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Ziegler-Natta Catalysis

IV. The Stereospecificity in the Polymerization of Olefins and Conjugated Dienes in Relation to the Crystal Structure of $\mathrm{TiCl_3}(\alpha,\beta)$

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The principles on which our recent theory of stereospecific propene polymerization with α-$\mathrm{TiCl_3/AlR_3}$ was based, appear applicable to a much wider field. Not only can the molecular structures of diene polymers prepared with the same catalyst system be explained but also the change in molecular structure of polymers on variation of the crystal structure of the solid phase of the catalyst.

It is deduced from crystal chemistry that, whereas at the surface of the layer-lattice modifications of $\mathrm{TiCl_3}(\alpha,\gamma)$ only one kind of active center is present (α_{I}), there exist two kinds at the crystal surface of β-$\mathrm{TiCl_3}$, one with a single and the other with two chlorine vacancies (β_{I} and β_{II}).

From the structure of the active centers and their situation at the crystal surface it follows that (1) in the presence of α-$\mathrm{TiCl_3}$ monoolefins polymerize to isotactic products whereas conjugated dienes give *trans*-1,4 polymers; (2) in the presence of β-$\mathrm{TiCl_3}$ monoolefins can form polymer molecules ranging from fully isotactic to atactic, whereas conjugated dienes give mixtures of *trans*-1,4 and *cis*-1,4 polymers.

Theory and experiment appear to be in fair agreement.

I. Introduction

The theory of the stereospecific polymerization of propene with α-$\mathrm{TiCl_3/AlEt_3}$ proposed in preceding contributions (*1–3*) implies that the molecular structure of the polymer depends in a subtle but well-defined way on the structure of the active center and on its situation in the crystal surface. As these structural and textural features are intimately connected with the crystal structure, it is plausible that different modifications of $\mathrm{TiCl_3}$ should lead to polymers of different stereospecificity. This is indeed borne out by the experimental facts (*4*, *5*). The layer-lattice modifications (α- and γ-$\mathrm{TiCl_3}$) induce polymerization of propene to isotactic polymer and of butadiene to *trans*-1,4 polymer. The chain-lattice modification (β-$\mathrm{TiCl_3}$), however, converts propene into a product with a lower content of isotactic molecules, and butadiene into a mixture of *trans*-1,4 polymer and *cis*-1,4 polymer.

The present work endeavors to show that the same principles that furnished a detailed mechanism for the formation of isotactic polypropene provide a rational explanation of all facts mentioned above.

An essential argument of the theory is that the crystal surfaces of the $\mathrm{TiCl_3}$ modifications contain titanium ions incompletely coordinated by chlorine ions and therefore carrying one or more vacancies ($\square$). These surface sites, $\mathrm{TiCl_5}\square$ or $\mathrm{TiCl_4}\square_2$, on reaction with the alkyl aluminum compound will form the active centers $\mathrm{TiCl_4R}\square$ and $\mathrm{TiCl_3R}\square_2$, respectively. In the following the situations at the crystal surfaces of α- and β-$\mathrm{TiCl_3}$ will continually be compared. In the first section the surface structure of α-$\mathrm{TiCl_3}$, discussed formerly (*2*) will be summarized as a basis for dealing with the corresponding feature of β-$TiCl_3$. From the surface structure the properties of the active centers readily follow.

The second section will discuss the consequences of these structural features for the stereochemical course of the polymerization of propene. Finally it will be shown that the same factors, in combination with the specific properties of the conjugated dienes lead to an explanation of the structural phenomena in their polymerization.

II. SURFACE STRUCTURE AND ACTIVE CENTERS

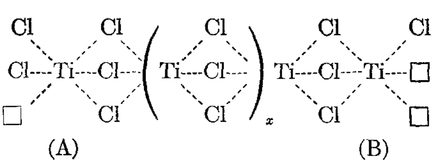
a. α-$TiCl_3$

In the α-$TiCl_3$ (2) lattice titanium ions are so arranged in the hexagonal close-packing of the chlorine ions that the crystal may be considered as built up of elementary sheets, each consisting of two chlorine layers sandwiching a titanium layer. These elementary sheets are perpendicular to the c axis and have the composition $(TiCl_3)_n$.

In view of the electroneutrality requirement part of the titanium ions in a sheet of finite dimensions will be surrounded by five chlorine ions and one chlorine vacancy. For energetic reasons the chlorine vacancies are located at the edges of the sheets. Calculations show that each titanium ion at the edge carries one chlorine vacancy and thus forms a potentially active site, $TiCl_5\square$. It follows that in the real crystal these sites will be found at faces formed by combination of sheet edges. Four of the chlorine ions of a $TiCl_5\square$ group are bound to a second titanium ion also; the fifth chlorine ion is linked to the central titanium ion only and therefore is loosely bound. The coordination sites of the loosely bound chlorine ion and of the vacancy, though both belonging only to the central titanium ion are, however, not equivalent. They differ in the number of surrounding chlorine ions.

