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THE FORMATION OF ISOTACTIC POLYPROPYLENE UNDER THE INFLUENCE OF ZIEGLER-NATTA CATALYSTS

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IN a previous publication [1] on the mechanism of the ethylene polymerization with heterogeneous Ziegler-Natta catalyst systems it was pointed out how an ethylene molecule is interposed between a Ti-ion and an alkyl group. The active center of the catalyst in the growth reaction was considered to be a Ti-ion in the surface layer of α-$TiCl_3$ of which one octahedral position is occupied by an alkyl group and another octahedral position is empty (chlorine vacancy). In this way a hole in the surface layer of the chlorine lattice is formed adjacent to the alkyl group. A monomer molecule can be incorporated in this hole and by means of a π-bond it can be attached to the alkyl-bearing Ti-ion.

Besides providing a better understanding of the driving force of the growth reaction and the possibility to explain the unique position of Ti and its neighbouring elements in producing the most active catalysts, the proposed

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[1] P. Cossee, Tetrahedron Letters No. 17, 12 (1960).

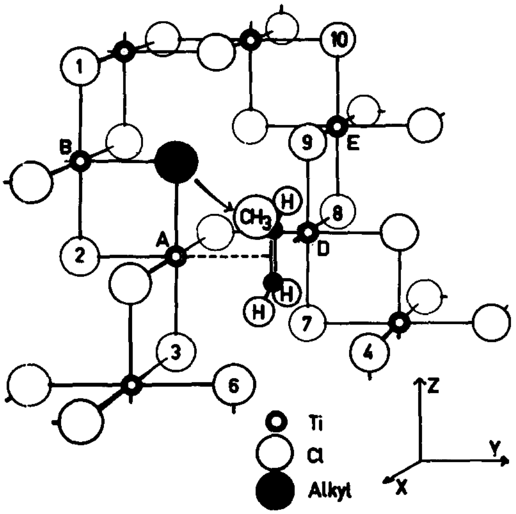

Fig. 1 Schematic drawing of part of the α-$TiCl_3$ lattice showing "active center" with monomer C_3H_6-molecule in Cl-vacancy

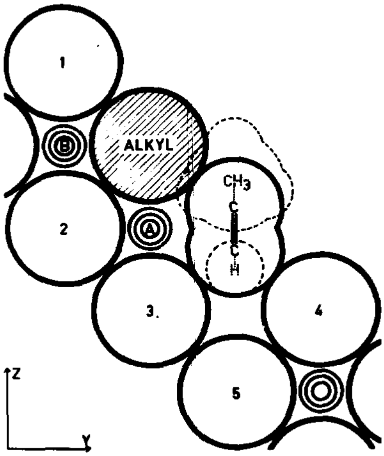

Fig. 2 ZY-Cross-section through reacting monomer

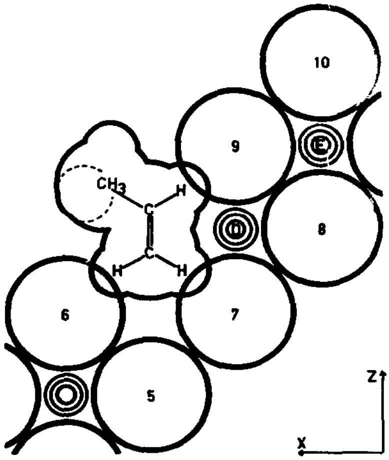

Fig. 3 XZ-Cross-section through reacting monomer

mechanism accounts for the formation of isotactic material when propylene is polymerized under the influence of α-$TiCl_3$ and Al-alkyls. It has already been pointed out by Natta[2] that the crystal structure of the solid phase is of direct importance for the stereospecificity of the reaction.

In order to understand this specificity the situation at the surface of α-$TiCl_3$ must be considered in some detail. This is done in Figures 1, 2 and 3. Figure 1 is a three-dimensional schematic picture of a $TiCl_3$ lattice with the active Ti-ion carrying the alkyl group R and a molecule of C_3H_6 inserted in the chlorine vacancy in the right orientation to form a π-bond with the active Ti-ion (for a discussion of the π-bond see ref. 1). Only the relative positions of the nuclei are given. Figs. 2 and 3 are cross sections through the monomer in the Cl-vacancy parallel to the YZ and XZ planes of Fig. 1 respectively. In Figs. 2 and 3 the Van der Waals radii are drawn to scale in order to demonstrate how the monomer molecule exactly fits into the chlorine vacancy. (Corresponding Ti- and Cl-ions in the various figures are indicated by the same letter and number respectively.)

