SOME ASPECTS OF THE MECHANISM OF THE STEREOSPECIFIC POLYMERIZATION OF α-OLEFINS

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INTRODUCTION

α-Olefins can be polymerized stereospecifically to give crystalline isotactic polymers and, in the case of propylene, under certain specific conditions, also crystalline syndiotactic polymers.

The most active and stereospecific catalyst systems in the polymerization to isotactic polymers consists of a halide of some transition metal (e.g. violet $TiCl_3$ or other metals of the second period) and a halide of an organo-metallic compound of a light metal (e.g. AlR_3, AlR_2Cl)[1,2]. Other systems which are active in this polymerization are prepared from only one transition metal compound [e.g. $TiCl_3CH_3$ (refs. 3, 4) or $Ti + TiCl_3$ (ref. 5)]. The last named systems are less active and are also often less stereospecific. All the systems quoted so far are heterogeneous in hydrocarbon diluents. The most interesting catalyst systems for the polymerization of propylene to syndiotactic polymer also consist of a transition metal compound (e.g. VCl_4, VAc_3) and an organometallic compound of a light metal (e.g. AlR_2Cl)[6]. These systems are homogeneous—or anyhow very dispersed—in hydrocarbon solvents, and active and very stereospecific in the polymerization under consideration at sufficiently low temperatures, e.g. $< -50°C$. These different catalyst systems are generally called Ziegler–Natta catalysts.

Since the discovery of these processes by Natta[7], which dates back to 1954, several hypotheses have been put forward as to the nature of the catalytic complexes that are active in the stereospecific polymerization and the causes determining stereospecificity[8]; however, none of these hypotheses has been supported so far by completely demonstrative experimental data. The catalyst systems, which have been investigated or considered in more detail by various workers are those quoted first; these are bimetallic and active in the polymerization to isotactic polymers.

The discussions on these systems not only concern the reaction mechanism, but also the nature of the components of the catalytic complexes and of the metal–carbon bond the polymeric chain grows on. For instance, it has not been demonstrated so far whether for the bimetallic systems considered [e.g. the systems $TiCl_3$—$Al(C_2H_5)_2Cl$], the catalytic complexes contain or do not contain both metals, and whether the polymeric chain grows on a Ti—C or Al—C bond.

In this communication, it is my desire to particularly discuss these topics, essentially on the basis of the experimental data (most of which are recent)

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mostly obtained at the Industrial Chemistry Department of the Polytechnic Institute of Milan.

NATURE OF THE ACTIVE METAL–CARBON BONDS

It is generally accepted that the stereospecific polymerization processes of α-olefins are of the anionic coordinated type as proposed by Natta[9] and that the growth of the polymeric chains occurs by insertion of the monomeric units on a metal–carbon bond of the catalytic complex.

In the catalyst systems mentioned above, prepared from compounds of only one transition metal (such as $TiCl_3$—$TiCl_3CH_3$), the active bond clearly is the Ti—C bond[4]. Although these systems are less active and less stereospecific than the bimetallic ones, it is fairly reasonable to expect that in the latter the polymer chain grows on the transition metal–carbon bond.

This hypothesis is also supported by theoretical considerations, such as those put forward by Cossee[10], and by experimental ones. For instance, in the homogeneous catalyst systems based on VCl_4, and on an organometallic compound of Al, the polymerization of propylene occurs on the vanadium–carbon bond, although the catalyst system is bimetallic; this fact can be deduced from the thermolability of the complexes that maintain their catalytic activity only at low temperatures[6].

RATE CONTROLLING STEP OF THE PROPAGATION PROCESS

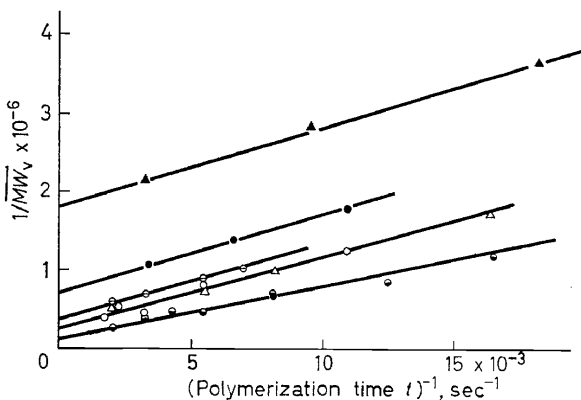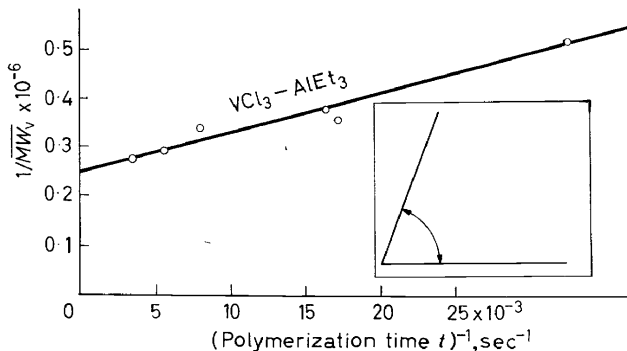*Figure 1* reports, as a function of the reciprocal of the polymerization time,