b. β-$TiCl_3$

Whereas here too the chlorine ions form a hexagonal close-packing, the titanium ions are arranged in such a way that the crystal can be considered as built up of elementary chains parallel to the c axis, with the composition $(TiCl_3)_n$. Every chain contains a straight row of titanium ions, filling all octahedral interstices of the chlorine lattice along the row. A typical feature is that the chlorine ions belonging to a chain are coordinated directly with two titanium ions of the same chain but not with titanium ions of a neighboring chain. In view of the requirement of electroneutrality each chain should carry an average of three chlorine vacancies (2). For energetic reasons they will be found at the ends of a chain since it is there that chlorine ions are bound to one titanium. Thus the structure of an individual chain probably is



Apparently at the surface of β-$TiCl_3$ two kinds of surface sites are possible:

(A) The first type has one chlorine vacancy and two loosely bound chlorine ions. As a consequence it has a formal charge of

$$(3 - 3 \times \tfrac{1}{2} - 2 \times 1)e = -\tfrac{1}{2}e.$$

(B) In the second type there are two chlorine vacancies and one loosely bound chlorine ion, resulting in a formal charge of $+\frac{1}{2}e$.

Note that (A) differs from the $TiCl_5\square$ of α-$TiCl_3$, which has one loosely bound chlorine ion and whose formal charge therefore is zero.

The situation at the surface of the β-$TiCl_3$ crystal can be deduced in an analogous way as for α-$TiCl_3$ (2) from the structure and the habit of the crystal. β-$TiCl_3$ forms needles (6) with their longest dimension parallel to the c axis. Apparently the elementary chains are bundled in the way given schematically in Fig. 1. The crystal will have its main faces parallel to the c axis; these will exclusively contain chlorine ions. However, a crystal of finite dimensions will also have faces making an angle with the c axis. Geometrically this means that, reckoned from the outside to the inside, every chain will be longer than its predecessor by a certain number of $TiCl_3$ units, each consisting of a trigonal pyramid with three chlorines at its base and a titanium at its apex, as shown in Fig. 1.

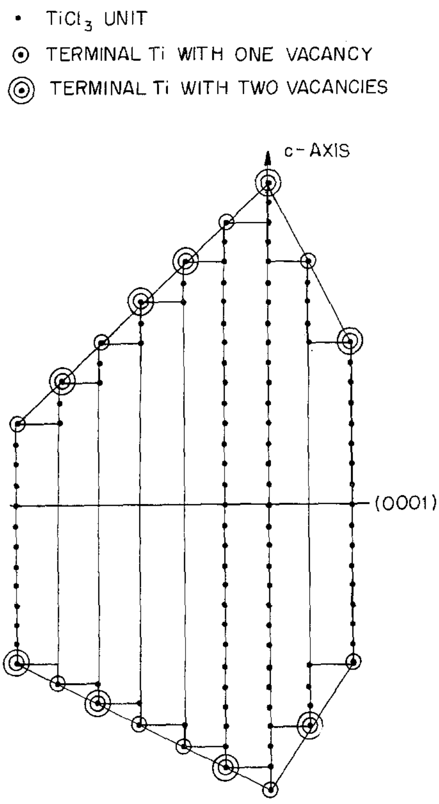


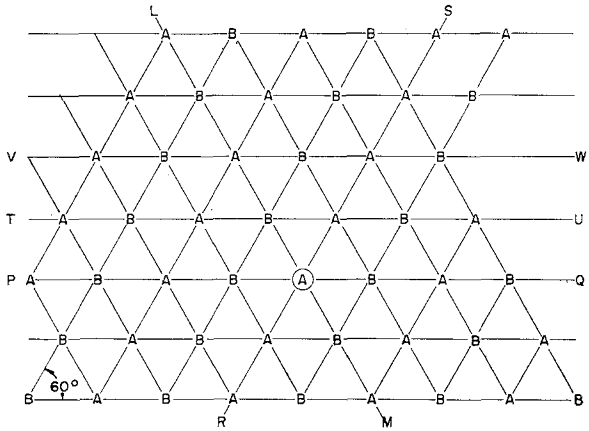
FIG. 1. β-$TiCl_3$ crystal; cut parallel to c axis.

At these faces there should be equal numbers of $TiCl_5\square$ (A) and $TiCl_4\square_2$ (B) in order to ensure over-all electroneutrality. Their distribution should be such that electroneutrality is attained within the smallest possible domain. The ideal distribution of equal amounts of opposite charges is that on a square array as realized for Na^+ and Cl^- at the (100) face of sodium chloride. The symmetry properties of β-$TiCl_3$ exclude the presence of such an array at its crystal surface. It will be shown, however, that it is possible to approach this ideal situation rather closely. Starting with a hypothetical (0001) plane with a distribution of (A) and (B) as given in Fig. 2(a), a crystal face making a sharp angle with the c axis can be built up by stacking $TiCl_3$ units onto (A) and (B) sites in (0001) according to a certain pattern. Suppose that, in Fig. 2(a) n $TiCl_3$ units are added per site along TU, 2 n along VW, and so on. The faces so obtained have the Miller indices $(n\ \bar{n}\ 0\ 2)$ on the basis of the elementary cell given by Natta *et al.* (7). How (A) and (B) will be distributed at these faces is shown schematically in Fig. 2(b). It appears that the greater the value of n, the larger the deviations of the distribution of opposite charges from the ideal square array.

