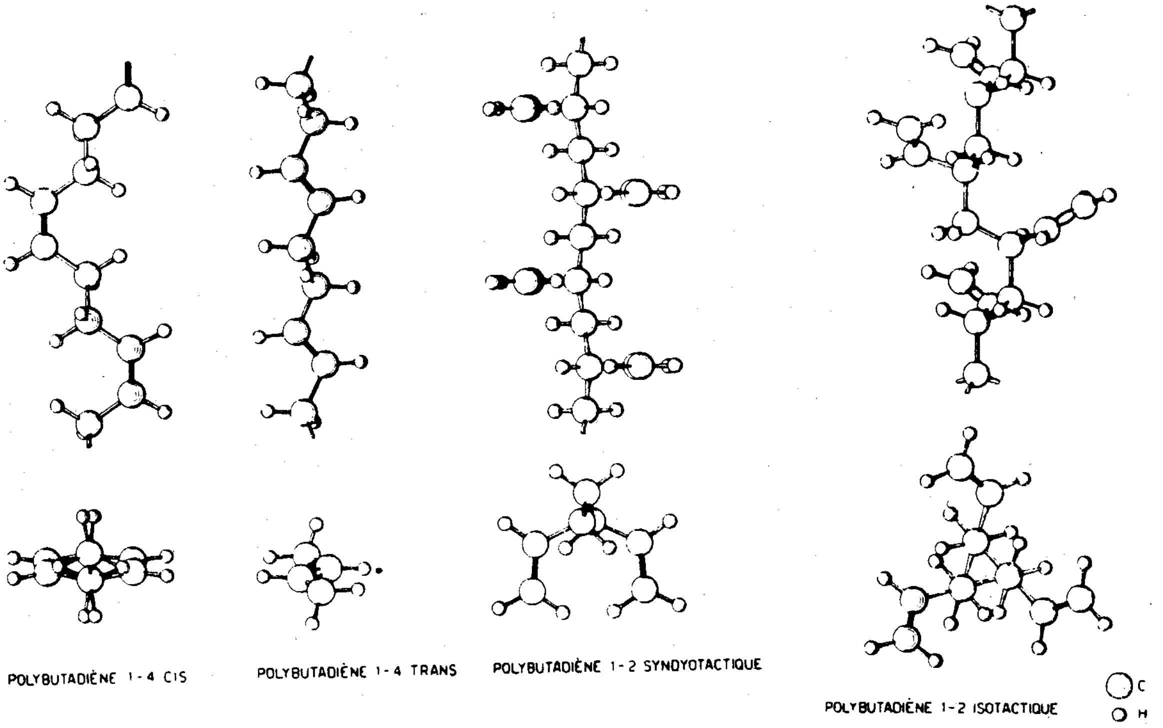


FIG. 4. – Chain structure of the polybutadiene chains determined by Natta-Corradini by X-Ray for the four crystalline stereoisomers.

responding respectively to the two types of geometrical stereoisomery [4] which are present in nature in hevea-rubber and in guttapercha, but also other stereoisomers which do not exist in nature, such as the isotactic and syndiotactic polymers, obtained by 1-2 or 3-4 enchainment of monomeric units deriving from conjugated diolefins [5].

In fig. 3 the structures of the stereoisomeric polymers which we prepared from butadiene are shown, while in fig. 4 we represent the conformation which the same chains assume in crystals, whose structures were determined by us. [6].

Catalytic complexes in coordinated anionic catalysis.

In some of my previous papers I have discussed the kinetics of the polymerization and indicated the composition of some catalysts which promote the stereospecific polymerization of alpha-olefins.

Those papers show that most of these catalysts have one charactestic in common, i. e. that of being formed by metallorganic complexes of strongly electropositive metals of small ionic diameter, in which carbon atoms, deriving from an anionic form, are coordinated. (table I) [7].

TABLE I.

Metal	Electronegativity (1)	Atom Radius *A*°	Ion Radius *A*° (2)
Li	*1,0*	*1,33*	*0,68*
Na	0,9	1,57	0,97
K	0,8	2,03	1,33
Rb	0,8	2,16	1,47
Cs	0,7	2,35	1,67
Be	*1,5*	*0,90*	*0,35*
Mg	*1,2*	*1,36*	*0,66*
Zn	*1,5*	*1,31*	*0,74*
Ca	1,0	1,74	0,99
Ba	0.9	1,98	1,34
B	2	0,88	0,23
Al	*1,5*	*1,26*	*0,51*
Si	1,8	1,17	0,42

(1) Electronegativity, according to L. Pauling.

(2) L. H. Ahrens: Ceohim. et Cosmochim. Act. 2, 155-169 (1952).

The underlined metals, that are highly electropositive and have small ion radius, give the more interesting metal alkyls for coordinated anionic catalysis.

While the practical applications of coordinated anionic catalysis have already reached a remarkable development, the study of the true nature of the catalysts is just at its very beginning and might represent a fascinating research in the field of the chemistry and structure of metallorganic complexes. It present, however, difficulties and complications, because the composition of the best heterogeneous catalysts now in use is mostly not well defined.

It frequently occurs in heterogeneous catalysis that the catalytic activity is connected with the existence of surface irregularities, of reticular gaps or of solid phases whose composition is not well definied. No wonder, therefore, if the same thing happens also in the case of heterogeneous anionic catalysis, in which the catalytic action is related to the existence of active centers on the surface of the catalyst and of chemisorption compounds, whose composition differs from the overall composition of the catalyst itself.

It cannot any longer be doubted, however, that the activity of the best stereospecific catalysts in the alpha-olefin polymerization is connected with a coordinating action of strongly electropositive transition metal atoms, situated on the surface of a solid, microcrystalline phase (for inst. of low-valence halides) which promotes the chemisorption of metallorganic compounds.

It is of significance to recall here that many halides of polyvalent metals (some of which corresponding to the highest valence of the same transition metals which in their lower valence state are employed now in anionic catalysis) may act as Friedel-Crafts catalysts, that is as catalysts of cationic type.

The electropositivity of a transition metal atom increases as its valence decreases. Only low valence compounds of transition metals can operate in a coordinated catalysis of the anionic type, but not those of poorly electropositive metals (e. g. platinum, palladium etc.) which are inactive, even if in a low valence state. The compounds formed by Platinum (II) or Palladium (II) halides with olefins, which were in the past the best known, stable compounds of well defined composition of metal halides with olefins, do not act as catalysts. This is due to the fact that in the olefin molecule bound in these complexes there is no considerable change in the nature of the olefinic double bond, while catalysis either cationic or anionic requires the presence of bonds of the ionic type, in which carbon ions take part.

Crystallizable complexes of transition metals, having a definite composition and having by themselves catalytic action in anionic polymerization of ethylene even in homogeneous phase, such as $(C_5H_5)_2\,TiCl_2\,Al(C_2H_5)_2$ have been obtained by us only in a few particular cases, but their catalytic action is always rather poor. Their X-ray examination in our laboratory demonstrates the existence of Al-Cl-Ti bridges, with a

Ti-Cl distance of about, 2,5 A^{o} and a *Ti-Cl-A l* angle of about 90°. These compounds although they do polymerize ethylene [8], do not polymerize alpha-olefins at all, and therefore no stereospecific action can be ascribed to them.

The most interesting catalysts, the ones which are stereospecific in the polymerization of alpha-olefins, act only in an heterogeneous phase [9].

