

The Different Crystalline Modifications of TiCl_3 , a Catalyst Component for the Polymerization of α -Olefins. I: α -, β -, γ - TiCl_3 . II: δ - TiCl_3

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INTRODUCTION

It is known that the most stereospecific catalysts for the polymerization of α -olefins to isotactic polymers are formed by organometallic complexes of transition metals, acting on the surface of a solid phase having a crystalline substrate, which is formed by a transition metal halide, the metal being in a valency state lower than the maximum.¹

Transition metal compounds of the TX_3 type, characterized by a layer lattice, give rise to the most stereospecific catalysts (violet TiCl_3 , VCl_3 , etc.). The study of the catalytic behavior of different types of TiCl_3 has given highly interesting results and allowed us to reach conclusions that agree very well with the classical principles of heterogeneous catalysis.^{2,3}

According to our research work, TiCl_3 may occur at least in four different crystalline modifications. Besides the violet (α) form, which was discovered long ago and can be obtained in several ways by reducing TiCl_4 at high temperature, and the brown (β) modification, which can be obtained only at lower temperatures,⁴ two other violet modifications exist. One of them (the γ -modification) was first described and its structure studied by us⁵; it can be obtained by reducing TiCl_4 with organometallic aluminum compounds, at temperatures between 150 and 200°C.; in this case it always contains appreciable amounts of AlCl_3 , which is present as a solid solution. AlCl_3 cannot be easily separated through sublimation or solvent extraction. An AlCl_3 content always leads to a small contraction of the a constant. This is due, we believe, to the solubility of AlCl_3 (which has the same cubic close packing of chlorine atoms and the same layered form that characterize the γ - TiCl_3 crystal structure) in the lattice of γ - TiCl_3 . The hypothesis of the formation of a compound (e.g., $3 \text{TiCl}_3 \cdot \text{AlCl}_3$) should be rejected, because the composition of the samples examined by us was variable, while differences in the corresponding x-ray spectral intensities were practically undetectable. Moreover, we never observed Debye reflections, which could be attributed to a superstructure.

In Part 1 of this communication we will summarize the essential structural features of the three (α , β , and γ) crystalline modifications of TiCl_3

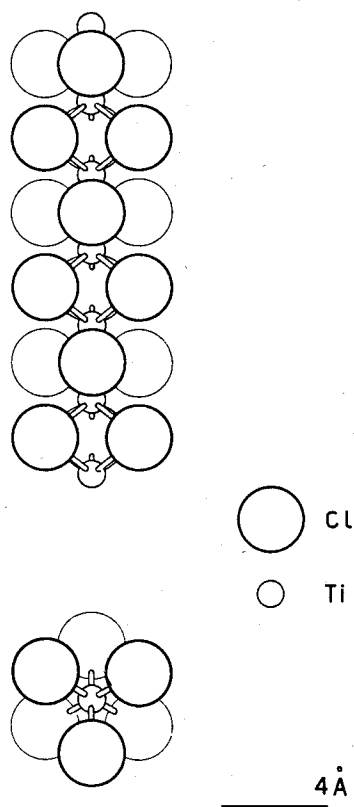


Fig. 1. Stereochemical model of the linear macromolecule $(\text{TiCl}_3)_n$, which can be considered as the structural unit in $\beta\text{-TiCl}_3$.

already known. In Part II, we will describe the x-ray powder spectrum of $\delta\text{-TiCl}_3$, which clearly shows an essentially disordered structure, and discuss the concepts from which we have found the best-fitting statistical model for the structure of this modification.

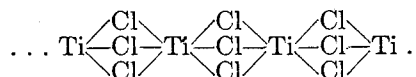
$\delta\text{-TiCl}_3$ was obtained by prolonged grinding either from α - or $\gamma\text{-TiCl}_3$ samples, containing appreciable amounts of AlCl_3 , or from samples completely free from it; this modification still shows, in the x-ray powder spectra, some typical characteristics of the α - and γ -layer modifications.

PART I: THE REGULAR (α , β , γ) CRYSTALLINE MODIFICATIONS OF TiCl_3

Fiber-Shaped and Layer Structures of TiCl_3

A first general distinction between the different crystalline modifications of TiCl_3 can be made from the structural standpoint: (1) modifications having a fiber-shaped structure, (β -modification), (2) modifications having a layer structure (α -, γ -, and δ -modifications).