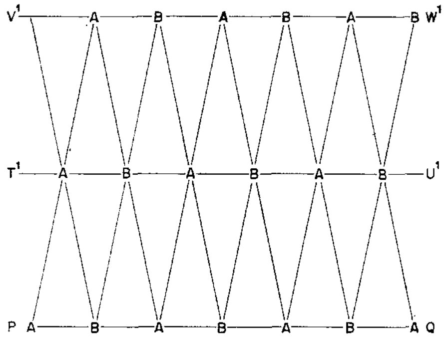
However, when the steps starting from (A) in Fig. 2(a) along the directions RS and LM are of unequal height $(n,\ p)$ faces are obtained with a more favorable (A), (B) distribution. Generally these faces have the Miller indices $[np(\bar{n} - \bar{p})2]$. In particular when $p = 1$ and $n = 3$, (A) and (B) form a nearly rectangular array. The angle between the rows in this array is 88° and the identity periods differ only by a factor of 1.24. Therefore it is assumed that this face $(3\ \bar{1}\ \bar{2}\ 2)$ will preferentially occur at the surface of β-$TiCl_3$ crystals. Figure 3, in which the loosely bound chlorine ions have been omitted, shows this practically rectangular arrangement of chain-end titanium ions.

Note that half of the chain-end titanium ions lie on top of a triangle of chlorine ions with a *corner* towards the outside of the crystal whereas the other ones have a *side* of the chlorine triangle protruding. Along one side of the rectangular array the situations are the same but they alternate along the other side and along the diagonals.

Figure 4 shows the same structure, but now with the loosely bound chlorine ions inserted. At sites (A) the two chlorine ions can be arranged in three ways on the three available coordination sites. At sites B the loosely bound chlorines may occupy three positions or possibly an intermediate position. No attempt has been made to find the thermodynamically most favorable position for the loosely bound chlorine ions. Figure 4 merely demonstrates the arrangement of the (A) and (B) active sites and shows that geometrically two kinds of (A) and two kinds of (B) sites are present depending on whether a corner or a side of the triangle protrudes.



(a) 0001 PLANE, ⊥ c-AXIS



(b) FACE MAKING A SHARP ANGLE WITH c–AXIS

Fig. 2. Faces of β-$TiCl_3$.

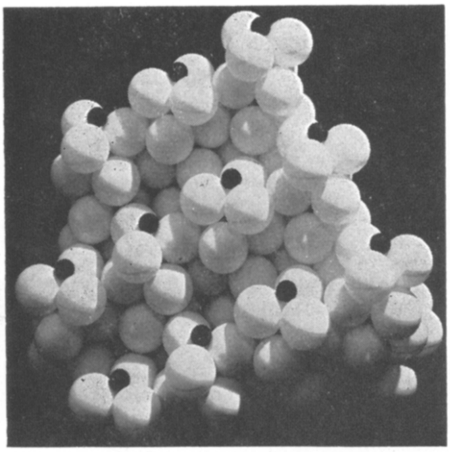


Fig. 3. Position of Ti in the (3 $\bar{1}$ $\bar{2}$ 2) face of β-$TiCl_3$. Loosely bound Cl omitted.

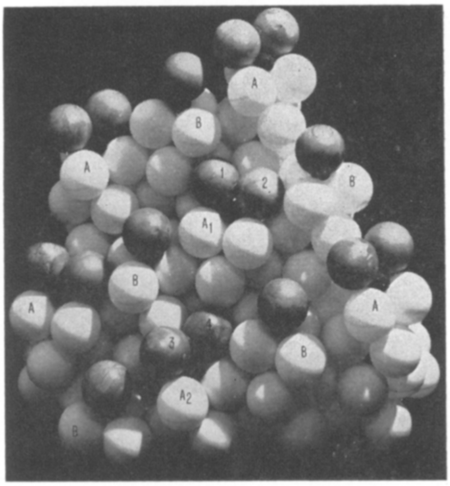


Fig. 4. The (3 $\bar{1}$ $\bar{2}$ 2) face of β-$TiCl_3$ with the loosely bound Cl (dark).

c. *Active Centers*

On the assumption that in all cases the essential function of the alkyl aluminum compound is the substitution of an alkyl group for a loosely bound chlorine ion, the properties of the active centers are easily found.

α-$TiCl_3$. The active center (α_I) is the octahedral unit $TiCl_4\square R$. All chlorine ions are firmly bound. The sites of □ and R are crystallographically nonequivalent (*3*).

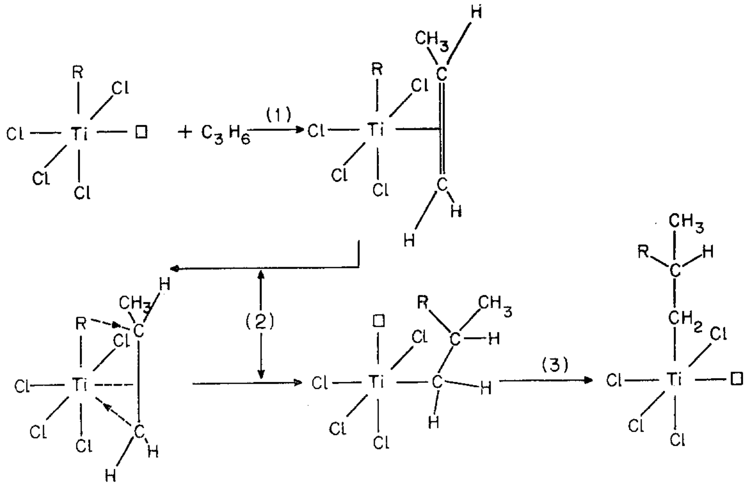
β-$TiCl_3$. A site (A) will be converted into an octahedral unit $TiCl_4\square R$. However, at this active center (β_I) three chlorine ions are firmly and one is loosely bound. In principle, therefore, the latter chlorine ion, the alkyl group, and the vacancy may change positions around the central titanium ion.