Figure 1. Reciprocal of the viscosity average molecular weight *vs.* the reciprocal of the polymerization time for isotactic polybutenes (pentanic residues) obtained at 0°C by different catalyst systems based on violet $TiCl_3.C_4H_8$:333 g/l. toluene [▲, $TiCl_3ARA$–$BeEt_2$; ●, $TiCl_3HRA$–$BeEt_2$; ⊖, $TiCl_3ARA$–$AlEt_2Cl$; △, $TiCl_3ARA$–$AlEt_2I$; ○, $TiCl_3HRA$–$AlEt_2Cl$; ◓, $TiCl_3ARA$–$AliBu_2Cl$]

the behaviour of the reciprocal of the viscosity molecular weight of isotactic polybutenes obtained at sufficiently low temperatures by different catalyst systems based on violet $TiCl_3$. The slopes of these straight-lines is proportional to the reciprocal of the propagation rate constants of the polymeric chains[11, 12]. As can be seen, the slope is practically independent of the type

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of organometallic compound used to prepare the catalyst system, even if the overall catalytic activity varies to a great extent when passing from one catalyst system to the other.

On the other hand, the propagation rate constant of the polymer chains strongly depends on the nature of the transition metal. As shown in *Figure 2*,


Figure 2. Reciprocal of the viscosity average molecular weight *vs.* the reciprocal of the polymerization time for isotactic polybutenes (pentanic residues) obtained at 0°C by VCl_3–$Al(C_2H_5)_3$. Comparison with the systems based on violet $TiCl_3.C_4H_8$:333 g/l. toluene [Inset: average slope for systems based on violet $TiCl_3$]

in fact, the propagation rate of the macromolecules is higher for the systems based on VCl_3 than for those based on violet $TiCl_3$[11, 12].

The activation energies for the propagation processes were also evaluated from data of this type, as it was observed that the activation energy of the systems based on VCl_3 is quite lower than that of the systems based on $TiCl_3$[11, 12]. As shown by these results, the kinetic-determining step of the propagation process of the macromolecules is that involving an interaction of the olefin with the transition metal.

The data reported in *Figure 3* also show that the propagation rate of the
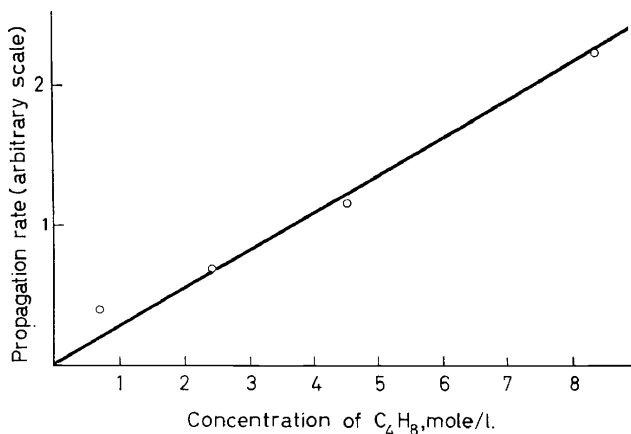
Figure 3. Rate of propagation of the isotactic polymer chains of polybutene *vs.* concentration of the monomer. $TiCl_3ARA$–$Al(C_2H_5)_2Cl$. T = 0°C

polymer chains is in practice a linear function of the concentration of the monomer[12]. These data and the kinetic data concerning the overall polymerization process[13] suggest that the kinetic-determining step is that involving the complexation of the olefin with the transition metal belonging to the catalyst complex and not the insertion of the monomeric unit on the metal–carbon bond.

This conclusion is in agreement with the results obtained by Natta, Danusso and Sianesi[14] from the study of the stereospecific polymerization of the styrenes substituted on the aromatic ring, and with the experimental results attained by Carrick and coworkers[15] on the ethylene–propylene copolymerization by different catalyst systems.

VALENCY OF THE TRANSITION METAL IN THE CATALYTIC COMPLEX

The valency of the transition metal in the catalytic complex has been studied by us. In particular we investigated the homogeneous systems based on vanadium and an organometallic compound, which are stereospecific at low temperatures in the polymerization of propylene to syndiotactic polymer[16].

Electron paramagnetic resonance measurements of these systems led us to conclude that such a valency must be equal to 3. The transition metal in the active catalyst complexes of these systems should be present as VCl_2R (ref. 16).