We say that the β -modification of TiCl_3 shows a fiber-shaped structure because we found that it can be considered as formed by structural units of the type:



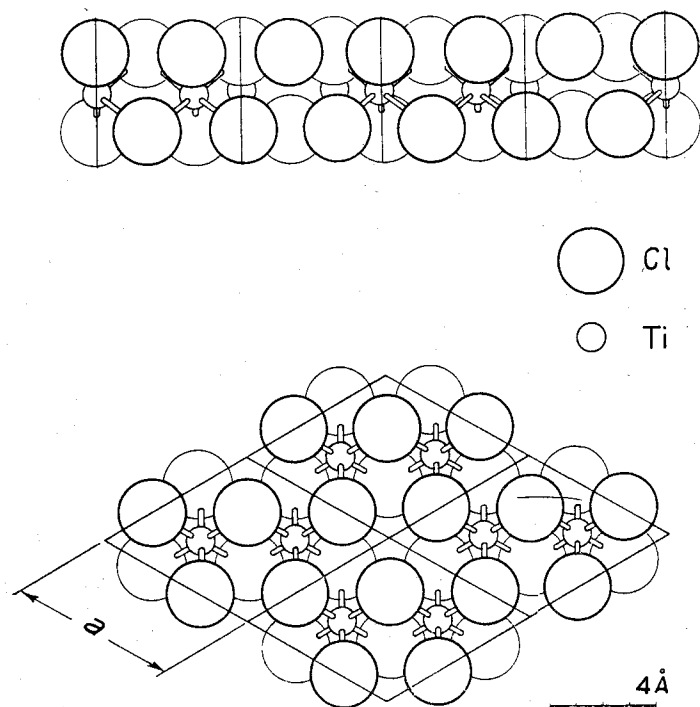


Fig. 2. Stereochemical model of the structural layer which characterizes the layer modifications (α , γ , and δ) of $TiCl_3$.

This modification can therefore be considered as a linear polymer of $TiCl_3$ (see Fig. 1).

The three other modifications (α , γ , δ), while differing very markedly from the β -modification in structure, show such clear analogies among themselves that one can argue a priori that the main chemical and physical properties must coincide. The essential property common to the three modifications consists in their being constituted of *bidimensional* macromolecules of $TiCl_3$, which are identical in the three modifications, and only differ in their mode of packing (layer structures). In each macromolecule, or *structural layer*, each titanium atom is linked to each of the three adjacent ones by two bridge bonds determined by chlorine atoms (see Fig. 2).

It is interesting to point out that both in the β - and in the layer or violet modifications, every titanium atom is placed in such a position that it can coordinate six chlorine atoms octahedrally.

(1) β -Modification of $TiCl_3$

This modification has been described by us from the structural standpoint⁴ on the basis of a hexagonal unit cell containing two monomeric units ($TiCl_3$) and having the following constants: $a = b = 6.27$ A., $c = 5.82$ A., $\gamma = 120^\circ$, space group = $P6_3/mcm$. Titanium atoms are placed in the special position corresponding to the fractional coordinates⁶ ($2b$) $x = 0$, $y = 0$, $z = 0$, whereas chlorine atoms are placed in the special position corresponding to the coordinates ($6g$) $x = 0.315$, $y = 0$, $z = 1/4$. Ti—Cl distances are 2.45 A. (to be compared with the distance of 2.46 A. in the

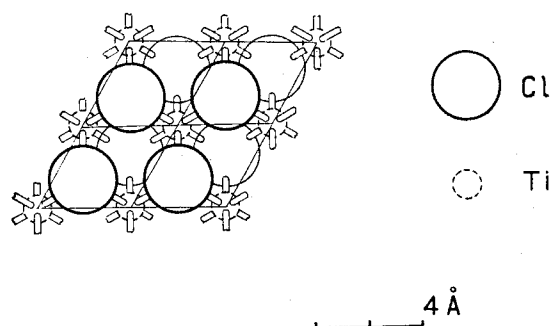


Fig. 3. Basal projection illustrating the subcell chosen by Reed and MacWood for the structural description of α - TiCl_3 .

layer modifications of TiCl_3 , and of 2.21 Å. in TiCl_4), whereas the distances between chlorine atoms belonging to the same row along the c axis



are much lower (3.42 and 3.51 Å.) than those between atoms belonging to different rows (3.72 Å.).