A site (B) will form the active center (β_{II}), $TiCl_3\square_2R$. All chlorine ions are firmly bound. Theoretically R has three coordination sites at its disposal. It might either easily change its coordination site or be imagined to occupy an intermediate position, giving rise to a nearly tetrahedral arrangement around the titanium ion.

III. THE POLYMERIZATION OF PROPENE

a. α-$TiCl_3$

The propagation is visualized (*3*) as proceeding according to the following scheme:



where (1) represents the chemisorption of monomer by π bonding. Owing to the situation of the active center in the crystal surface there is only one reactive position of the monomer that can lead to incorporation of the monomer according to reaction (2). As the sites of vacancy and alkyl group are not equivalent the newly formed larger alkyl group shifts back (3) to the favored position, thereby restoring the original stereochemical situation.

One thing is apparent already: When variations are induced in the steps described above by virtue of the specific properties of other active centers such as β_I and β_{II} a polymer of a different molecular structure may result.

b. β-$TiCl_3$

β_I centers. Theoretically R, the loosely bound Cl, and □ may be distributed in six different ways over the three coordination sites. These distributions may be classed in two sets: in one R, Cl, and □ are in clockwise, in the other in anticlockwise sequence. Interchanging the positions of R or Cl with □ reverses the sequence.

The two sets correspond to the two arrangements of R and □ at α_I. In the latter case the situation is unambiguous as soon as a favored position of R has been defined but in the case of β_I the problem arises of choosing between six arrangements. Even if it were possible to eliminate three or more of them this would not automatically mean that the remaining ones belong to one set. This reasoning already suggests that the presence of a loosely bound chlorine ion at β_I (difference with α_I) might entail nonidentity of successive incorporation steps and therefore lead to a polymer of irregular structure. However, to what extent this is true in practice will depend on the situation of the active centers β_I in the crystal surface.

Consider the active center which will be formed from (A_1) in Fig. 4. For steric reasons the coordination site of the vacancy on the outside of the crystal will be favored by the alkyl group. As the loosely bound Cl(1) has seven next chlorine neighbors and Cl(2) has six, Cl(1) might be removed preferentially. The active center then will be in a situation closely resembling that of the active centers α_I at α-$TiCl_3$ and isotactic polymer will be formed.

Energetically, however, the positions Cl(1) and Cl(2) do not differ greatly so that it is quite feasible for Cl(2) to be removed in the reaction with $AlEt_3$. Then the immediate surroundings are hardly asymmetrical so that two reactive positions of the propene molecule are possible; an irregular polymer will then be formed. Moreover, it is conceivable that the above situations pass into each other by a shift of Cl(1) to the site of Cl(2) and *vice versa* during the course of the polymerization reaction. At (A_2) with two coordination sites towards the outside the position of Cl(4) will be inaccessible to R for steric reasons; it will prefer one of the outside positions. For the remaining loosely bound chlorine ion this might also apply because at (4) it has eight next neighbors and at (3) only three. Then the propene would accommodate itself in a hole surrounded by five chlorine ions and an alkyl group; isotactic polymer would be formed. However, when during the polymerization the loosely bound chlorine should shift from (3) to (4) the situation would become favorable for the formation of irregular polymer.

Thus the conclusion seems warranted that there will be active centers β_I at which a single arrangement of R, Cl, and $\square$ is preferred, at least temporarily, but that there also will be active centers where several arrangements are equally probable. Then it only depends on the activation energy of the transition between these arrangements whether successively arriving propene molecules encounter sterically identical or different situations.

β_{II} centers. When propene is chemisorbed at the site of one vacancy its methyl group presumably will point towards the other vacancy and *vice versa*. As a reason can hardly be seen for the propene favoring one position above the other it is to be expected that the polymer formed at β_{II} will have a randomly irregular structure.

In view of the above it is to be expected that on the average considerably more atactic material will be formed with brown β-$TiCl_3$ than in the presence of the violet modifications α- and γ-$TiCl_3$. The fact that with catalyst systems containing "brown $TiCl_3$" as the solid phase, polymers ranging from low to medium isotacticity are formed may be related to the fact that these brown catalysts, which are generally prepared through reduction of $TiCl_4$ by alkyl aluminum compounds, contain a fair amount of $AlCl_3$ in solid solution (*8*). Though the bulk structure still may be that of β-$TiCl_3$ the surface structure may be different from that of pure β-$TiCl_3$. Moreover, even at room temperature these solids of β-$TiCl_3$ structure gradually transform into the γ-$TiCl_3$ structure (*8*). If the surface layers in particular should be involved in this transition a small degree of conversion would suffice for a radical change in the β/γ ratio at the surface and thus in the irregular/stereoregular ratio in the polymer.