By analogy, we think that in the heterogeneous systems based on titanium which are stereospecific in the polymerization of α-olefins, the catalytic complexes contain $TiCl_2R$. It may be pointed out here that pure $TiCl_3R$ is not active in the polymerization of α-olefins[3, 4]. Similar conclusions were also reached by Rodriguez and Van Looy[4], who studied the behaviour of systems prepared from $TiCl_3$, $TiCl_2$, $TiCl_3R$ and $TiCl_2R_2$.
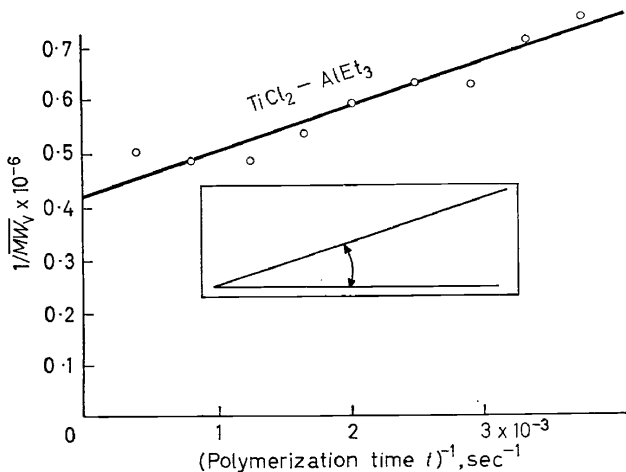

Figure 4. Reciprocal of the viscosity average molecular weight *vs.* the reciprocal of the polymerization time for isotactic polybutenes obtained at 0°C by $TiCl_2$–$Al(C_2H_5)_3$. Comparison with the systems based on violet $TiCl_3.C_4H_8$:333 g/l. toluene [Inset: average slope for systems based on violet $TiCl_3$]

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According to these workers, this conclusion can be extended to the systems based on $TiCl_2$ (ref. 4). As a proof of these hypotheses we observed[12] that in the systems based on $TiCl_2$ the propagation rate of the isotatic polymeric chains is equal to that of the systems based on $TiCl_3$. This is shown by the data reported in *Figure 4* where a comparison is made of the results concerning the two types of systems mentioned above.

Therefore, in the case of systems based on $TiCl_2$, an oxidation of titanium from the bivalent to the trivalent state must be considered to take place at least with regard to the transition metal belonging to the catalytic complex.

BIMETALLICITY OF THE CATALYTIC COMPLEXES

The simplest hypothesis that can be deduced from the results reported so far is that the stereospecific catalytic complexes are of the monometallic type, e.g. consisting of $TiCl_2R$ on the surface of a crystalline substrate of $TiCl_3$. The organometallic compound (e.g. AlR_3) used in the preparation of the catalyst should exclusively alkylate the transition metal compound.

However, we studied this topic more thoroughly and concluded that the experimental data obtained by us agree better with the hypothesis that the catalytic complexes that are active in the stereospecific polymerization of α-olefins are, at least partially, bimetallic as proposed by Natta in his first hypotheses[9]. A first set of data supporting this hypothesis was obtained by comparing the reducing powers of some organometallic compounds in the presence of VCl_3, and the activity of the corresponding systems in the polymerization of propylene.

The relative value of the reducing power of the organometallic compounds was evaluated with the aid of e.p.r. measurements, carried out on samples of VCl_3 treated with different organometallic compounds[17].

The e.p.r. analysis reveals the presence of bivalent vanadium. By assuming that the organometallic compound alkylates VCl_3 to VCl_2R and that the latter decomposes to VCl_2, the amount of VCl_2 that is present in said samples should be practically equal to the total amount of VCl_2R that forms during
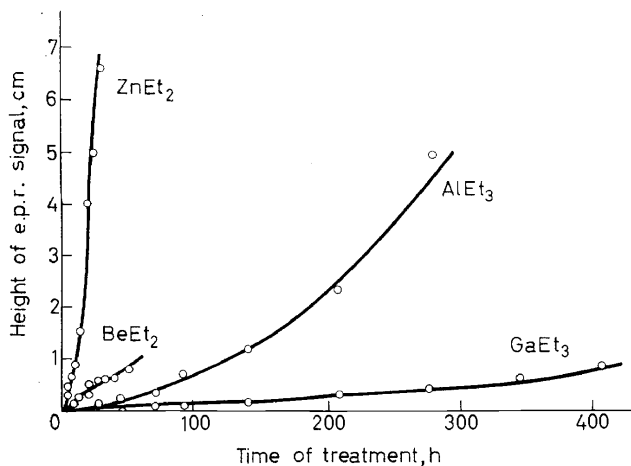
Figure 5. E.p.r. analysis of VCl_3 samples treated at 90 °C with some organometallic compounds

the whole run. The results obtained from these runs are reported in *Figures 5* and *6* which show the height of the e.p.r. signal *vs.* the time of treatment of VCl₃ at 90° with some organometallic compounds.

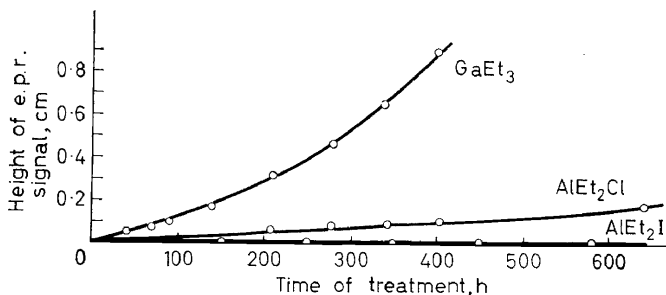*Figure 6.* E.p.r. analysis of VCl₃ samples treated at 90 °C with some organometallic compounds

These results have been compared with the catalytic activity of the corresponding systems. In order to establish a more correct comparison, the activity was evaluated by considering the amount of macromolecules that form within a given time, rather than the amount of polymerized monomer. This comparison is reported in *Table 1*. We see that no parallelism exists

