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Ziegler-Natta Catalysis III. Stereospecific Polymerization of Propene with the Catalyst System $TiCl_3$-$AlEt_3$

E. J. ARLMAN AND P. COSSEE

From the Koninklijke/Shell-Laboratorium, Amsterdam, Holland

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The stereospecificity of the polymerization of propene under the influence of α-$TiCl_3$ and alkyl aluminum compounds is explained. The explanation rests exclusively on quantum chemical principles and the crystal chemistry of transition metal trichloride layer structures, subjects described in two preceding papers.

The active centers formed by alkylation of titanium ions at those faces of the surface where chlorine vacancies are available are shown to possess the asymmetry necessary for the appropriate orientation of the α olefin in the π complex with the exposed titanium.

The nonequivalence of the crystallographic sites of vacancy and alkyl group at the active center ensures that the growing alkyl group will move back to its original position after each incorporation of a new monomer.

Thus the polymerization consists of a sequence of sterically identical steps which leads to isotacticity of the product.

I. INTRODUCTION

When propene is polymerized with a catalyst system consisting of α-$TiCl_3$ and $Al(C_2H_5)_3$, highly stereoregular polymers are obtained. The configuration of the asymmetric carbon atoms appears to be the same throughout one polymeric chain (*1*). Natta (*2, 3*) has already pointed out that in this particular process a solid catalyst is required. He drew attention to the fact that the various modifications of $TiCl_3$ (α, β, and γ), when used as catalysts in the polymerization of propene, yield products differing in percentage of isotacticity. The highest stereoregularity was obtained when well-crystallized α-$TiCl_3$ was used.

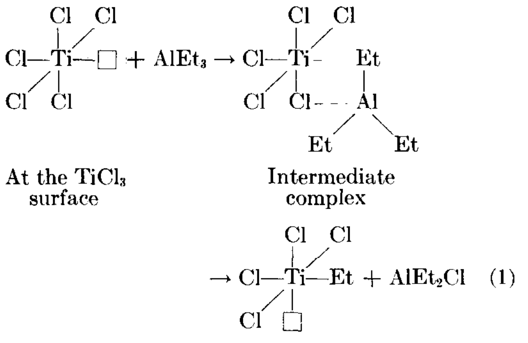
The importance of the particular crystal structure of the solid catalyst was stressed also by Patat and Sinn (*4*) and by Fontana and Osborne (*5*). Theories explaining stereoregularity in terms of hydrogen bonding between alkyl groups and halogen ions have been developed (*5, 6*); various investigators (*7, 8, 9*) have proposed models in which the steric repulsions between substituents on the asymmetric carbon atom already incorporated and on the newly entering one play an important rôle, whereas Topchiev *et al.* (*10*) presume that the regularity of the crystal surface by itself is sufficient to explain stereoregularity. Boor (*11*) was the first to put forward the theory that chlorine vacancies at the surface of transition metal halides play an important rôle in stereospecific polymerization. He worked out this idea in some detail for a bimetallic propagation mechanism (*12*).

In previous work (*13, 19*) an explanation for stereospecificity in terms of a monometallic mechanism was given. The active center was postulated to be a pentacoordinated titanium ion. Four corners of the octahedron around the central titanium ion are occupied by chlorine ions, on the fifth corner is an alkyl group (growing chain), whereas the sixth position is vacant and allows of the accommodation of a monomer molecule. The first contribution of this series (*14*) (to be referred to as paper I) described the reaction at such an active center in terms of molecular orbitals. The second contribution (*15*) (to be referred to as paper II) gave a detailed analysis of the number of pentacoordinated titanium ions and of their preferred location at the surface of α-$TiCl_3$ crystallites. General characteristics of the geometry around these exposed titanium ions were derived.

In the present contribution the stereospecific polymerization of propene is discussed making use of the concepts developed in papers I and II. It relates the formation of isotactic polymer to the structure of the $MeCl_3$ layer lattice and to the location of and the symmetry around pentacoordinated Ti ions at the surface of the crystallites.