In spite of the difficulties encountered in establishing the true chemical nature of the active centers which catalyze the stereospecific polymerization of alpha-olefins, a great number of experimental data are now available, which allow to establish that such a catalytic action is always connected with the existence of metallorganic complexes, mostly electron deficient molecules, in which the carbon atom, in order to be coordinated with the central strongly electropositive metals, must be rich in electrons and therefore must derive from an anionic form, which may be originated by the polarization of the olefinic double bond.

Homogeneous catalysts for the polymerization of ethylene and diolefins.

Some simple metallorganic compounds act even in homogeneous phase in the anionic polymerization of ethylene. However, not all the metallorganic compounds containing a carbon-to-metal bond and having a certain percentage of ionic nature show a catalytic action in ethylene polymerization.

The simple, most typically ionic metal alkyls, such as the alkyls of the metals from sodium to caesium, for which the ionic character of the carbon-to-metal bond has been evaluated as comprised between (47 % (*Na*) and 57 % (*Cs*) [10] are not, by themselves, catalysts in the polymerization of alpha-olefins and polymerize only diolefins, however, in a non stereospecific way.

Even the metallorganic compounds of the alkaline-earth metals, from calcium to barium, do not polymerize ethylene. These metals, in fact, have no tendency to form stable complexes and form labile complexes only in particular cases, in which they make use of the outer *d* orbitals. This type of coordination is stabilized by the presence of several complexable groups belonging to the same molecule (polydentate complexes). The coordination of water in the hydrates of the ions of these metals is not an exception to these rules because it may be explained by the fact that water is associated in polymeric molecules, so that these hydrates present an analogy with the polydentate complexes.

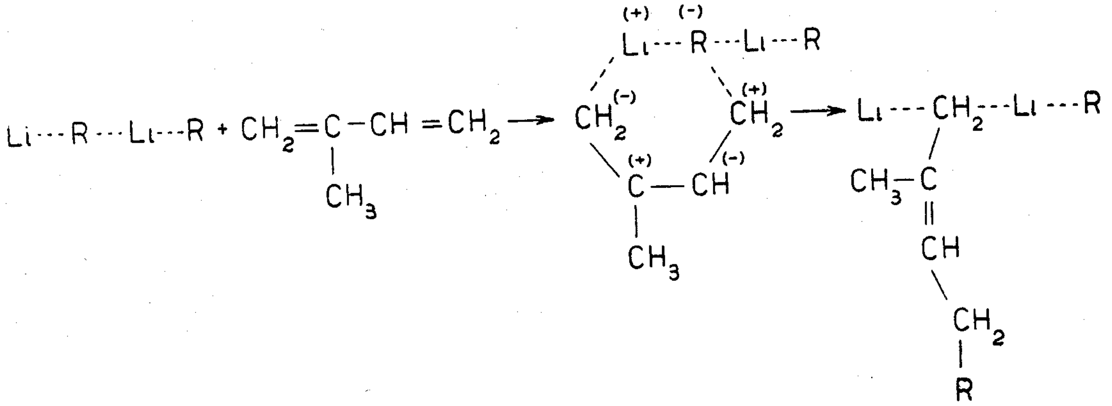
Aluminum-alkyls (ionic character of the bond = 22 %) and lithium-alkyls (43 %) polymerize ethylene to low polymers while with alpha-olefins they only yield dimers [11].

Already from a comparison of the behaviour of several simple metal-alkyls, one can observe that in ethylene polymerization the strongest catalytic action is shown by the alkyls of metals having the smallest ionic diameters (*Be*, *Al*). These metals are, as it is known from mineral chemistry, the ones among the metals of the first subgroup of the first three groups in the periodic table, which most easily originate complexes.

Boron, which also has a very small ionic diameter, and of which a large series of metallorganic compounds is known, gives by itself only metallorganic compounds which do not show any marked catalytic action in the polymerization of alpha-olefins and this is due to the low electropositivity of the metal. (2,0 in the Paulings electronegativity scale).

In the case of lithium, it is known that its alkyls are mostly associated in a dimeric form Li_2R_2 [12]. Its catalytic action may be connected with the resonance between the two forms: $Li^+(R_2Li)^- \leftrightarrow (LiR_2)^- Li^+$ related to the ionic nature of the $Li - C$ bond.

A lithium alkyl in an hydrocarbon solvent is a stereospecific catalyst for the polymerization of isoprene [13], with formation of the polymer having a 1-4 cis enchainment, while in ether solution it loses its stereospecificity, yielding a polymer containing atactic monomeric unit with 1-2 enchainment. The small Li^+ $(CH_2)^-$ distance and the ability of lithium to give complexes is most probably the reason of the stereospecific 1-4 cis polymerization.



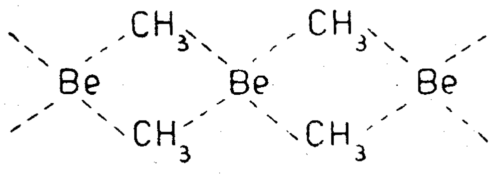
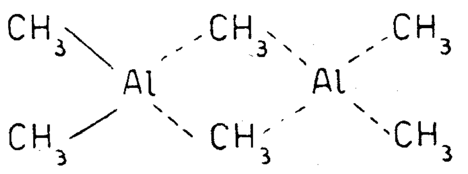
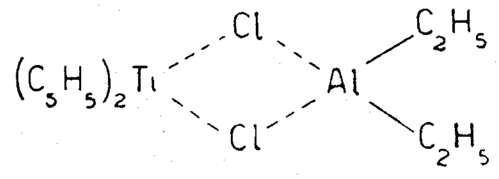
The sodium alkyls, like the alkyls of other strongly electropositive metals having a greater diameter and a smaller tendency to give complexes, do not polymerize ethylene and are not stereospecific catalysts in the polymerization of diolefins.

Metallorganic complexes containing transition metals in a low valence state, for inst. the complexes obtained by reaction between transition metal compounds and metal alkyl compounds of metals (like aluminum, lithium, etc.) having small ionic radius may, according to the type and composition of the complex itself, respectively yield prevailingly stereounitary polymers of 1-4, trans, 1-4 cis, 1-2 isotactic or 1-2 syndiotactic enchainment or polymers with random distribution of the different isomeric units (4) (5).

I will mention, as an example, certain complexes obtained by reaction between aluminum alkyls and chromium acetyl-acetonate. By low ratios (lower than 6) between AlR_3 and *Cr* acetyl-acetonate used in the preparation of the catalyst, in the polymerization of butadiene a polymer with 1-2 syndiotactic enchainment is obtained. By higher ratios a polymer with the same enchainment, but having an isotactic structure is obatined.

A similar behaviour is shown by other complexes containing oxygen or nitrogen, as for inst. those obtained from alcoholates, carbonyls, carbylamines of transition metals by the action of aluminum alkyls. Their stereospecificity and their activities depend from the ratios between the reactants. These complexes do not act as catalysts in the polymerization of alpha-olefins, but some of them polymerize ethylene. In this last case, where there is no possibility of stereoisomerism in the polymerization products, the ratio between the titanium compounds (for inst. *Ti* alcoholates) and aluminium alkyls influence only the activity of the catalysts and the molecular weight of the polymers. By low ratios, ethylene dimerization to 1-butene occurs [14], while by higher ratios a polymerization to not branched high polymers takes place [15].