Table 1. Comparison between reducing power and catalytic activity

SCALE OF THE REDUCING POWER ON VCl₃ AT 90°C
$Al(C_2H_5)_2I(=O) < Al(C_2H_5)_2Cl < Ga(C_2H_5)_3 < Al(C_2H_5)_3$
$< Be(C_2H_5)_2 < Zn(C_2H_5)_2 < Cd(C_2H_5)_2 < LiC_4H_9$

SCALE OF THE CATALYTIC ACTIVITY IN THE POLYMERIZATION OF
PROPYLENE WITH VCl₃ AT 90°C
$Zn(C_2H_5)_2 < LiC_4H_9 < Cd(C_2H_5)_2 < Al(C_2H_5)_2Cl < Al(C_2H_5)_2I$
$< Ga(C_2H_5)_3 < Be(C_2H_5)_2 < Al(C_2H_5)_3$

between catalytic activity and reducing power of the organometallic compound used to prepare the catalyst. For instance, aluminium diethylmonochloride, which exhibits a relatively low reducing power, gives rise with violet TiCl₃ to catalytic systems that are more active than those based on diethyl zinc, which exhibits a relatively high reducing power. These data also suggest that in the catalyst systems considered above, not all VCl₂R molecules that form within a certain time by the action of the organometallic compound on VCl₃ give rise to the formation of a macromolecule.

A significant result supporting the hypothesis that the catalytic complexes are at least partially bimetallic, is indicated in *Figure 7*[17]. This figure compares the rate of polymerization of propylene with time, for a run carried out at constant temperature and pressure of the olefin.

In the first part of the run, a-TiCl₃ was allowed to react with Zn(C₂H₅)₂ in the presence of propylene. In the particular system considered, the polymerization does not occur to any significant extent during this stage; subsequent addition of Al(C₂H₅)₃ immediately activates the system. The polymerization

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rate obtained is practically equal to that corresponding to the same system free from $Zn(C_2H_5)_2$. This leads to the interpretation that the alkylating and the reducing power of diethyl zinc (and of the mixtures of diethyl zinc and triethyl aluminium) is higher than that of triethyl aluminium, while its complexing power is lower.
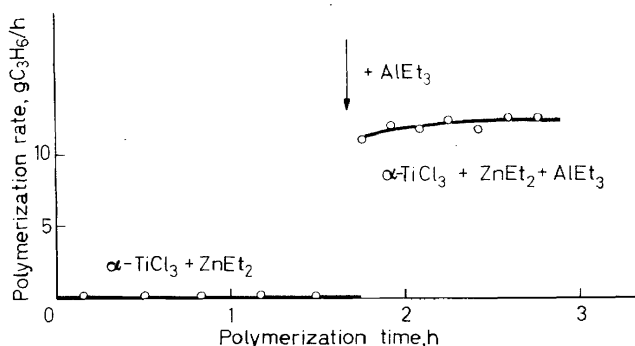

Figure 7. Rate of propylene polymerization in the presence of a catalyst system α-TiCl₃–$Zn(C_2H_5)_2$ before and after addition of $Al(C_2H_5)_3$. Reagents used: n-heptane: 250 cm³; α-TiCl₃: 0·30 g; $Zn(C_2H_5)_2$: 0·70 cm³; $Al(C_2H_5)_3$: 0·45 cm³; $p_{C_3H_6}$: 950 mm Hg; T = 20°C

During the first part of the run several transition metal–carbon bonds and $TiCl_2R$ compounds are formed which, being relatively unstable in the system considered, decompose rapidly. In accordance with this hypothesis, we observed[17] that the catalyst systems based on $Zn(C_2H_5)_2$ and $TiCl_3$ are more active, e.g. at 15°C than at 70°C. The addition of aluminium alkyl to the system $Zn(C_2H_5)_2$–$TiCl_3$ should stabilize the transition metal–carbon active bonds, by the formation of bimetallic surface complexes.

The values of stereospecificity of the different bimetallic catalyst systems based on violet $TiCl_3$ do not agree with the hypothesis that the active centres are exclusively monometallic; actually, if it were so, it can be assumed that when increasing the reducing power of the organometallic compound, a given transition metal halide should give rise to catalyst systems with ever increasing or ever decreasing stereospecificities. On the contrary, e.g. in the case of violet $TiCl_3$ the stereospecificity of the different catalyst systems increases in the order[12] $Al(C_2H_5)_3 < Ga(C_2H_5)_3 < Al(C_2H_5)_2Cl < Be(C_2H_5)_2$, while the reducing power of the aforementioned organometallic compounds increases in the order: $Al(C_2H_5)_2Cl < Ga(C_2H_5)_3 < Al(C_2H_5)_3 < Be(C_2H_5)_2$ (ref. 17).