Finally, the distance between adjacent titanium atoms belonging to the same row (linear macromolecule) is 2.91 Å.; it is much lower than the distance between titanium atoms linked by bridge bonds of chlorine atoms in the layer modifications (3.54 Å.), and it equals the Ti—Ti contact distance in metallic titanium. Very short metal-metal distances in bridge bonded structures have been observed *inter alia* in $\text{Be}(\text{CH}_3)_2$ ⁷ and $[\text{Al}(\text{CH}_3)_3]_2$.⁸

(2) α - and γ -Modifications of TiCl_3

The structure of the α -modification of TiCl_3 was described for the first time by Klemm⁹ in 1947 by means of Debye spectra, and subsequently more accurately studied by Reed and MacWood¹⁰ with the aid of Weissenberg methods. It shows a succession of structural layers corresponding to a hexagonal close packing of chlorine atoms. Titanium atoms are also distributed in layers, repeating every two layers of chlorine atoms, perpendicular to the direction of the threefold axis.

Klemm has assigned to the unit cell the following constants: $a = b = 6.12$ Å., $c = 17.50$ Å., $\gamma = 120^\circ$, space group = $R\bar{3}$. The unit cell contains 6 monomeric units (TiCl_3). Titanium atoms have been placed in (6c) 0, 0, $1/3$; chlorine atoms have been placed in (18f) $1/3$, 0, 0.079.⁶

A more accurate investigation performed by Reed and MacWood has demonstrated that all the x-ray reflections given by this modification may be accounted for on the basis of a subcell, containing $2/3$ of monomeric units (TiCl_3), having the following constants (see Fig. 3): $a = b = 3.56$ Å.; $c = 5.87$ Å.; $2/3\text{Ti}$ (a): $x = 0$, $y = 0$, $z = 0$; 2Cl (c): $x = 2/3$, $y = 1/3$, $z = 0.246$; space group = $P\bar{3}m1$.

Reed and MacWood also observed several diffuse streaks, which are to be attributed only to titanium atoms whose positions in the lattice cannot be

exactly defined. In a paper to be published we will propose, on a mathematical basis, statistical models of succession of the structural layers either for the α - TiCl_3 crystals showing the streaks described by Reed and MacWood, or for the crystals prepared by us which also show several streaks but of rather different kinds.

The structure of the γ -modification was described for the first time by us in 1959.⁵ In this modification, the succession of structural layers is such that it determines a cubic close packing of the chlorine atoms. The unit cell of this modification also belongs to the hexagonal system and contains six monomeric units (TiCl_3). The size of the unit cell and the coordinates of the atoms are:⁶

$$a = b = 6.14 \text{ \AA}, c = 17.40 \text{ \AA}$$

$$\text{Ti atoms: 1st set, } (3a) \frac{1}{9}, \overline{1/9}, 0$$

$$\text{2nd set, } (3a) \frac{7}{9}, \overline{7/9}, 0$$

$$\text{Cl atoms: 1st set, } (6c) \frac{1}{9}, \overline{1/9}, 0.254$$

$$\text{2nd set, } (6c) \frac{4}{9}, \overline{4/9}, 0.254$$

$$\text{3rd set, } (6c) \frac{7}{9}, \overline{7/9}, 0.254$$

Space group $P3_112$

The data reported above show the great analogy existing between the values of constants of the unit cells of these two modifications and an identical relative position of the atoms inside each structural layer. This confirms the statement made above that these two modifications may be considered as constituted of *identical* structural layers that differ only in their mode of packing.