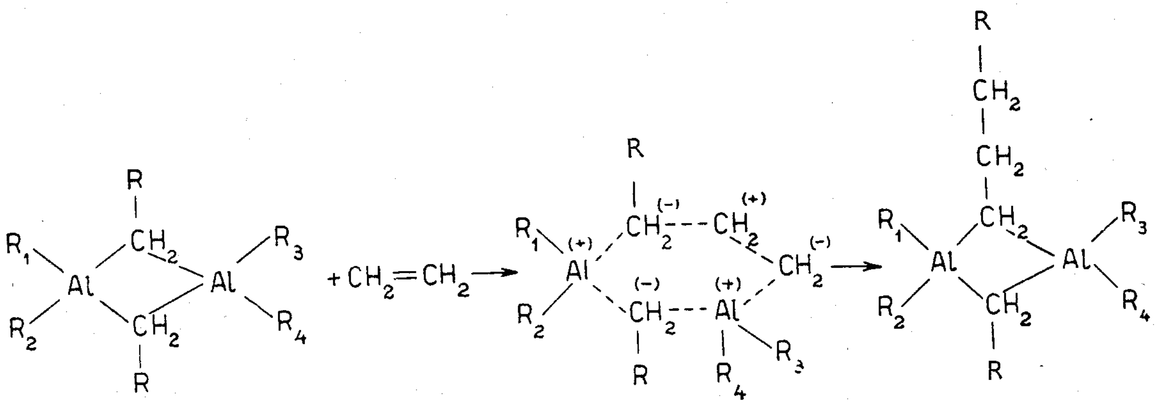
TABLE II.

	Angle	Distance *C-M* Å	
	Me-C-Me	bridge	terminal
	66°	1.93	—
	70°	2.24	1.99
	90°	~ 2.5 (*Ti* — *Cl*)	—

Aluminum or berillium alkyls have a tendency to form complexes and this is demonstrated by the fact that some of them are usually in an associated form (dimers). The X-rays and electron-rays analysis of the aluminum-trimethyl dimer has made it possible to calculate the distance *C-Al* for the two carbon atoms forming a bridge between the two *Al* atoms. This distance is 2,24 A^{o} and, being much greater than the distance existing in the four terminal *C-Al* bonds (1,99 A^{o}), is the cause for the easier dissociability of that bond.

The *Al-C-Al* angle of the bridge is very small (70°) because of the particular type of bond in the bridge between the two metallic atoms and the alkyl group. (The so called « 3-center » bonds whose molecular orbitals appear to be composed by the hybrid orbitals of two *Al* atoms and one *C* atom). [16].

In this case the catalytic action in the polymerization of ethylene to linear polymers may be interpreted as a penetration of a carbon anion (rich in electrons) deriving from a polarized ethylene molecule $CH_2 = CH_2 \rightarrow {}^{-}CH\text{-}CH_2{}^{+}$, in the coordinating field of action of the electron deficient complex, with simultaneous dissociation of a metal alkyl bridge bond, and as a competitive action of the carbon anion of the polarized olefin with the carbon atom, which is also negatively polarized, which was before a part of the bridge between the two metallic atoms.

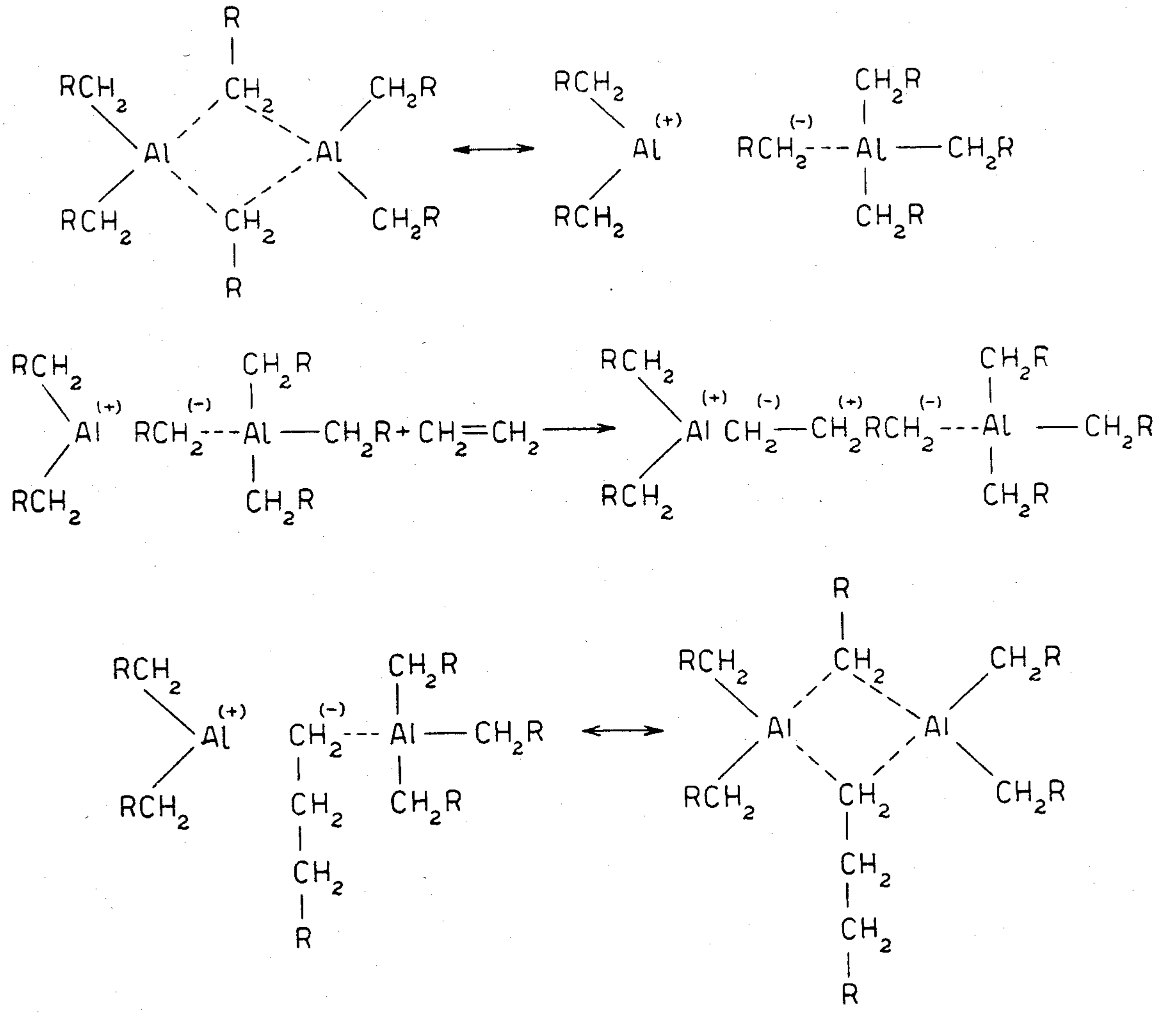


The greater distance of the carbon of the metallic atom bridge can justify a greater dissociability of that bond in comparison with the dissociability of the terminal *C-Al* bonds.

The fact that the solubility of ethylene in heptane and its dissolution heat (contrary to what happens with methylether) are not increased in the presence of aluminum alkyl demonstrates that no process takes place with a low activation heat which joins the ethylene molecule, by means of its π electrons, to the electron deficient molecule of the aluminum alkyl.

A different interpretation of the ethylene addition mechanism can be considered taking into account the electric conductivity of the aluminum alkyl solutions in hydrocarbons. This conductivity is attributed by Bonitz

[18] to a ionic dissociation. Also in this case the insertion of an ethylene polarized molecule between the two ions of opposite charge is considered.