Fig. 3 demonstrates that as a consequence of the bulkiness of the methyl group in the propylene molecule the only possibility to insert the monomer into the hole is with the CH_2-group pointing into the lattice. This explains why the polymerization is exclusively a "head-to-tail" one. Figure 3 also demonstrates that, once the notion of a CH_2-group pointing into the lattice and a CH_3-group protruding out of the surface is accepted, only two different orientations of the monomer are possible: one as shown in Fig. 3, the other with the C=C double bond horizontal. In the $TiCl_3$ lattice, however, one third

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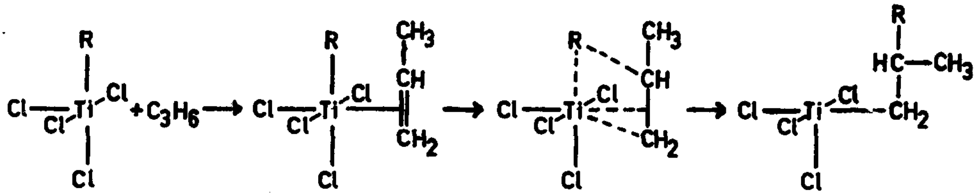
[2] G. Natta, J. Polymer Sci. 34, 21 (1959).

of the available octahedral metal positions in an occupied layer is empty (see Fig. 1). This means that in the orientation indicated in Fig. 3 the CH_2-group is pointing into an empty octahedral hole of the lattice, whereas in the other possible orientation this CH_2-group would be pointing towards another titanium ion.

Although it is theoretically not yet predictable which of the two non-equivalent orientations is favoured, we may assume that one of them is preferred. The orientation of each reacting monomer is thus completely fixed.

When according to the reaction scheme



described in the previous publication [1] the alkyl group R has migrated to th $C\begin{matrix}H\\CH_3\end{matrix}$ - group of the propylene monomer, the active Ti-ion retains both an alkyl group and a vacant coordination position which have, however, mutually chang place. The alkyl group R' is one unit larger and the configuration at the ne asymmetric carbon atom (in the situation drawn in Figs. 1, 2 and 3) is such that seen from Ti into the growing chain the sequence $CH_3 \rightarrow H \rightarrow R$ is in a clockwise order.

If now the reaction proceeds by introduction of the next monomer molecule into the new vacant position this monomer will again prefer to point its CH_2-group towards the <u>empty octahedral metal position</u>. The pattern of Ti in α-$TiCl_3$ is now such that after the interposition of the monomer between Ti and growing alkyl group the sequence $CH_3 \rightarrow H \rightarrow R'$ is again in a clockwise

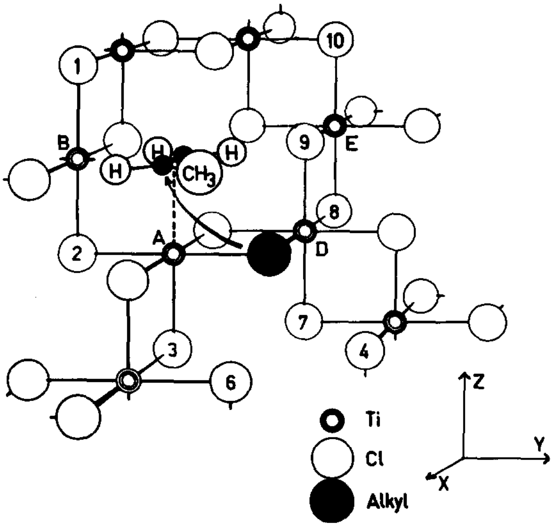


Fig. 4 Schematic drawing of the situation after migration of alkyl group R according to reaction path indicated by the arrow in Fig. 1.

The next monomer C_3H_6-molecule is placed in the new Cl-vacancy. Reaction path of alkyl group R' is indicated.

order. This is demonstrated in Fig. 4. The proposed mechanism together with the above considerations on the $TiCl_3$-lattice thus explains the occurrence of isotactic material in a natural way. It is also clear from Figs. 2 and 3 that only α-olefins may be successfully polymerized.

It is at the same time obvious that the other carbon atom of propylene will obtain a well-defined configuration when cis- or trans-1-deutero-propylene is polymerized. This is in close agreement with Natta's [3] results in the field of di-isotactic polymers. A simple reasoning similar to that above shows that from trans-1-deutero-propylene one obtains threo-poly-1-deutero-propylene.

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[3] G. Natta, Makromolekulare Chemie 35 (1960) 94.