IV. THE POLYMERIZATION OF CONJUGATED DIENES

In comparison with the α monoolefins, the conjugated dienes present the following new features:

(1) the possibility that one or both carbon–carbon double bonds are involved in π bonding of monomer with the transition metal;

(2) the appreciable double-bond character of the C_2–C_3 bond in conjugated dienes, which is the cause of their existing in two conformations, viz. single *cis* and single *trans*. It has been derived (*9, 10*) that for butadiene the energy difference between the s *cis* and the s *trans* is 2.3 kcal/mole so that under normal conditions s *trans* largely predominates. This is corroborated by electron diffraction (*11, 12*) and spectroscopy (*13, 14*).

a. α-$TiCl_3$

At the active center α_I, with its one vacancy, butadiene will be chemisorbed

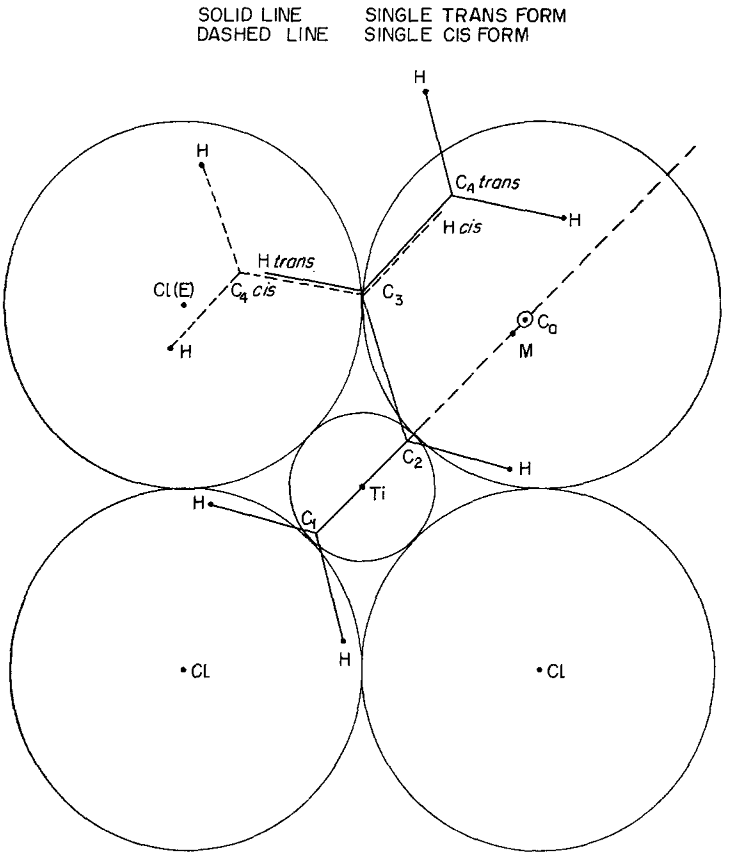


FIG. 5. Reactive position of butadiene at the active center α_I. The butadiene is projected perpendicularly onto the $TiCl_3R$ plane.

through one of its double bonds. The chemisorption complex is comparable to $Fe(CO)_4C_4H_6$ (*15*), where butadiene occupies one coordination site. The infrared spectrum of the latter complex reveals that only one double bond is used in π bond formation. For energetic reasons the conformation of the butadiene may be assumed to be *trans*. This contrasts with the complex $Fe(CO)_3C_4H_6$ (*16*), which shows no absorption typical for a free double bond. From X-ray diffraction (*16*) it appears that the diene occupies two coordination sites and is in the *cis* conformation, all its carbon atoms being equidistant from the Fe atom.

The assumption that butadiene is chemisorbed at α_I in the *trans* conformation by means of one terminal double bond (C_1–C_2) leads to the reactive position shown in Fig. 5. The plane of the butadiene is supposed to be parallel to that of the square $TiCl_3R$. Calculation on the basis of van der Waals and ionic radii shows that the distance between the two planes will be about 2.86 Å.* When in this reactive position the Ti–R bond is weakened as a consequence of the π bond formation, the first carbon of R, C_a, has not only the possibility to react with C_2—as in the case of propene—but it may also react with C_4. The essential argument is that C_a preferentially reacts with C_4 instead of with C_2 because the distance C_4–C_a in the chemisorption complex is shorter than C_2–C_a.

Once this is accepted it follows readily that *trans*-1,4-polybutadiene is formed. When C_a reacts with C_4 concertedly a new σ bond between Ti and C_1 is formed with

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* In the corresponding case of the *cis* conformation this distance would be 2.97 Å.