II. The Active Center

On the basis of the view that on the surface of the layer-lattice crystals chlorine vacancies are present (paper II) the formation of active centers may be assumed (*16*) to consist of alkylation of the pentacoordinated Ti ions according to:



This reaction is considered to represent the essential rôle of the trialkyl aluminum in these catalyst systems. The feasibility of reaction (1) was demonstrated by the study of the interaction of crystalline $ScCl_3$ with $ZnEt_2$ (labeled by Zn^{65} and C^{14}) in isooctane solution. After careful elimination of the excess of zinc diethyl by repeated washings the crystalline residue was found to contain Et and Zn at a ratio substantially higher than two (*17*). This proved that the scandium chloride had been alkylated at its surface.

Additional evidence for the assumption that a partly alkylated surface of a transition metal compound is essential for catalytic activity is provided by the investigation of the catalyst system $TiCl_2$–azo compound (*18*). When a small amount of 4,4′-azoheptane is deposited on the surface of $TiCl_2$ powder, the latter becomes catalytically active for ethene polymerization after the azo compound has been decomposed by gentle heating; typical Ziegler polyethene is formed at atmospheric pressure at 100°C. Apparently the radicals $(C_3H_7)_2\dot{C}H$ oxidize Ti(II) at the surface to form Ti(III)-$CH(C_3H_7)_2$ as the catalytic species.

It is further remarked that reaction (1) does not involve reduction of the trivalent transition metal ion. Indeed reduction is not essential for catalytic activity as suggested by the study of the system $ScCl_3$–$AlEt_3$ (*16*). In the case of $TiCl_3$ it might occur to a minor extent, resulting in additional active centers or in some titanium ions having two chlorine vacancies. We will assume that under normal conditions reduction is only of secondary importance. Equation (1) suggests that the number of active sites should be of the same order of magnitude as the number of naturally available chlorine vacancies at the crystal surface. This is borne out by the reasonable agreement between the number of chlorine vacancies calculated (*15, 16*) for crystals of 1 μ, 1.4×10^{-3} eq/mole, and the number of active sites determined radiochemically (*2*) for $TiCl_3$ crystals of similar size, 6×10^{-3} eq/mole.

The crystallographic location where reaction (1) takes place obviously will be that where chlorine vacancies are already present. In paper II it has been shown that the vacancies should occur preferentially not at the usually best developed face (0001) of the layer lattice crystals but at the other faces, formed by the combined edges of the elementary crystal sheets. It further has been argued that of the five chlorine ions around an exposed titanium ion one is always loosely bound, being attached directly only to one Ti ion. Therefore this ion will be removed in reaction (1). As the remaining four chlorine ions, which are attached directly to two Ti ions, are firmly bound, only the sites of the loosely bound chlorine ion and of the vacancy are available for the alkyl group and the monomer participating in the propagation step. These sites, however, are not equivalent (paper II). This important fact is demonstrated in Fig. 1. The black sphere in Fig. 1a has four and that in Fig. 1b seven of its twelve surrounding sites occupied. If we draw the plane of the crystal surface through ions 1, 2, and 3 the alkyl group in Fig. 1b lies in that plane but that in Fig. 1a outside it.

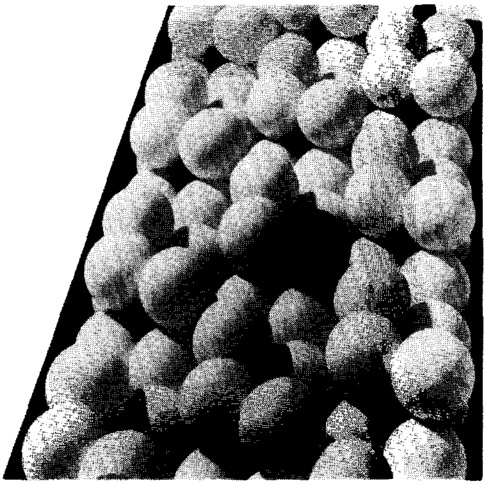


Fig. 1a.