With regard to the polymerization of propylene to syndiotactic polymer, the data agree better with the hypothesis that the stereospecific catalyst complexes in the syndiotactic sense are bimetallic. It was actually observed that the systems based on VCl_4 and $Ga(C_2H_5)_3$ give rise to atactic polypropylenes[12], while the use of $Al(C_2H_5)_2Cl$, instead of $Ga(C_2H_5)_3$ allows one to obtain highly syndiotactic polymers[6]. This different behaviour was attributed to the fact that $Al(C_2H_5)_2Cl$ presents higher complexing

properties than those of $Ga(C_2H_5)_3$. Actually $Al(C_2H_5)_2Cl$ is a dimer, while the molecule of $Ga(C_2H_5)_3$ is monomeric. The alkylating power of $Al(C_2H_5)_2Cl$ on the contrary, is not much lower than that of $Ga(C_2H_5)_3$ (*Figure 6*). Therefore, we are led to conclude that in the systems based on $Al(C_2H_5)_2Cl$ and on a vanadium compound, $Al(C_2H_5)_2Cl$ is complexed with VCl_2R that forms, giving rise to catalyst complexes that are stereospecific in the polymerization of propylene to syndiotactic polymer. On the other hand, $Ga(C_2H_5)_3$ should not give rise to such complexes, and in the corresponding catalyst systems, uncomplexed VCl_2R should give rise to the atactic polymer. Therefore, in the case of these homogeneous catalyst systems, the bimetallic catalytic complexes should be stereospecific, while the monometallic ones should be only active and nonstereospecific.

INFLUENCE OF THE TRANSITION METAL HALIDE

The scale of stereospecificity reported in the previous section is peculiar to the systems based on violet–$TiCl_3$ and is not valid for the systems based on other transition metal halides, as shown in *Table 2*[12]. For instance, the system violet $TiCl_3$–$AlEt_3$ is less stereospecific than the system violet $TiCl_3$–$AlEt_2Cl$, while the reverse is true for the corresponding systems based on VCl_3.

Table 2. Stereospecificity (°) of catalytic systems in the polymerization of propylene at 70°C

Transition metal halide \ Organometallic compound	$Be(C_2H_5)_2$	$Al(C_2H_5)_3$	$Ga(C_2H_5)_3$	$Al(C_2H_5)_2Cl$	$Al(C_2H_5)_2Br$	$Al(C_2H_5)_2I$
$\gamma TiCl_3$	96	83	86	92	95	99
β-$TiCl_3$	62	56	62	70	—	86
$TiBr_3$	42	49	61	77	72	—
VCl_3	88	67	86	37·5	48	50
$CrCl_3$	15	17	—	60	—	—
$TiCl_2$	91	75	81	71	62	84

(°) Indicated as % of polypropylene not extractable by boiling *n*-heptane.

These comparison data among the different catalyst systems, however, do not agree with the hypothesis of simply monometallic stereospecific catalytic complexes. As is known, the structure of the crystalline substrate of the transition metal halide conditions the stereospecificity of the catalyst system. It is known, for instance, that violet $TiCl_3$ (α, γ and δ)—characterized by a layer lattice[19]—generally yields catalyst systems which are more stereospecific than those obtained from β-$TiCl_3$ (brown)[12]. This result, however, does not show that systems based on β-$TiCl_3$ contain a lower percentage of stereospecific catalytic complexes than those based on violet $TiCl_3$. Actually, in order to clarify this aspect, some information is necessary, e.g. on the rate of formation of the polymeric chains with different stereoregularity for the different catalyst systems.

We observed in some runs that in the systems based on β-$TiCl_3$, the rate of formation of the stereoregular chains is much lower than the corresponding one for the systems based on violet[12] $TiCl_3$ (*Figure 8*); on the other hand, the rates of formation of the atactic macromolecules in the two

systems probably are little different one from another. Therefore it cannot be *a priori* stated that the differences in overall stereospecificity between the two systems, depend on percent differences in the number of stereospecific catalytic complexes with respect to the total active centres.
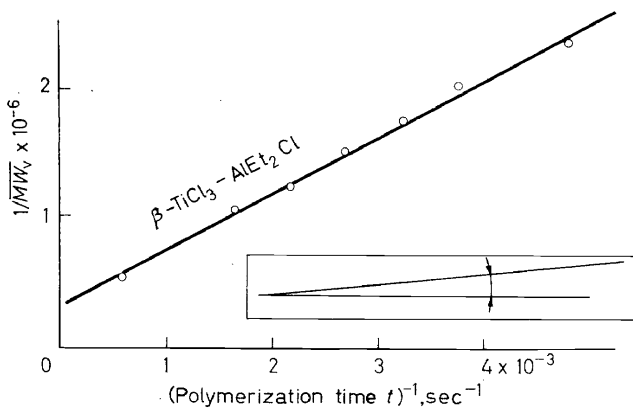

Figure 8. Reciprocal of the viscosity average molecular weight *vs.* the reciprocal of the polymerization time for isotactic polybutenes obtained at 0 °C by β-TiCl$_3$–Al(C$_2$H$_5$)$_3$. Comparison with the systems based on violet TiCl$_3$.C$_4$H$_8$:333 g/l. toluene [Inset: average slope for systems based on violet TiCl$_3$]

On the other hand, it must be observed that the use of a transition metal halide characterized by a crystalline layer lattice does not necessarily involve a high overall stereospecificity in the polymerization [see e.g. the data reported in *Table 2* concerning the system VCl$_3$–Al(C$_2$H$_5$)$_2$Cl]. It is, however, possible to obtain, also from β-TiCl$_3$, catalyst systems with a relatively high degree of stereospecificity, such as those containing Al(C$_2$H$_5$)$_2$I (*Table 2*)[12].