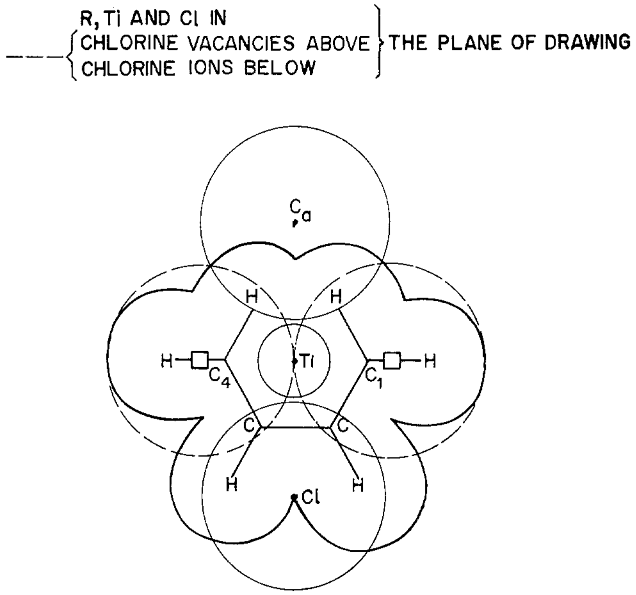


FIG. 6. Butadiene at an active center β_{II}.

conservation of the *trans* conformation of the monomer. Only occasionally will C_a add to C_2, causing the polymer to contain a few per cent of monomer units with vinyl groups as side chains. $C_4{-}C_a < C_2{-}C_a$ depends on the bond length Ti–C_a. It follows from simple geometry that it applies if Ti–C_a is greater than 2.15 Å, corresponding to the point M in Fig. 5.

No experimental data on the Ti–C_a distance in compounds of trivalent titanium are available, but a reasonable estimate can be based on data regarding $TiCl_3CH_3$. From its infrared spectrum the force constant (κ) of the Ti–C bond was calculated recently (*17*) to be $\kappa = 0.185 \pm 0.02$ Mdyne/cm. With the aid of Badger's formula (*18*), $\kappa^{-0.5} = 2.00(D_0 - 1.06)$, the equilibrium distance (D_0) for Ti–C is found to be $D_0 = 2.23 \pm 0.06$ Å.

Probably in a trivalent compound the Ti–C distance will be slightly larger so that Ti–C_a = 2.30 Å seems a fair estimate. The position of C_a in Fig. 5 is given in accordance with this. Apparently the above condition is fulfilled. With the distance between the butadiene plane and the $TiCl_3R$ plane of 2.86 Å the distances C_a–C_4 and C_a–C_2 are calculated to be 3.21 Å and 3.33 Å, respectively.

As a substantiation, results of Natta (*19*) and co-workers are mentioned. With α-$TiCl_3$/$AlEt_3$ polybutadiene containing 90% of 1.4-*trans*, 4% of 1,4-*cis*, and 6% of 1,2 units was obtained.

b. β-TiCl₃

β_I centers. It is to be expected that at β_I butadiene will be chemisorbed in the same way as at α_I. That in this case the subsequent reactive positions will not always be identical, owing to the mobility of R, Cl, and □ at the three available sites, is immaterial as long as the polymer does not contain asymmetric carbon atoms. Therefore at β_I centers *trans*-1,4 polymer will be formed.

β_{II} centers. The important feature of β_{II} is that it offers two coordination sites in the correct position for butadiene to be chemisorbed in the single *cis* conformation as a kind of bidentate ligand. The reactive position is assumed to be that given in Fig. 6. The plane of the butadiene is taken perpendicular to the bisector of the two free valencies of the titanium. Incorporation will again be due to weakening of the Ti–C_a bond under the influence of the π bond. C_a will add to a terminal carbon atom, say C_4, and concertedly a σ bond between Ti and C_1 will be formed with conservation of the

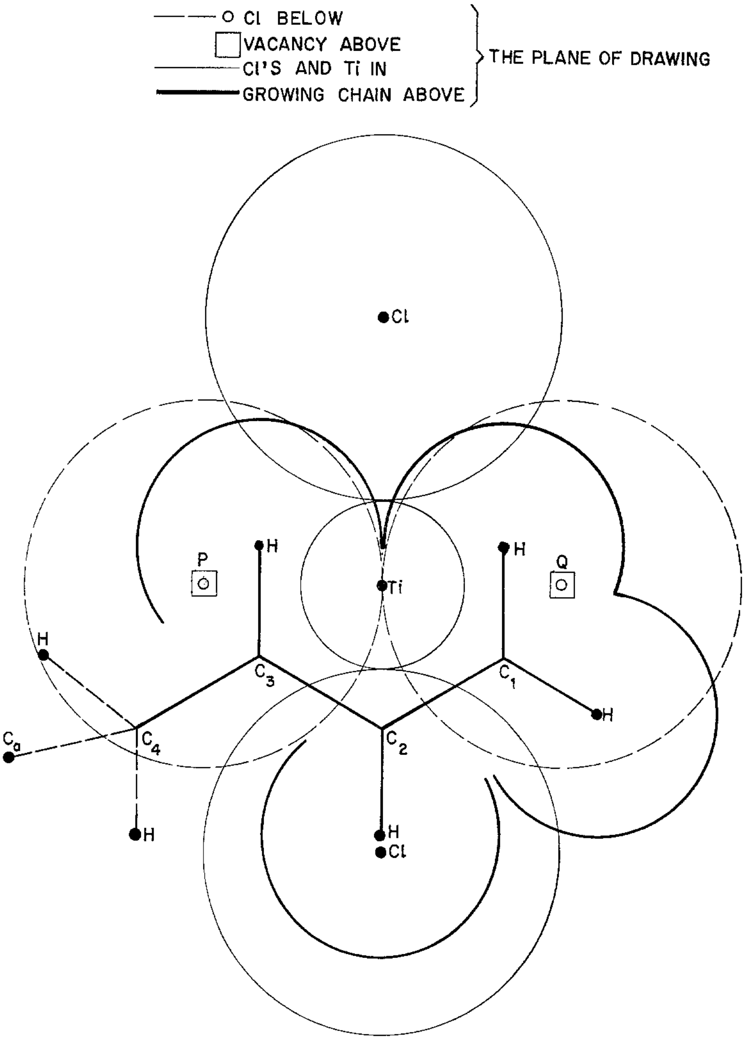
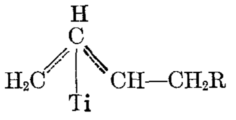


FIG. 7. π-Allyl complex of growing chain on an active center α_I or β_I.

cis form of the chemisorbed molecule. Thus at β_{II} *cis*-1,4 polymer is formed.