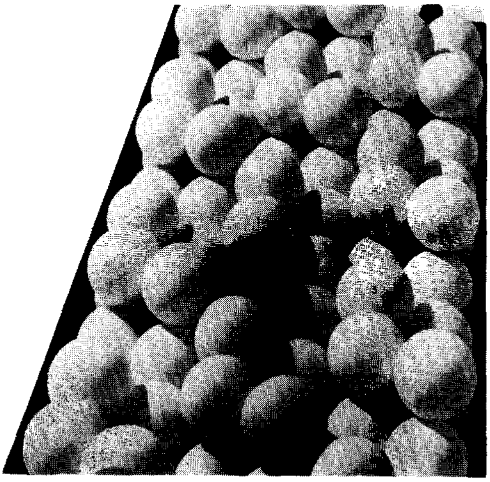


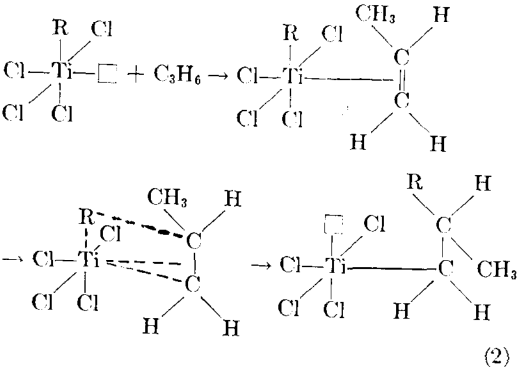
Fig. 1b.

Fig. 1. Nonequivalence of the sites of alkyl group and chlorine vacancy in model C_{II} of $(10\bar{1}0)$. Black sphere represents an alkyl group.

The active center thus emerges as consisting of a square base having three chlorine ions and the alkyl group at its corners and the titanium ion in the middle. This square is anchored by the fourth chlorine ion to the inside of the crystal and carries a vacancy at its outside. The plane of these square bases always includes an angle of 54°44′ with (0001) and therefore in most cases is in an oblique position towards the other crystal faces. As a consequence two of the chlorine ions of the square base lie more to the inside of the crystal and thus are more or less blocked whereas one lies more to the outside and is to a certain extent exposed.

III. Mechanism

In paper I it was postulated that a propene molecule reacts at the active center according to:



(2)

If we postulate that the reaction can only proceed provided the C=C double bond is parallel to the titanium-carbon bond (see paper I) this gives us four alternatives for the position of the propene molecule. Of these, two are ruled out for steric reasons, because they would require space for the bulky CH_3 over the blocked chlorine ions, which is not available.

Looking down on the square base around an exposed titanium ion (Fig. 2) one readily verifies that the plane perpendicular to

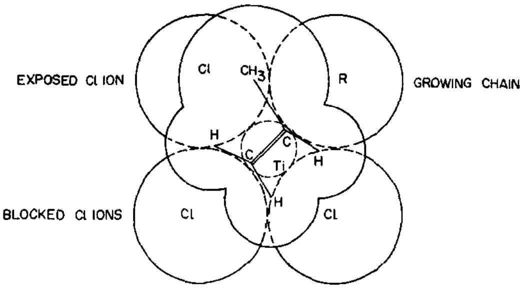


FIG. 2. Reactive position of propene on an active center. The propene molecule is projected perpendicularly onto the $TiCl_3R$ plane.

this square base and going through the titanium–carbon bond is not a plane of symmetry, because the exposed and the corresponding blocked chlorine ion differ in their surroundings. Hence for the reacting propene molecule the two remaining orientations are not equivalent. In one of them the methyl group would cover a blocked chlorine ion for the greater part. However, this will be practically impossible because of the steric hindrance of the surrounding chlorine ions. In the other orientation the methyl group of the propene will protrude out of the crystal; consequently this will be the preferred one (Fig. 2).

In the above way one requirement for stereoregular polymerization, viz. the fixation of the monomer at the active center exclusively in one orientation, is fulfilled. For the special case of isotactic polymerization a second requirement is that the process consist of identical steps.

Equation (2) shows that after the incorporation of the monomer the alkyl group and the vacancy have changed sites. However, these two sites were shown above not to be equivalent (Fig. 1). Therefore we may assume that one of them is preferred and that consequently after one propagation step the alkyl group will move back to the favored position so that the process may be continued with a step identical to the previous one.