It must also be observed that the boiling *n*-heptane extractable fractions of polypropylene, obtained by the systems based on brown TiCl$_3$, contain relatively high percentages of syndiotactic product, which appears crystalline by x-rays[12]. Also this result suggests that each catalyst system considered here contains different types of active catalytic complexes.

The different total behaviour of the systems based on violet TiCl$_3$ and on brown TiCl$_3$ might be connected with the different reactivities of the two types of TiCl$_3$ with the organometallic compounds. For instance, brown TiCl$_3$, due to its lower lattice energy, might react more easily than violet TiCl$_3$, with a given organometallic compound to give organometallic complexes both on the surface and in solution.

STUDY OF THE STERIC IRREGULARITIES IN THE MACROMOLECULES

Nuclear magnetic resonance analysis threw more light on the structures of the different types of macromolecules contained in the crude polypropylenes that can be obtained by the stereospecific catalyst systems considered by us[20].

The most significant results obtained in this respect concerning the crude
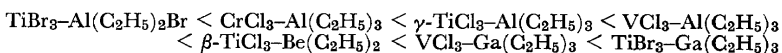
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polymers fractionated by ethyl ether extraction and subsequently by boiling *n*-heptane extraction can be listed as follows:

(1) The boiling ethyl ether extractable polymer fractions consist of amorphous macromolecules, although their stereoisomeric compositions are different depending on the catalyst system used (*Table 3*).

Table 3. Polymerization of propylene at 70°C

The catalyst systems are listed according to the increasing contents of inversion of steric configuration of the monomeric units in the ether fractions

$TiBr_3–Al(C_2H_5)_2Br < CrCl_3–Al(C_2H_5)_3 < \gamma\text{-}TiCl_3–Al(C_2H_5)_3 < VCl_3–Al(C_2H_5)_3$
$< \beta\text{-}TiCl_3–Be(C_2H_5)_2 < VCl_3–Ga(C_2H_5)_3 < TiBr_3–Ga(C_2H_5)_3$

(2) The boiling *n*-heptane extractable fractions generally consist of block macromolecules mostly of the isotactic type. However, block macromolecules of segments of the isotactic, syndiotactic and atactic type are also present in these fractions[12].

(3) The presence of stereoblock polymer containing syndiotactic segments, crystalline by x-rays, in the heptanic fractions is particularly high with some catalyst systems (e.g. systems containing brown $TiCl_3$ and $Be(C_2H_5)_2$ or $Ga(C_2H_5)_3$ (ref. 12). In other cases, the crystalline syndiotactic product is practically absent (e.g. for the polymer obtained by any system based on VCl_3)[12].

(4) The polymer left as residue after boiling *n*-heptane extraction generally consists of macromolecules either completely isotactic or containing long isotactic blocks[12].

These data first of all suggest that the catalyst systems considered contain different types of catalytic complexes, which respectively give rise to the formation of atactic, isotactic and syndiotactic macromolecules or segments. The relative percentage of these different complexes varies when passing from one catalytic system to the other, and does not only depend on the nature of the transition metal, but also on the alkylating and complexing powers of the organometallic compound used to prepare the system.

The presence of isotactic and syndiotactic stereoblock macromolecules, moreover, allows one to support Natta's hypothesis[9, 21] that for the isotactic catalytic systems here considered, the steric configuration of the monomeric units that polymerize is first of all conditioned by the asymmetry of the catalytic complex rather than by the structure of the monomeric unit previously entered in the chain, as supposed by other authors[22].

The fact that the catalytic complexes, stereospecific in the polymerization of α-olefins to isotactic polymers, must be intrinsically asymmetric is in agreement with the investigations carried out by P. Pino[23] on the polymerization of racemic α-olefins. This hypothesis is also in agreement with the preparation of optically active polymers from monomers that do not contain asymmetric carbon atoms, in the presence of asymmetric catalysts[24].

The hypothesis that, at least in some cases, the steric configuration of the monomeric units which polymerize depends more on the asymmetry of the

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catalytic complex than on the reacting unit, is also supported by the preparation of crystalline ethylene-*cis*-butene-2 alternating copolymers[25]. These polymers are of the *erythro*-diisotactic type; therefore all butene units polymerize with the same configuration even if one ethylene unit is inserted.

STERIC INVERSION PHENOMENA OF MONOMERIC UNITS

In order to improve our knowledge on the mechanism of formation of the non-completely isotactic macromolecules, which are found in the crude polymers of propylene, we systematically studied polymers obtained under different operating conditions by the catalyst system γ-TiCl$_3$–Al(C$_2$H$_5$)$_2$I[12, 26]. This system is the most stereospecific among those known so far for the polymerization of propylene to isotactic polymer[2]. The crude polymers were fractionated by subsequent extractions with boiling ethyl ether, *n*-heptane, and *n*-octane.