Soluble, well defined compounds which act as catalysts in the polymerization of ethylene are e. g.:

Metal alkyls, mostly existing in polymeric forms (for inst. dimers) polymerizing ethylene to low polymers, such as:

$$Li_2\ (C_2H_5)_2\ ;\ Be_2\ (C_2H_5)_4\ ;\ Al_2(C_2H_5)_6$$

Soluble crystallizable metallorganic complexes polymerizing ethylene both to low and high polymers:

$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	melting point 126-130°C
$(C_5H_5)_2TiCl_2AlClC_2H_5$	» » 88-92°C

Other soluble catalysts are not crystallizable (for inst. the reaction products between *Ti* alcoholates and *Al* alkyls), but the most active catalysts in the polymerization of ethylene are those insoluble in hydrocarbons, described in the next paragraph.

Heterogeneous catalysts.

The simple metal alkyls considered in the proceeding chapter, and even the most active of them (aluminum, berillium, lithium alkyls) polymerize ethylene in a rather slow way through a stepwise addition process. They allow, when used alone, only to obtain rather low ethylene polymers, of average molecular weight below 10.000, which are of scarce practical interest.

The reason of this is probably the fact that in the polymerization at elevated temperatures the chain termination step is very fast, while it is very slow at low temperatures and, when the linear polymeric chain becomes very long, the polymer has a tendency to crystallize, thus blocking as inclusions the small diameter metals strongly linked to the chain end.

The Ziegler's polymerization process [17] for the low pressure polymerization of ethylene to very high molecular weight polymers, uses catalysts obtained by reaction of a metal alkyl with some transition metal compounds. The first catalysts described by Ziegler and most widely studied both in Europe and in America are those obtained by reacting $TiCl_4$ with aluminum trialkyls. The reaction, which is a very complex one, takes place in several stages. The first step of titanium alkylation is followed by a successive stage of homolytic decomposition of the titanium mono-alkyl compound. During this stage free radical are formed and at the same time a reduction of titanium from valence 4 to 3 or less takes place. If *Al*-triethyl is used the free ethyl radicals disproportionate, for the most part, to ethane and ethylene, and the latter partially polymerizes to polyethylene.

The reaction between $TiCl_4$ and AlR_3 can be considered as taking place in several steps:

I) Alkylation of $TiCl_4$ and homolytic decomposition of organo-titanium compounds:

$$TiCl_4 + Al(C_2H_5)_3 \rightarrow Al(C_2H_5)_2Cl + TiCl_3C_2H_5$$

$$TiCl_3C_2H_5 \rightarrow TiCl_3 + \cdot C_2H_5$$

$$TiCl_4 + 2Al(C_2H_5)_3 \rightarrow TiCl_2(C_2H_5)_2 + 2Al(C_2H_5)_2Cl$$

$$TiCl_2(C_2H_5)_2 \rightarrow TiCl_2C_2H_5 + \cdot C_2H_5$$

$$TiCl_2C_2H_5 \rightarrow TiCl_2 + \cdot C_2H_5$$

$$2 \cdot C_2H_5 \rightarrow C_2H_4 + C_2H_6$$

II) Formation of insoluble complexes of the type:

$$TiX_2Y + R'AlR''_2 \rightarrow X_2TiYR'AlR''_2$$

an example of this type of complexes is given in the soluble crystallizable compound $(C_5H_5)_2$ $TiCl_2Al(C_2H_5)_2$, which can be formed by addition of one mol. of $(C_5H_5)_2$ $TiCl$ to one mol. of $AlCl(C_2H_5)_2$.

Only when the alkylation of $TiCl_4$ is carried out with Al-dimethyl-monochloride the greater stability of the CH_3^- ion in comparison with the CH_2^- ion allows the separation and even the purification by distillation of the $TiCl_3 \cdot CH_3$ compound. [19]. The latter decomposes, however, very fast by mild heating yielding the brown form of $TiCl_3$ which crystallizes in needles. According to our X-rays measurements this form is isomorphous with the TiJ_3 form describeb by Klemm [20].

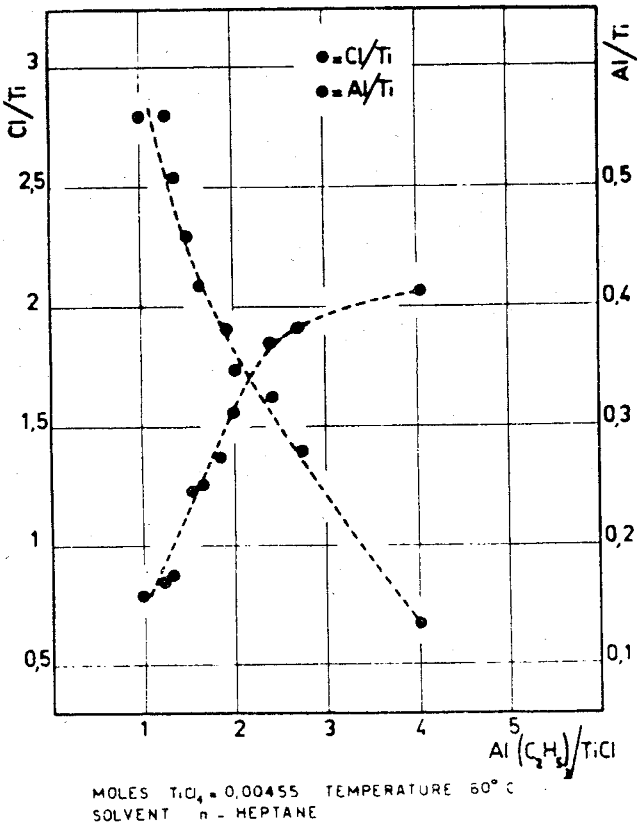


FIG. 5. – Composition of the catalysts obtained in the reaction between $Al\,(C_2H_5)_3$ solution (0.729 mol/l) and $TiCl_4$ solution in n-heptane (0.0455 mol/l) at 60°C, in function of the Al/Ti ratio.

In general, when higher alkyl aluminum compounds are reacted with a titanium tetrahalide, a precipitate is obtained whose composition varies according to the Al/Ti ratio, (fig. 5) the temperature, the time (fig. 6), and the kind of alkyl group used.

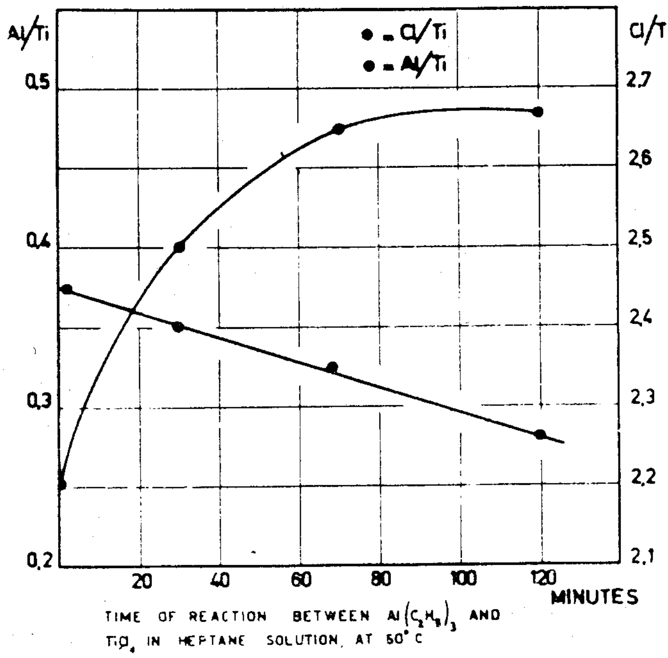


FIG. 6. – Composition of the catalysts obtained by reacting $Al\,(C_2H_5)_3$ and $TiCl_4$ $(Al/Ti = 1.5)$ in heptane solution, et 60°C, at different reaction times.