PART II: THE δ -MODIFICATION OF TiCl_3

Discussion of X-Ray Powder Spectrum

The powder spectrum of δ - TiCl_3 shows some sharp lines together with some diffuse reflections of halos. The number of sharp lines appears to be remarkably lower than those detectable in the corresponding spectra of the α - and γ -modifications. The corresponding reflections, on the basis of a hexagonal unit cell having the same dimensions of those of α - and γ - TiCl_3 (i.e., $a = b \cong 6.13 \text{ \AA}$, $c \cong 17.40 \text{ \AA}$), possess Bragg indexes satisfying the relationships $h = 3m$, $k = 3n$, $l = 3p$ ($m, n, p = \text{integer numbers}$).

Reflections of this type are the only ones that appear in both the α - and γ -modifications with the same indexes and intensity, suggesting that the structure of the δ -modification is in some way similar to the α - and γ -structures. Clearly, the presence of halos in addition to the above-mentioned reflections indicates some type of disorder in the layer structures. Two halos are more characteristic and intense (data recorded on most of the examined samples). One has a maximum at $2\theta = 17.2^\circ$ ($\text{Cu K}\alpha$) ($d =$

5.13 Å.), halo concentrated toward the lowest 2θ values, strong. A second halo has a maximum at $2\theta = 33.8^\circ$ (Cu $K\alpha$) ($d = 2.65$ Å.), symmetrical, very strong.

The first halo appears with similar shape and intensity in the spectra of the α - and sometimes of the γ -modification. A distribution of x-ray intensity lying in this 2θ region must be due to diffraction by the titanium atoms alone. In α -TiCl₃ it has been indeed explained by Reed and MacWood as originated from $10l$ (l continuous and small) streaks, owing to disorder in the succession of titanium atoms layers. As the intensity in reciprocal space may be approximately assumed to be uniformly distributed along the $(10l)$ zone (l continuous) and the difference in Bragg angles ($\theta(10l) - \theta(100)$) tends to zero as l^2 , for l small, the shape of the halo must be disymmetric in respect to its maximum, ending very sharply toward the low (2θ) angles, and being more and more diffuse at high angles.

The halo at $2\theta = 33.8^\circ$ ($d = 2.65$ Å.) is much stronger and characteristic than the 17.2° halo, since it lies intermediate between the sharp lines at $2\theta = 32.9^\circ$ ($d = 2.72$ Å.) and $2\theta = 35.6^\circ$ ($d = 2.52$ Å.), which are typical for the α -modification (reflection with $(11\bar{3})$ and (113) indexes) and for the γ -form (reflection with $(11\bar{4})$ indexes), respectively, and it appears to substitute them in the new form. This has suggested to us the idea that the mode of packing of the structural layers in the new form should be in some way a statistical "average" between the corresponding modes of packing in the α - and γ -forms.

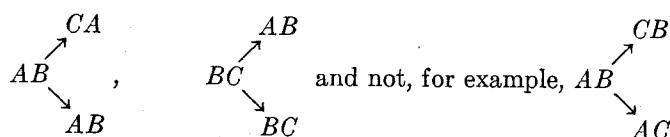
A Possible Explanation for the 33.8° Halo

The intensity of the $113 + 11\bar{3}$ (α -TiCl₃) and $11\bar{4}$ (γ -TiCl₃) reflections, while being invariant with respect to the distribution of titanium atoms in the octahedral coordination sites, within each structural layer (see Reed and MacWood¹⁰ and our work⁵), depends only on the mode of close packing (hexagonal or cubic) of chlorine atoms. In an analogous way, we have supposed that the halo under consideration could be justified by a somewhat irregular succession of structural layers, leading to a statistical structure in which hexagonal and cubic successions of chlorine atoms would take place. Depending upon the presence of the 17.2° halo, in a first approximation titanium atoms have been considered as equally distributed in all octahedral sites within each structural layer. Under these conditions, it is possible to discuss the origin of this halo, referring to fictitious structural layers described by the same "subcell" introduced by Reed and MacWood.