Measurements of the viscosity, molecular weight, conventional melting temperature, crystallinity by x-rays, and in some cases by n.m.r. analysis, were performed on the crude polymer and on the most significant fractions thus obtained.

Some significant results obtained in these runs are reported in the *Tables 4–6* which show that the percentage of ethyl ether extractable polymer is always relatively low. These products are partially (about 40 per cent)

Table 4. Polypropylene fractions obtained by γ-TiCl$_3$–Al(C$_2$H$_5$)$_2$I system
(Pressure 500–2000 mm Hg, γ-TiCl$_3$ 10–40 mmoles/l., Al/Ti 1 : 8)

Polymer. temp. (°C)	Ether extract (%)	Heptane extract (%)	Octane extract (%)	Heptane residue (%)
84	1·5–3	7–10	60–80	87–90
66	1·5–2	3–5	15–50	94–96
46	∼0·4	0·5–1	6–10	∼99
27·5	0–0·4	0·5–1	6–10	∼99

Table 5. Characteristics of polypropylene fractions obtained by
γ-TiCl$_3$–Al(C$_2$H$_5$)$_2$I system (see *Table 4*)

Polymer. temp. (°C)	Heptane extract†		Octane extract‡	
	Melting temp. (°C)	X-rays cryst. (%)	Melting temp. (°C)	X-rays cryst. (%)
84	149–155	70–75	∼170	74–80
66	151–155	70–75	∼168	74–80
46	145–150	not determined	165–170	74–80
27·5	150	63	170–172	74–80

† $\overline{MW}_v$ between <10 000 and 25 000.
‡ $\overline{MW}_v$ between 100 000 and 200 000.

Table 6. Characteristics of polypropylene residues obtained by
γ-TiCl$_3$–Al(C$_2$H$_5$)$_2$I system (see *Table 4*)

Polymer. temp. (°C)	Heptane residue†		Octane residue‡	
	Melting temp. (°C)	X-rays cryst. (%)	Melting temp. (°C)	X-rays cryst. (%)
84	170–172	75–80	173–174	∼78
66	170–171	75–80	∼172	75–80
46	172–173	75–80	173–174	75–80
27·5	173–175	75–80	174–176	75–80

† $\overline{MW}_V$ from 30 000 to 2 000 000 depending on the operating conditions.
‡ $\overline{MW}_V$ from 400 000 to 2 000 000 depending on the operating conditions.

crystalline (x-ray analysis). Their viscosity average molecular weight is about 10 000 and their melting temperature is 105–115°C.

The properties of the heptanic and octanic extracts are indicated in *Table 5* and those of the residues in *Table 6*.

We have demonstrated that the lower value of the melting temperature of the heptanic extracts is due both to the relatively low value of the molecular weight and to a lower steric regularity of the polymer.

The results obtained in this study have been quantitatively interpreted by calculating a coefficient of steric irregularity of the polymeric chains starting from their melting temperature. Calculations were done using the simplified equation originally proposed by Flory[27] for copolymers. With the aid of experimental data the influence of the molecular weight of the polymer on its melting temperature was also taken into account.

Although the coefficient of steric irregularity calculated does not represent the number of inversions of steric regularities along the polymeric chains, parallelism seems to exist between these two quantities.

Table 7. Coefficients of steric irregularity in polypropylene fractions
obtained by γ-TiCl$_3$–Al(C$_2$H$_5$)$_2$I system (see *Table 4*)

Ether extract	∼0·2
Heptane extract	0·05 – 0·1
Octane extract	0·02 – 0·05
Heptane residue	0·005–0·03
Octane residue	0·000–0·02

The coefficients of steric irregularity evaluated for the different fractions are indicated in *Table 7*. The data obtained can be correlated one with another by the relationship (see *Figure 9*):

$$n = A + B/p_{C_3H_6}$$

where
n = coefficient of steric irregularity
A, B = factors as function of temperature onlv
$p_{C_3H_6}$ = partial pressure of propylene.

This equation is identical with that already reported by us in a pre-liminary paper[28].

These results have been interpreted by admitting that the inversions of steric regularity of the monomeric units which polymerize are due to at least two processes: the rate of one depends on the polymerization temperature, and the other also depends on the olefin pressure. The first of these processes may be due to a variation of stereospecificity of the
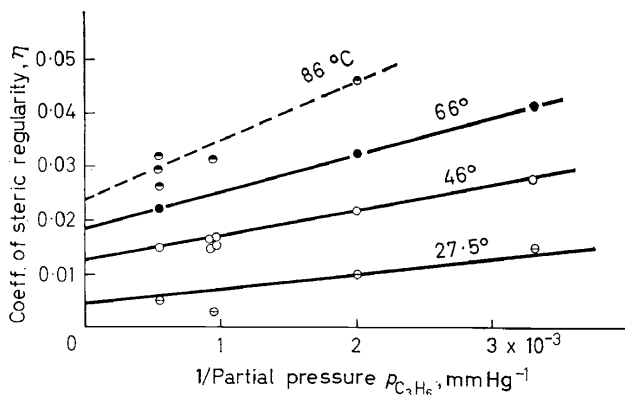

Figure 9. Coefficients of steric irregularity in crude polypropylenes obtained by γ-TiCl₃–Al(C₂H₅)₂I at different temperatures *vs.* the reciprocal of the partial pressure of the monomer

catalytic complex the polymeric chain grows on; alternatively, it may be due to a decomposition of the complex and subsequent dissociation of a part of it containing the growing chain, followed by the subsequent re-association of this part on another site in order to give a catalytic complex with a different stereospecificity with respect to the preceding one.