As a consequence, this precipitate exhibits a catalytic action which varies with its composition and with the time, but which is in some cases very high, particulary by Al/Ti ratios of about 2. Such a precipitate contains, besides titanium and chlorine, also aluminum and alkyl groups. Doubtless it contains those elements combined with other in complexes whose formation is partly due to character of a Lewis' acid of the *Al*-trialkyl. In fact it is not possible even by accurate washing with inert solvents to separate completely the aluminum alkyl compounds from the diand trivalent titanium halides.

It must be assumed that in such complexes the compound $AlClR_2$ or AlR_3 is combined with a tri- or divalent titanium compound, according to the conditions in which the catalyst is prepared.

The fact that the primary process in the reaction of $TiCl_4$ with AlR_3 is an alkylation, leading to the formation of an alkylated titanium compound (which decomposes yielding free radicals) induced many chemists to think that the $TiCl_4$-AlR_3 system could act as the initiator of a free radical type polymerization and that monomeric units, absorbed in ordered succession on the surface of a solid phase, could add to each other thus forming sterically ordered structures [21].

The formation of free radicals, which is observed during the formation of the catalyst, can in fact start the polymerization of certain monomers (e. g. styrene, diolefins) but not that of aliphatic alpha-olefins to high polymers, when the process is carried out at low temperature and low pressure, in the presence of solvents.

At firts the study of the Ziegler's catalysts presented some difficulties and their kinetics of polymerization appeared very intriguing because they are quite unstable, and their activity varies during the time. They polymerize ethylene and some of them, if prepared in particular conditions, and with particular ratios between metalkyls and transition metal compounds, may polymerize alpha-olefins, but their sterecspecificity is generally poor.

In studying the alpha-olefin polymerization we were able to obtain certain highly stereospecific catalysts, yielding substantially only isotactic polymers and others yielding only atactic polymers [22].

The most interesting results, from both theoretical and practical standpoint in producing isotactic polymers were achieved by us by means of catalysts which show a high stability in the time. We obtained them by contacting insoluble crystalline halides (with layer lattices) of di-or trivalent transition metals with organometallic compounds. Such catalysts may, if suitable metallorganic compounds are used, (*Al*-triethyl, *Be*-diethyl, etc.) be highly stereospecific and yield isotactic, highly crystalline polymers.

On the contrary, by means of the same organometallic compounds absorbed on amorphous carriers containing transition metal compounds, amorphous atactic polymers are obtained.

Characteristics of the coordinated anionic catalysis.

Before giving an interpretation of some aspects of stereospecificity and trying to explain its causes, the exposition of some characters of coordinated anionic catalysis may be useful.

Independently of their stereospecificity, the catalysts used by us represent a special type of catalyst, since in many cases they make it possible to obtain polymers having a chemical constitution which is different from that for the previously known polymers, and this even in the case of the atactic polymers of alpha-olefins. It was possible to demonstrate in fact, through infra-red examination, that the new alpha-olefin polymers have a greater regularity of structure, and particularly a head-to-tail enchainment more regular than that of polymers obatined by other processes.

We are of the opinion that the difference between the more classic anionic mechanism and the mechanism which we attribute to our processes is to be ascribed to the particular coordination bonds contained in the catalysts used by us.

The arguments in favour of the hypothesis of a coordinated anionic catalysis are the following:

1) The linear, regular head-to-tail structure of the macromolecules, obtained by polymerization of $CH_2 = CHR$ monomers, in which R is an alkyl group, according to the greater tendence of the CH_2 group (in comparison with the CHR group) to give a carbanion able to be coordinated in a metallorganic complex.

2) The nature of the terminal groups contained in the macromolecules of poly alpha-olefins, characterized by the presence of terminal vinylidenic groups at one end of the chain and generally, at the other end, of terminal alkyl groups corresponding to the normal saturated alkyl containing the same number of carbon atoms as the normal chain of the polymerized olefins [23].

3) The presence, in the most active catalysts, of at least two different metals which are, all of them, highly electropositive and able to form complexes.

4) The stronger catalytic activity of the complexes containing metallic ions, which have a small atomic radius and generate locally more intense electric fields: berillium (ionic radius 0,35 Å), aluminum (0,51 Å), and, among the monovalent ions, lithium (0,68 Å).

5) The electric conductivity of ionic type, with migration of the groups richer in alkyls toward the anode, shown by the solutions of the alkyl metal compounds (such as an aluminum trialkyl) and of their catalytically active soluble complexes.

6) The different reactivity of the monomers in the catalysis which follows a reverse order in respect of that of the cationic catalysis, (with exclusion of those monomers containing substituents which can poison the catalysts). The reactivity of propylene and butene is lower in comparison with ethylene according to the presence in their molecule of the electron releasing $-CH_3$ group.

7) The nature of the chain propagation:

$$\text{I (Complex)}-CH_2\text{-}CHR\text{-}P + CH_2 = CHR \rightarrow$$
$$\rightarrow \text{(Complex)}-CH_2\text{-}CHR\text{-}CH_2\text{-}CHR\text{-}P$$

and of the chain termination which leads to the formation of a vinylidene bond through transfer of an hydride ion from the $-CHR$ group of the last monomeric unit to the catalytic complex, which can then initiate a new polymeric chain:

$$\text{II (Complex)}-CH_2\text{-}CHR\text{-}P \rightarrow \text{(Complex)}-H + CH_2 = CR\text{-}P$$
$$\text{III (Complex)}-H + CH_2\text{-}CHR \rightarrow \text{(Complex)}-CH_2\text{-}CH_2R$$

This transfer is the easier, the more electron-donor is the R group, and it is to be assumed therefore that an hydride ion transfer is involved. This may explain the lower molecular weight of poly alpha-olefins, with respect to polyethylene or polystyrene.

8) The fact that the molecular weight is not lowered, contrary to what happens in radicalic polymerization, when the polymerization is carried out in the presence of certain solvents (e.g. cumene, isoctane, etc) known for their ability to pick up free radicals.

9) The constant rate of polymerization during the time, observed when using stabilized catalysts. The solid catalyst is not consumed, unlike to what occurs with all the radicalic initiators.

10) The decrease of molecular weight with increasing of alkyl aluminum concentration (fig. 7) which can be explained by a transfer of ionic nature, or as a dissociation of the catalytic complex, followed by its reconstitution with a different aluminum alkyl compound.

The addition of a monomer molecule to the organometallic compound may be considered a ionic reaction with heterolitic rupture of the metal-to-carbon bond comparable to the ionic type addition of an halogen to an olefin. This addition requires a polar environment which, in the absence of polar solvents, is made possible by a polar surface.

An increase of catalytic activity, attributable to a polar environment, has been observed by addition of crystals having a layer lattice consisting of atoms having a different polarity.

One of the most important characters of the anionic catalysis is the high instability of the carbanion, which is conserved also when it is coordinated in complexes with a highly electropositive transition metal.

The carbanions are in fact stable only in the absence of protons which would transform the carbanion into a more stable alkyl group, and in the absence of nucleophylic groups, capable of forming anions more stable than the carbanion and to coordinate themselves in a more stable way to the highly electropositive metal of the metallorganic compound.