It follows that in the presence of β-$TiCl_3$, butadiene may be expected to give a mixture of *trans*-1,4 and *cis*-1,4 polymer. This is in accordance with results described by Natta (*20*). The product of the polymerization of 1,3-butadiene at 15°C with a system β-$TiCl_3/AlR_3$ could be separated by extraction into two-thirds having a *trans*-1,4 structure (>90%) and one-third having a *cis*-1,4 structure (>90%). Apparently the two kinds of active centers are largely independent of each other. This is understandable if we bear in mind the relatively large distances between the active centers at the crystal surface, which for the face represented by Figs. 3 and 4 are 6.90 and 8.70 Å.

Although the above mechanism adequately explains the formation of *trans*-1,4 polymer at α_I and β_I and of *cis*-1,4 polymer at β_{II} active centers, it is conceivable that the presence of a C–C in the growing chain in the "allyl" position with respect to the titanium should entail connection of the growing chain to the metal not by a σ bond, $Ti{-}CH_2{-}CH{-}CH_2{-}R$ (I) but by way of a π-allyl complex (II), as proposed by Natta and Porri (*21*). For situation (I) one coordination site of the



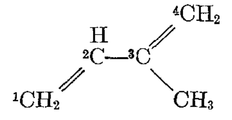
(II)

Ti is required whereas a complex as in (II) probably occupies two sites, as is shown in Fig. 7, for which the results of the X-ray investigations (*22, 23*) of $(C_3H_5PdCl)_2$ have been taken into account. The plane of the allyl group is taken perpendicular to the bisector of the two free valencies of the titanium. If the growing chain should be connected to the titanium in this way, it would have to be assumed that the monomer to be chemisorbed induces the allyl structure (II) to pass into the alkyl structure (I) prior to the above-described steps that lead to incorporation.

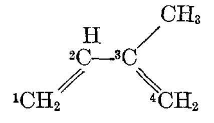
c. C_5 Homologs of 1,3-Butadiene

1,3-Butadiene being the simplest example of a conjugated diene, the question arises whether the mechanisms proposed also apply to its homologs. A full discussion of this problem is outside the scope of this contribution, the more so as generalizations in this field are extremely dangerous. Only a few remarks will be made regarding the C_5 homologs, viz. 3-methyl-1,3-butadiene-(isoprene) and 1,3-pentadiene (piperylene).

Under normal conditions the single *trans* conformation will be prevalent with these dienes too. For isoprene the conformations are simply

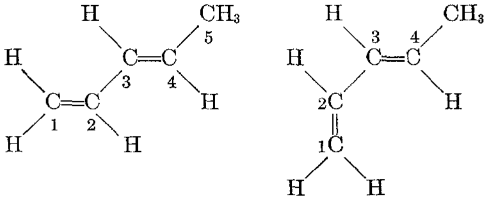


and



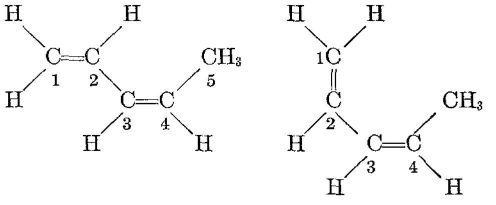
but in the case of piperylene ordinary *cis*–*trans* isomers exist so that four conformations have to be considered according to the scheme in the next column.

trans Isomer



(I) Single *trans* (II) Single *cis*

cis Isomer



(III) Single *trans* (IV) Single *cis*

For steric reasons conformation (IV) cannot be realized with all carbon atoms in one plane, so that it will hardly occur. In all cases it will be the C_1C_2 double bond that is involved at the α_I active centers of α-$TiCl_3$. The C_4C_3 double bond carries two bulky groups; this will sterically prevent the formation of the chemisorption complex in this position. This hypothesis is supported by the fact that 2-methylpropene (isobutene) and butene-2 (*cis* and *trans*) do not polymerize.

Although the presence of the methyl group will prevent isoprene in its single *trans* conformation from approaching the Ti of the active center as closely as butadiene, its reaction in the presence of α-$TiCl_3$ does lead to *trans*-1,4 polymer (*19*).

When the *trans* isomer of piperylene is polymerized it will be chemisorbed in conformation (I). Reaction with the alkyl group of the active center at C_4 then leads to *trans*-1,4 polymer with a fixed configuration at C_4: The product is an isotactic *trans*-1,4 polymer. When the *cis* isomer of piperylene is polymerized it will be chemisorbed in its conformation (III). The only difference with (I) is that now the methyl group (5) points towards the alkyl group of the active center instead of away from it.