The hypotheses justify the formation of stereoblock polymers consisting of segments that contain monomeric units of different steric configurations. In our opinion, the process of steric configuration inversion, the rate of which also depends on the monomer pressure, is strictly connected with the growth of the polymeric chain on a given catalytic complex. According to this hypothesis, every monomeric unit during such growth might probably polymerize with an opposite steric configuration to that preferentially induced by the catalytic complex.

DISCUSSION

On the basis of the data reported so far, it is possible to put forth a hypo-thesis on the nature of the stereospecific catalytic complexes in the isotactic polymerization of α-olefins. The hypotheses put forward by us are very close to those already proposed by Cossee and Arlman[10, 29]; the most im-portant difference is that we think that the stereospecific catalytic complexes are, at least partially, bimetallic.

For convenience, we shall refer to the systems based on violet TiCl₃. In these systems, titanium is hexacoordinated. In agreement with several

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authors[2, 4, 13, 29, 30], we think that the catalytic complexes form on the side surfaces of the hexagonal crystals of $TiCl_3$, where Ti atoms are accessible. The coordination number of these atoms is lower than 6, due to the vacancy of some chlorine atoms. These vacancies should be necessary for the co-ordination of the olefin to the Ti atom of the catalytic complex.

The Ti–C bond of the complex, which is active in the polymerization, forms by a surface alkylation of $TiCl_3$ to $TiCl_2R$ by the action of the organo-metallic compound used to prepare the catalyst. Such a compound, or its derivative, would then be complexed to the surface $TiCl_2R$, thus stabilizing the Ti–C bond.

The catalytic complex thus obtained, therefore, might be of the same type as that shown in the *Figure 10*, where P = growing polymeric chain. The Ti atom of this complex is asymmetric. The complexation of the
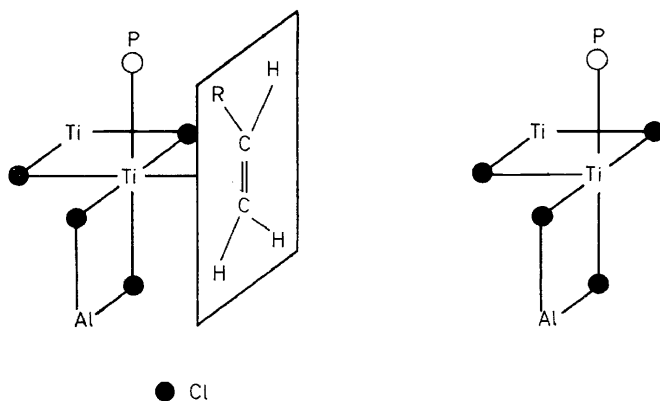
Figure 10. Schematic model of a stereospecific catalytic complex in the polymerization of α-olefins to isotactic polymers

monomeric units with such an atom before the polymerization always tends to occur by preferentially presenting the same face: thus, by sub-sequent polymerization, an isotactic polymeric segment is obtained.

According to our data, the rate of growth of the isotactic polymeric chains on the complexes considered is independent of the nature of the light metal atom present in the complex. Actually, we believe that such a metal stabilizes the Ti–C bond. Therefore, it can be assumed that the degree of stability and consequently of reactivity of such bond also depends on the nature of the light metal of the complex. These statements are not in contrast if we accept that the kinetic-determining step of the process of formation of the polymeric chains is the complexation of the monomer to the transition metal and not its insertion on the Ti–C bond.

CONCLUSIONS

The basic conclusions drawn by us from our investigations on the stereo-specific polymerization of α-olefins by Ziegler–Natta catalyst systems can be summarized as follows. (i) The polymeric chain grows by insertion of the monomeric units on a transition metal–carbon bond. (ii) The transition

metal in the catalytic complex is trivalent. (iii) In the catalytic systems prepared from a transition metal compound and from an organometallic compound, the stereospecific catalytic complexes are—at least partially—bimetallic.

These conclusions are valid both for the systems yielding isotactic polymers and for those yielding syndiotactic polymers of propylene. (i) The catalytic bimetallic complexes, which are stereospecific in the isotactic sense, are situated on the surface of the solid substrates. Their stereospecificity seems to be mainly due to their own asymmetry. (ii) The kinetic-determining step of the polymerization process to isotactic polymer seems to be is the complexation of the monomeric unit to the transition metal of the catalytic complex, before its insertion in the polymeric chain. (iii) The different catalytic systems, which are active in the polymerization of α-olefins to prevailingly isotactic polymers, contain different types of catalytic complexes, which can be either stereospecific, in the isotactic or in the syndiotactic sense, or not. Not all these complexes are necessarily on the surface of the solid substrate. The relative percentage of these different complexes particularly depends on the nature of the components of the catalytic system.

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