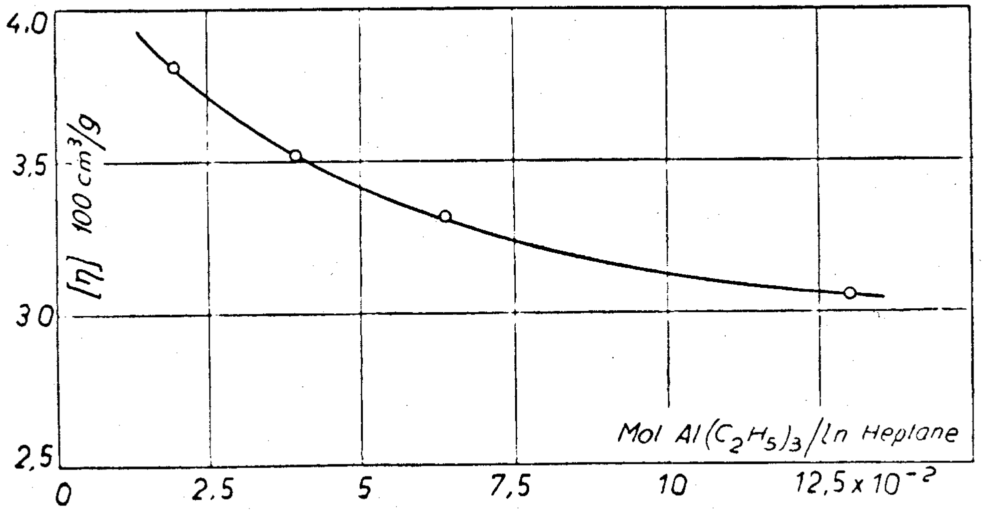


FIG. 7. - Molecular weight (expressed by intrinsic viscosity) i polypropylene as a function of $Al(C_2H_5)_3$ concentration in the catalytic system.

In the case of coordinated cationic catalysis it is not the carbon ion but the ion with which the latter is combined which coordinates itself in a complex: while in the case of coordinated anionic catalysis it is the carbanion itself which is coordinated. As we will see, this difference allows to explain from the point of view of stereospecificity, the different behaviour of certain anionic catalysts.

In a cationic catalyst, such as the one formed e. g. from Al_2Cl_6 in the presence of an alkyl chloride, complexes of the type $(AlCl_4)^{-}R^{+}$ are present. The chlorine of the alkyl chloride which takes part in the formation of the complex enters into a symmetric $(AlCl_4)^-$ anion.

The chlorine which was bound to be alkyl chloride loses its identity and we can admit that a large diameter ion $(AlCl_4)^-$ corresponds to the carbon cation. This is the cause of the lack of stereospecificity in cationic catalysis with catalysts based on aluminum chloride.

On the contrary in the case of coordinated anionic catalysis, e. g. with *Ti-Al* complexes, the same carbanion initially partaking of an alkyl metal compound coordinates itself in a complex in which the electropositive character of the transition metal favours the coordination of a negatively polarized carbon atom.

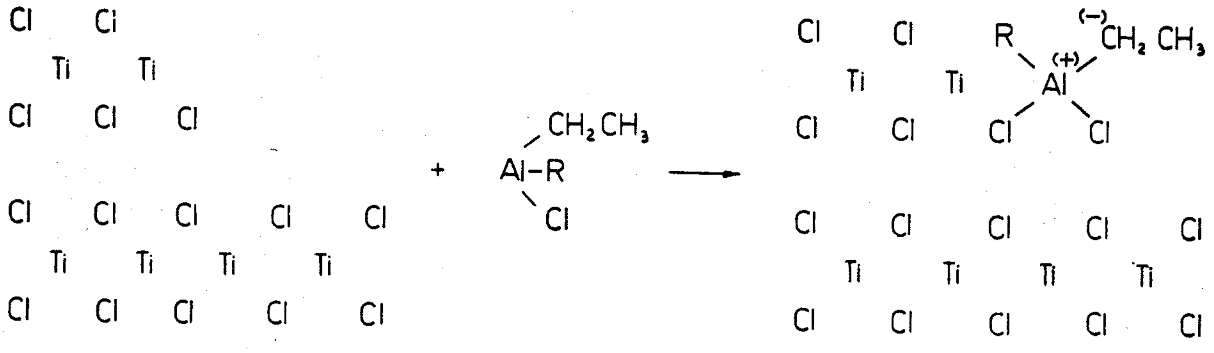


FIG. 8.

The formation of bridge bonds between two metals (for inst. observed in the aluminum alkyls and in the crystallizable metallorganic *Ti-Al* complexes previously decribed), the preferential coordination of ions of a given type in the bridge linkage and the asymmetries of the dimetallic complex, can determinate a defined position of the carbon anion in certain complexes. This clearly appears when the complex is formed by chemisorption on the border of a crystalline surface, as it is schematically represented in fig. 8 in the case of the layer lattice of the violet $TiCl_3$ crystals.

This can be the reason for the higher stereospecificity of the coordinated anionic catalysis and for the fact that, in the alpha-olefin polymerization, the most active catalysts are given only by asymmetric bimetallic complexes, containing as central atoms, atoms of two different metals (or atoms of different valence of the same metal) and not by complexes containing equivalent atoms of one single metal.

It should be kept in mind that the most stereospecific catalysts are those in which the carbanion is coordinated to a metal cation having a very small diameter (e. g. *Al*, *Be*, *Li*) and in fact the highest stereospecificity is observed with alkyl berillium compounds. (Table III).

TABLE III.

Metal of the metal organic compound	Ionic radii of the metal	% of polypropylene not extractable in boiling *n* - heptane
Be	0,35 Å	94 ÷ 96 %
Al	0,51 Å	80 ÷ 92 %
Mg	0,66 Å	78 ÷ 85 %
Zn	0,74 Å	30 ÷ 40 %

The catalyst obtained with violet $TiCl_3$ and $Be(C_2H_5)_2$ yields an higher fraction of polypropylene insoluble in boiling *n*-heptane. The percentage of this highly crystalline fraction can be assumed as an index of the stereospecificity of the catalyst.

Transition metal complexes and stereospecificity.

It has already been briefly discussed that only transition metals of a high electropositive character, in a low valence state, can lead to the formation of catalysts suitable for the anionic polymerization of alpha-olefins to high polymers.

Simple organometallic compounds of transition metals, in which an alkyl group is bound to the metal by a strongly polarized bond, are not known. In most of the transition metal organometallic compounds, which in general have poor stability, the bonds are merely of the covalent type (which decompose with an homolytic mechanism) or of the covalent « delocalized » type (in which a metal atom is bound jointly to an electron rich system of several carbon atoms).

In the complexes of some not very electropositive metals (platinum, palladium, etc.) with olefins, of the type: $Pt_2Cl_4\ (C_2H_4)_2$ the olefinic double bond remains mostly unmodified in the complex and the whole olefin molecule acts with two of its π electrons as a donor to the vacant orbitals dsp^2 of the metal. Such olefinic compounds do not behave as catalysts in the polymerization of olefins which requires a polarization of the reacting monomer molecules.

In some compounds of the covalent « delocalized » type (for inst. biscyclo-pentadienyl compounds of transition metals) the central atom can yield metallorganic compounds in which also a σ type bond is stabilized. (e. g. diphenyl-bis-cyclo-pentadienyl-titanium).

The nature of the organometallic bond and particularly its ionic character are modified when a metallic atom becomes part of a complex, as it appears from the change in conductivity of its solutions in hydrocarbons.

The processes of heterogeneous anionic catalysis throw now a new light on a particular field of the chemistry of complexes, i. e. of the complexes formed by chemisorption on solid crystalline surfaces.

In particular cases, with crystalline supports, chemisorption may occur connected with epytaxy phenomena, which can impart to the chemiadsorbed molecule coordination numbers different from the normal ones. In general to a different coordination number corresponds a different hybridation of the molecular orbitals.