However, this situation is not seriously hindered sterically; in the neighborhood of the methyl group of (III) the growing chain consists of $Ti–CH_2–CH=CH$ and therefore is not bulky. So, with the *cis* isomer too, isotactic *trans*-1,4 polymer is expected to be

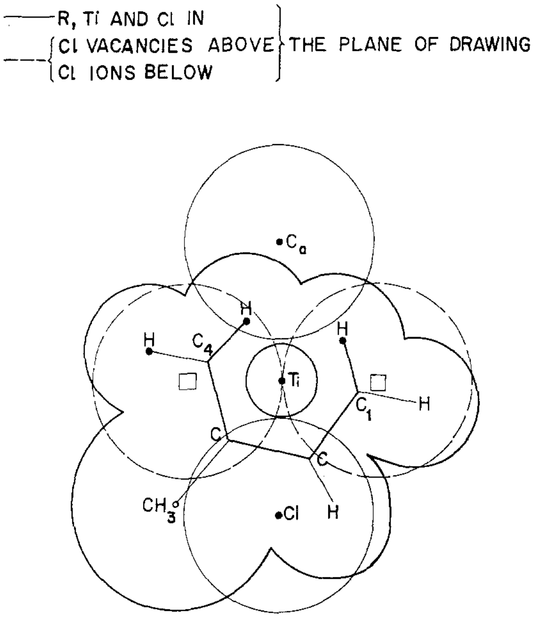


FIG. 8. Isoprene at an active center β_{II}.

formed. If a mixture of *cis-* and *trans-*piperylene is used, the monomer in conformations (I) and (III) will be incorporated randomly so that a 1,4 polymer with an irregular arrangement of the methyl groups is obtained.

The above is in agreement with the experimental evidence given by Natta and coworkers (*23*) for piperylene in a catalyst system containing VCl_3 (isomorphous with α-$TiCl_3$). The polymers from the *trans* and the *cis* isomer were identical and melted at 95°. With mixtures of *cis-* and *trans-*piperylene 1,4 polymers with lower melting points were obtained.

Extension of the discussion of the polymerization of butadiene in the presence of β-$TiCl_3$ to isoprene and the like makes one expect that at the β_I centers *trans-*1,4 and at the β_{II} centers *cis-*1,4 polymer will be formed. At β_{II} the bulky methyl group might cause the chemisorption complex (Fig. 8) to be less symmetrical than that of butadiene (Fig. 6). In consequence R might be envisaged as likely to react preferentially with C_4 so that the *cis-*1,4 polymer formed would have the methyl groups in regular positions along the chain. In conformity with the above, catalyst systems containing "brown $TiCl_3$" in general produce a mixture of *trans-*1,4 and *cis-*1,4 polyisoprene (*4*, *5*). However, with pure β-$TiCl_3$ predominantly *cis-*1,4 is formed (*19*).

The explanation of the variation of the *cis/trans* ratio in the polymer in dependence on the diene and the catalyst system (*19*, *25*) is a problem now being studied.

V. CONCLUDING REMARKS

It is emphasized that the theory presented deals with well-defined catalyst systems. They are supposed to contain pure $TiCl_3$ crystals of the ideal structure, reacting with alkyl aluminum compounds, exchanging chlorine against an alkyl group. That in quite a few cases polymerization takes place in accordance with the schemes proposed is viewed as an indication of the essential correctness of the approach. However, in practical systems deviations from ideal behavior might be encountered owing to compositional and/or structural impurity of the transition metal compound, to reactions with the alkyl aluminum compound going further than mere alkylation, to addition of foreign compounds reacting at the active sites or centers or with the alkyl aluminum compound, etc. Still more complications may arise when the solid phase is prepared *in situ;* then its composition, structure, and

TABLE 1

Crystal Structure of Catalyst and Molecular Structure of Polymers

Crystal structure of catalyst	Active centers			Structure of polymers	
	Composition	Location	Characteristics	α Olefins	1,3-Diolefins
Layer lattice $\mathrm{TiCl_3}$ (α,γ)	$\mathrm{TiRCl_4}\square$ (α_{I})	Edges of elementary sheets	1. All Cl firmly bound 2. Sites of R and □ nonequivalent	Isotactic	*trans*-1,4
Chain lattice $\mathrm{TiCl_3}$ (β)	$\mathrm{TiRCl_4}\square$ (β_{I})	Ends of elementary chains	1. One Cl loosely bound 2. R preferentially at outer site 3. Sites of $\mathrm{Cl_L}$ and □ nearly equivalent	Varying from atactic to isotactic	*trans*-1,4
	$\mathrm{TiRCl_3}\square_2$ (β_{II})	Ends of elementary chains	1. All Cl firmly bound 2. Sites of □'s equivalent	Atactic	*cis*-1,4

available surface will depend on the nature of the procatalysts and their reaction conditions. It is believed, nevertheless, that the present theory can serve as a background for the explanation of the effects of the numerous variables of the catalyst systems mentioned above.

The rationalizations obtained so far in this series of publications are summarized in Table 1.

It demonstrates that on the basis of a few principles a considerable amount of facts in the field of stereospecific polymerization of olefins can be explained in a consistent way.

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