We shall label the three planes of chlorine atoms not superposed in the c axis direction of a close-packed structure as A, B, C .¹¹ A will be generated by a $(0, 0, nc)$ translation from a fixed plane, B and C by a $(\frac{1}{3}a, \frac{2}{3}b, nc)$ and a $(\frac{2}{3}a, \frac{1}{3}b, nc)$ translation, respectively. A structural layer can now be simply described by indicating the succession of the two planes of chlorine atoms, i.e., by AB, AC, \dots

A First Statistical Model for the Succession of Structural Layers in $\delta-TiCl_3$

At first we supposed that any relative rotation or rearrangement of bonds within each layer was excluded. In such a case the succession of structural layers is bound to the condition that every structural layer is followed by the A , B and C layers and always in the same cyclic way, that is:



This is the same as to say that the various structural layers are obtained from the previous ones by simple translation, even if the succession of the said translations has to be assumed as disordered. Every disordered succession, however, may imply a greater probability that some succession modes, rather than others, take place.

In our case, we shall assume as different succession types:

$$\dots AB \rightarrow AB \dots, \dots CA \rightarrow CA \dots \text{ etc.} \quad (1)$$

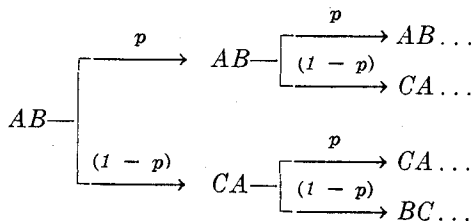
which recall the hexagonal mode of compact packing of the anions and:

$$\dots AB \rightarrow CA \dots, \dots CA \rightarrow BC \dots \text{ etc.} \quad (2)$$

which recall the cubic mode of compact packing of anions. Equations (1) and (2) can be differently probable. Obviously all the successions involving contiguity of anion layers of the same type must be excluded because no close packing of anion atoms could take place in such a case.

Expression of the Average Diffracted Intensity Obtained Starting from the First Postulated Statistical Model

We will start by indicating with p and $(1 - p)$ the probabilities that two contiguous structural layers follow each other according to the hexagonal or cubic type of succession, respectively. The following diagram can be given to illustrate the different probabilities of succession of various structural layers:



Calculation of the average diffracted intensity has given the following results. For the lines of the reciprocal lattice corresponding to the ratios between indexes:

$$h - k = 3n \quad (n \text{ integer number})$$

the diffracted intensity exactly corresponds to that obtainable from any

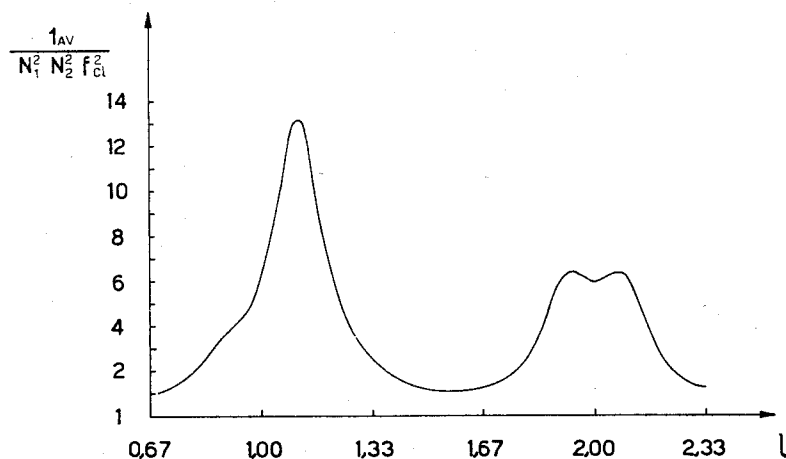


Fig. 4. Diagram showing the variation of I_{av} against l values along the reciprocal (10) line in δ -TiCl₃, assuming the first statistical model ($p = 0.63$).

regular structure (such as α -TiCl₃ and γ -TiCl₃), and gives rise to the same localized reflections. This result is in accordance with the experimental data for δ -TiCl₃.