It is known for inst. that aluminum exhibits in general in its liquid or gaseous non ionic compounds a coordination number 4, and to them a tetrahedric structure (sp^3) should be attributed.

If we consider however many solid crystalline compounds of aluminum, e. g. Al_2O_3 in which the strong field due to the small ionic diameter and to the charge of Al strongly attracts the oxygen ions, we observe a coordination number 6 (sp^3d^2), as in the crystal lattice of Al_2O_3 (corundum). When the anion bound to the aluminum has a very small diameter, e. g. in fluorine, the coordination number 6 of the metal becomes more stable especially in the crystal lattices.

It appears therefore possible that the aluminum present in the planar molecule of a monomeric AlR_3, which loses its planarity when aluminum assumes the coordination number 4 of the dimer, might assume a higher coordination degree in the case that it is chemically adsorbed in an epytactic way onto a lattice, the metal atoms of which present the coordination number 6.

It is already known that if the fields existing in the crystals are applied to atoms with different states of excitation, they can induce state changes which depend on the field direction and on its symmetry. For instance in the case of certain iron complexes, these fields can lead them to overcome the transition from the paramagnetic to the diamagnetic state.

We must therefore foresee that the field connected with the crystal lattice may act in modifying the coordination number and also the ionic character of a metal-to-carbon bond.

Asymmetry phenomena can occur with greater frequence in the surface chemisorbed compounds than in free molecules, as for inst. in solution. They may be caused by difference in the chemical composition among the coordinated groups, which are usually considered in the stereochemistry of complexes, and also by differences produced by the bond type or also by the topological differences between atoms having the same chemical nature, when these atoms instead of being inside, are on the plane surface or on the edges or on the corners of a crystalline lattice. Topological differences may cause also chemical differences; for inst.

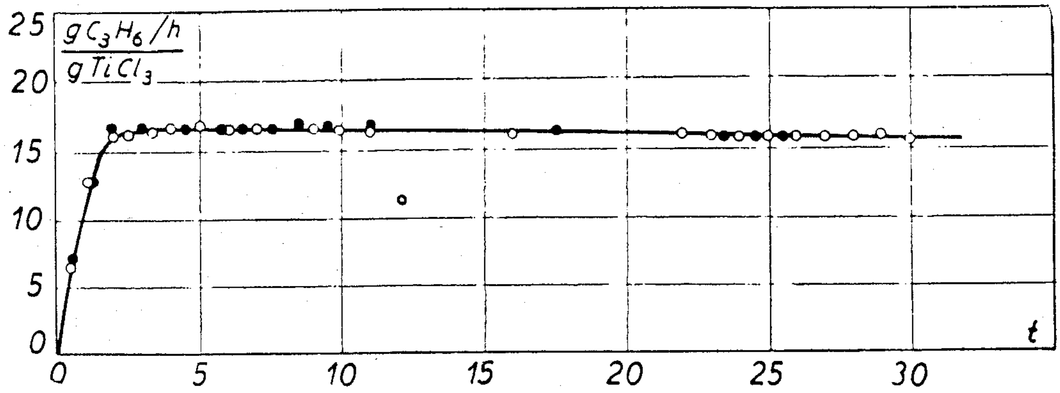


FIG. 9. – Constance of reaction rate (after a settling period) in the polymerisation of propylene with catalyst obtained from not ground crystals of violet $TiCl_3$ and $Al(C_2H_5)_3$. Temperature 70°C, $TiCl_3$ = 0,80 g/l, $Al(C_2H_5)_3$ = 4,5 mol/l, $[C_3H_6]$ = 0,62 mol/l.

an atom which lies inside the lattice appears to be non polarized or symmetrically polarized, while an atom which lies on the surface and particularly in an irregular part of the surface can present a particularly oriented polarization.

A molecule of the type $AlR'R''R'''$ or $AlClR'_2$ chemisorbed on the $TiCl_3$ crystalline surface, should show more easily optical stereoisomerism if it is adsorbed on irregular sites of the lattice surface, which presents locally asymmetric characters.

The higher stereospecificity of violet, well crystallized $TiCl_3$ and the induction phenomena (settling period with an increase of the catalytic activity during the time), observed in violet $TiCl_3$, can be attributed to the fact that in this type of $TiCl_3$ the (001) faces are well formed and therefore the alkyl aluminum compound is adsorbed more tenaciously by epytaxy on the border of these faces or on irregular sites, thus forming stable complexes with a particular asymmetrical steric configuration acting as catalysts in the polymerization. In figures 9 and 10 the kinetic curves relating to the propylene polymerization by means of $TiCl_3$ crystals are reported (fig. 9 = unground; fig. 10 = finely ground)

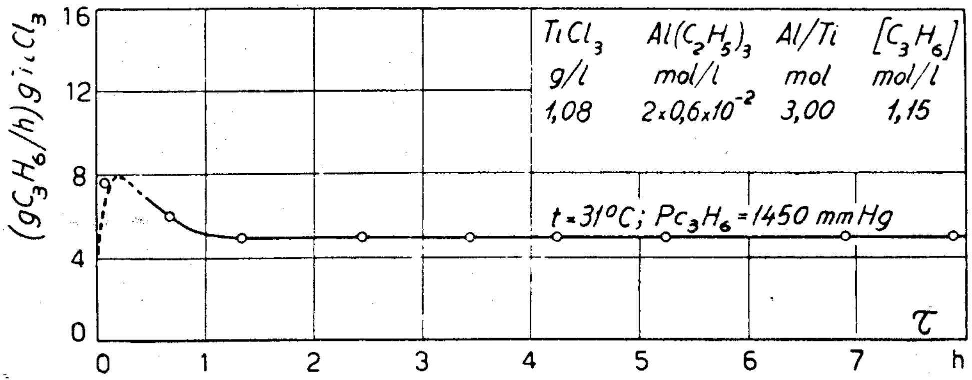


FIG. 10. – Constance of reaction rate (after a settling period) in the polymerizatln of propylene with catalyst obtained from ground crystals of violet $TiCl_3$ and $Al(C_3H_5)_2$.

The induction phenomenon observed in unground $TiCl_3$ can be attributed to an increase of the active centers, due to the formation of fresh surfaces caused by cleavage along the base planes of the crystals which occurs by a mechanical action due to the formation of bulky polymer on the edges of the crystalline laminae. With finely ground $TiCl_3$ such a phenomenon is observed in a lesser degree because it is masked by a recrystallization which acts in the opposite sense.

The determination of aluminum alkyls by means of C^{14} lebelled alkyls shows that only a portion of the aluminum alkyl adsorbed at low temperature on $TiCl_3$ (viz. the more tenaciously adsorbed) can initiate the polymerization of alpha-olefins.

If the adsorbed aluminum alkyl assumes, by epytaxy, the coordination number 6 of $TiCl_3$, asymmetry cases are foreseable even when the groups of different type, bound to the aluminum atom, are only three or even two. (fig. 11). For inst. a complex group of the type Cl_nAlR_2, epytactically partaking of a locally asymmetrical zone of the $TiCl_3$ lattice, should easily exhibit an optical type asymmetry.

If one of the R groups, coordinated with the asymmetrical complex of Al and with the $TiCl_3$, crystal lattice can exhibit in the activated state a ionic nature, it can become the initiator of a chain of asymmetrical addition reactions. The synthesis of isotactic polymers can thus take place, since each macromolecule, synthesized from a single active center, consists of monomeric units having the same steric configuration.