Two remarks should be made in relation to this supposition:

a. There is ample time for the alkyl group to move to the favored octahedral position in between two successive growth steps since the kinetics indicate that on the average most of the active sites are not occupied by propene (see paper I).

b. The two nonequivalent octahedral positions belong to rows in the cation lattice that have different distances to the solid and undisturbed part of the lattice. One position is nearly embedded in a surface of chlorine ions while the other is more prominent (Fig. 1). We may assume that the latter is the favored one since the nonpolar alkyl group will prefer being as much as possible in the nonpolar hydrocarbon medium in which the reaction is carried out.

The production of isotactic polypropylene according to reaction (2) thus follows in a logical way from the particular structure of the surface of $TiCl_3$ crystals and the direct environment of the pentacoordinated titanium ions therein.

IV. DISCUSSION

It is worth while to compare the present approach with that of a previous paper (*19*) in which the stereoregular reaction was discussed for the case in which the cation vacancies were situated in the (0001) faces of the crystal. There the positions of vacancy and alkyl group were equivalent. However, the monomer did not occupy equivalent positions in two successive steps. Actually one of these appears to be rather unfavorable for reaction since the C=C double bond and the Ti–alkyl bond are perpendicular to each other (see Fig. 4 of ref. *19*).

An adjustment in the sense of the present contribution is easily introduced. Since the monomer orientation with the C=C direction perpendicular to the Ti–C direction is not favorable for reaction nothing will happen and the monomer will eventually leave the vacancy. No reaction will take place until the alkyl group has migrated to its original position; after that a second step identical to the previous one will be possible, thus preserving isotacticity of the product also when formed at active sites in the (0001) faces. There are still, however, some disadvantages to this picture. As mentioned earlier the positions of vacancy, alkyl group, and all of the chlorine ions are equivalent in a (0001) face. In the time between two successive steps, not only may the alkyl group make the required jump to the neighboring vacancy, but conceivably a chlorine ion may also move into the vacancy. A sequence of such chlorine jumps may result in inversion of the symmetry of the active center or even loss of the active site, if alkyl group and vacancy should become separated.

The present picture, however, with active centers at the faces formed by layer edges excludes chlorine jumps. At these locations a jumping chlorine would have to move from an energetically favored site, where it is bound to two titanium ions, towards an unfavorable site, where it is only bound to the one titanium of the active center. Therefore the active sites at other faces than (0001) are expected to possess particularly stable configurations and reactions will be confined to sites of a vacancy and an alkyl group that belong to one Ti ion.

Another advantage of the present theory is that the postulated location of the chlorine vacancies at other crystal faces than (0001) is in agreement with microscopic observations (*20, 21*), which shows that polymerization does not occur on the $TiCl_3$ platelets but at their edges.

It should be stressed, however, that the explanation of the other features discussed previously (*19*), such as the rôle of Al alkyl in chain transfer and its influence on the degree of isotacticity, the specificity for α olefins, and the explanation of diisotacticity, remains valid.

A second comparison which suggests itself is with the theory of Boor (*12*), since this is the only other one taking the structure of α-$TiCl_3$ and the presence of vacancies explicitly into account.

Boor also makes use of the concept of vacancies on the edge of a crystal sheet. In discussing stereoregularity this author considers the edge of a single sheet only and consequently needs the steric influence of the Al alkyl which is thought to be present as a bimetallic complex with the active titanium ion. In our opinion an active site at the edge of a single sheet will give rise to an atactic polymer. Combination of sheet edges to a face is necessary in order to explain the orienting influence of the site symmetry on the incoming monomer molecule.

With the present approach also syndiotacticity can be fitted into the picture. When the rate of migration of the alkyl group to its original position is lowered and the coverage of active sites is increased, it becomes possible for a new monomer molecule to react before the alkyl group has migrated. When the same rules for steric hindrance are applied as in the case discussed in Section III the configuration around the new asymmetric carbon atom will be the mirror image of that around the previous one. It is in this way understandable that under suitable conditions, e.g. at very low temperatures, syndiotactic material may be formed.

The present contribution (III) completes the exposition of a theory of polymerization of α olefins by means of heterogeneous Ziegler-Natta catalysis. It shows that in terms of quantum chemistry (see paper I) and of crystal chemistry (see paper II) a logical picture of the main features of this type of catalysis can be given. Also when the present picture would in some details need modification in the future, its principal characteristics seem correct and of general validity. At any rate the way of thinking introduced may be fruitful for heterogeneous catalysis in general.

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