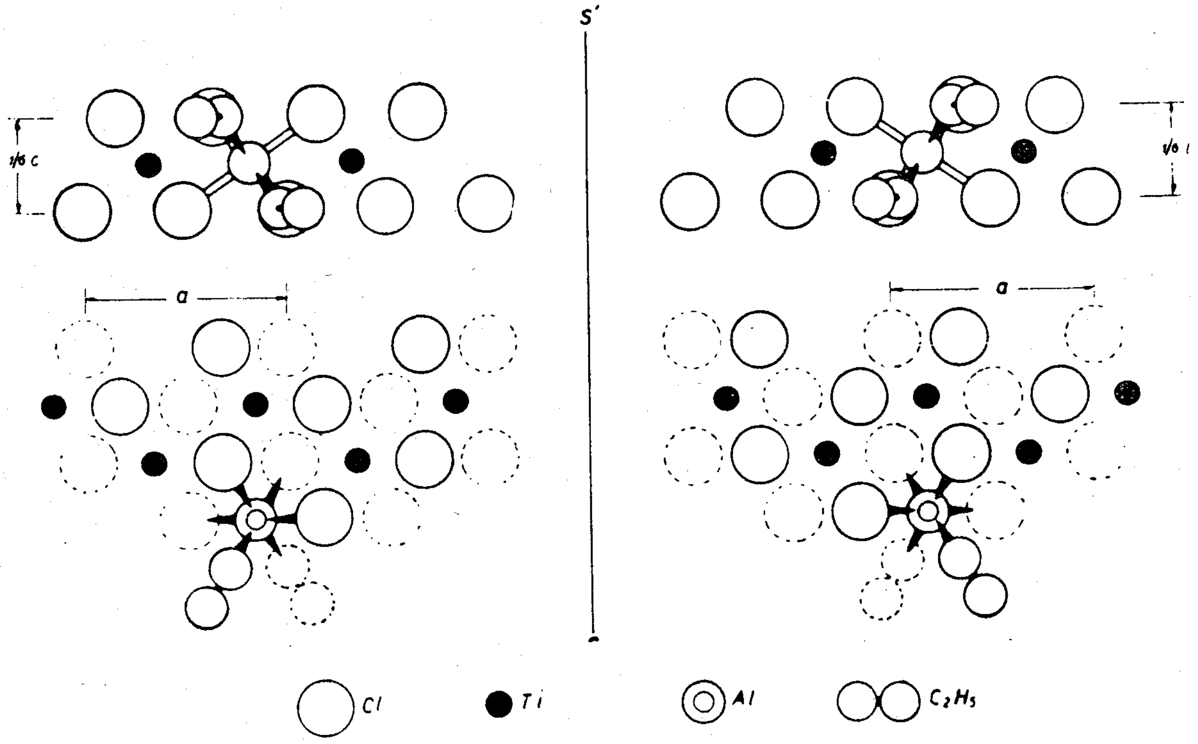


Fig. 11. - Schematic model of how an epitactic adsorption of $AlCl(C_2H_5)_2$ on the bordet of the basal plane of a crystal of $TiCl$, ($a = 6\ 12$ Å, $C = 17\ 50$ Å) may give rise to enantiomorphous active centers.

Since there is the same probability of having active centers of both enantiomorphic forms, the crude polymer will consist of a mixture of enantiomorphous macromolecules, each formed by a large number of sterically equal units.

A further research field, i. e. the isolation of asymmetric active centers, corresponding to only one of the two enantiomorphous isomeric forms, can be of remarkable interest, from the scientific point of view since it could solve the problem of asymmetric organic synthesis in the field of macromolecules.

REFERENCES

[1] G. Natta, *Opening lecture at the XVI International Congress of Pure and Applied Chemistsy* (Paris, July 1957), Experientia, Supplementum, VII, G. Natta, *Lecture presented at the International Symposium on Synthetic Rubber*, London (1957); « Rubber Plastics Age », **38**, 495 (1957).

[2] G. Natta, « Atti Accad. Lincei », (8) **4**, 61 (1955); G. Natta, « Chimica e Industria », **37**, 888 (1955); G.Natta,P. Pino, G. Mazzanti, ibid. **37**, 927 (1955); G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti, M. Peraldo, « Chimica e Industria », 38, 124 (1956); G. Natta, I. Pasquon, E. Giachetti, « Angew. Chemie », **69**, 213 (1957); G. Natta, G. Mazzanti, G. Crespi, G. Moraglio, « Chimica e Industria », **39**, 275 (1957); G. Natta, P. Pino, G. Mazzanti, « Gazzetta Chimica Italiana », **87**, 528 (1957); G. Natta. P. Pino, G. Mazzanti, P. Longhi, ibid. **87**, 549 (1957).

[3] G. Natta, P. Corradini, « Atti Accad. Lincei », (8) **4**, 73 (1955); G. Natta, P. Corradini, M. Cesari, « Rend. Accad. Lincei », (8) **21**, 365 (1956).

[4] G. Natta ,L. Porri, G. Mazzanti, « Italian Patent », 536.631, 12-3-1955.

[5] G. Natta, L. Porri, « Italian Patent », 538.453, 15 luglio 1955.

[6] G. Natta, P. Corradini, L. Porri, « Rend. Accad. Lincei », (8), **20**, 728 (1956); G. Natta, P. Corradini, « Angew. Chemie », **68**, 615 (1956); G. Natta, P. Corradini, « Rend. Accad. Lincei », (8), **19**, 229 (1955); G. Natta, L. Porri, P. Corradini, D. Morero, « Rend. Accad. Lincei », (8) **20**, 560 (1956).

[7] G. Natta, « Chimica e Industria », **38**, 751 (1956).

[8] G. Natta, P. Pino, G. Mazzanti, U. Giannini, « J. Am. Chem. Soc. », **79**, 2975 (1957).

[9] G. Natta, P. Pino, G. Mazzanti, P. Longhi, « Gazzetta Chimica Italiana », 87, 570 (1957).

[10] E. G. Rochew, D T. Hurd, R. N. Lewis, « *The Chemistry of organometallic compounds*, J. Wilye, New York pag. 18 (1957).

[11] x. Ziegler, « Brennstoff Chem. », **33**, 193 (1952).

[12] G. Wittig, *Lecture presented at the XVI International Congress of Pure and applied Chemistry*, Paris, July 1957.

[13] H. Hisch, V. Tobolsky, « J. Polymer Science », **25**, 245 (1957).

[14] H. Martin, « Z. Angew Chem. », **68**, 306 (1956).

[15] G. Natta, M. Farina, M. Ragazzini, « Italian Patent Application », 3900/56, 25 luglio 1956.

[16] E. Cartmell, G. W. Fowles, *Valency and molecular structure*, *Butterworths Scientific Publications*, London (1956) pag. 237.

[17] K. Ziegler, « Belgian Patent » 533.362, German priority 16 novembre 1953.

[18] E. Bonitz, « Ber., » 88, 742 (1955).

[19] Belgian Patent 533.477, German priority 16 dicembre 1955.

[20] W. Klemm, *Lecture presented at the XVI International Congress of Pure and applied Chemistry*, Paris, July 1957.

[21] H. N. Friedlander, Fall Meeting, 1956, American Chemical Society, Atlantic City, N. J.

[22] G. Natta, P. Pino, G. Mazzanti, « Italian Patent » 526.101, 3 dicembre 1954; « Italian Patent» 545.332, 16 dicembre 1954.

[23] G. Natta, P. Pino, G. Mazzanti, U. Giannini, E. Mantica, M. Peraldo, « Chimica e Industria », **39**, 19 (1957).