For the lines of the reciprocal lattice corresponding to the relation between the indexes:

$$h - k = 3n \pm 1$$

the expression of the average diffracted intensity for each layer is the following*:

$$I_{av.} = \frac{1}{2} \left\{ \varphi'^2 \frac{1 - A^2}{1 + A^2 - 2A \cos 2\pi (l \pm \sigma)} + \varphi''^2 \frac{1 - A^2}{1 + A^2 - 2A \cos 2\pi (l \mp \sigma)} \right\} \quad (3)$$

in which the double signs, respectively, correspond to the cases:

$$h - k = 3n \pm 1 \quad (l \text{ continuous})$$

and φ' and φ'' are the structure factors corresponding to two different structural layers. The first of them is formed by an A -type layer of chlorine atoms followed (in the positive direction of the c axis) by a B -type layer with a layer of titanium atoms interposed between them; the second structural layer is defined in an analogous way except for the inversion between A and B . Moreover:

$$A = \sqrt{3p^2 - 3p + 1} \quad \sin 2\pi\sigma = \frac{\sqrt{3}(1-p)}{2\sqrt{3p^2 - 3p + 1}}$$

$$\cos 2\pi\sigma = \frac{3p-1}{2\sqrt{3p^2 - 3p + 1}}$$

* The calculations leading to this expression and to eq. (4) were obtained by mathematical developments of the same kind as those followed for analogous problems by Hendricks and Teller,¹² Jagodzinsky,¹³ and others. We have dealt with these calculations in detail in other papers now in press.

Calculation of the diffracted intensity according to eq. (3), along the line of the reciprocal lattice characterized by the ratios $h = 1$, $k = 0$, l ranging from 0.67 to 2, has given, for the value of p corresponding to 0.63, the curve represented in Figure 4. This curve clearly explains, in both position and intensity distribution, the halo observed in $\delta\text{-TiCl}_3$ having its maximum at $2\theta = 33.8^\circ$ ($l = 1.10$).

Second Statistical Hypothesis and Related Calculations

A second particularly simple and acceptable hypothesis for the type of statistic succession among structural layers is the following.

It has been assumed that any of the four possible structural layers beginning with a layer of chlorine atoms different from B , that is, AB , AC , CA , CB , could follow a structural layer of the AB type. The succession probability among them has been assumed to be determined by the different probabilities of three layers of chlorine atoms for following each other according to the hexagonal or cubic model of compact packing. Thus, indicating by α the probability that three layers of chlorine atoms follow each other according to the hexagonal model, and by $(1 - \alpha)$ the succession probability according to the cubic model, the probabilities that the above-mentioned four layers follow an AB -type layer are the following:

	Probability:
$AB \begin{cases} \rightarrow AB \\ \rightarrow AC \\ \rightarrow CB \\ \rightarrow CA \end{cases}$	$\begin{matrix} \alpha^2 \\ \alpha(1 - \alpha) \\ \alpha(1 - \alpha) \\ (1 - \alpha)^2 \end{matrix}$

Calculation of the average diffracted intensity on the basis of this model has given the following results. For all the lines of the reciprocal lattice having $h - k = 3n$, we observed the appearance of the same sharp reflections, already deduced on the basis of the preceding model, common to the regular and δ -modifications of TiCl_3 . For all the lines characterized by the ratio between the indexes $h - k = 3n \pm 1$, the expression of the average intensity diffracted by every structural layer proved to be the following:

$$I_{av} = \frac{2\alpha(1 - \alpha)\{(4\alpha^2 - 4\alpha + 2)(\varphi'^2 + \varphi''^2 - \varphi'\varphi'' \cos 2\pi l) - (\alpha^2 + 2\alpha - 1)[(\varphi'^2 + \varphi''^2) \cos 2\pi l - \varphi'\varphi''] \mp \sqrt{3}(1 - \alpha)^2(\varphi'^2 - \varphi''^2) \sin 2\pi l\}}{(17\alpha^4 - 28\alpha^3 + 18\alpha^2 - 4\alpha + 1) - 4(2\alpha^4 + 2\alpha^3 - 5\alpha^2 + 4\alpha - 1) \cos 2\pi l + 4(2\alpha - 1)^2 \cos^2 2\pi l} \quad (4)$$

in which φ' and φ'' have the meaning already defined in the previous paragraph and the sign (\mp) in the numerator corresponds to the $h - k = 3n \pm 1$ conditions.

The value of α in correspondence of which the I_{av} curve, according to eq. (4), shows a maximum where $l = 1.10$, for $h = 1$ and $k = 0$, is 0.50. However, the poor resolution of such a curve (see Fig. 5) clearly disagrees with the shape of the observed halo; small variations in the value of α do not lead to a detectable modification in the shape of the curve, so that the

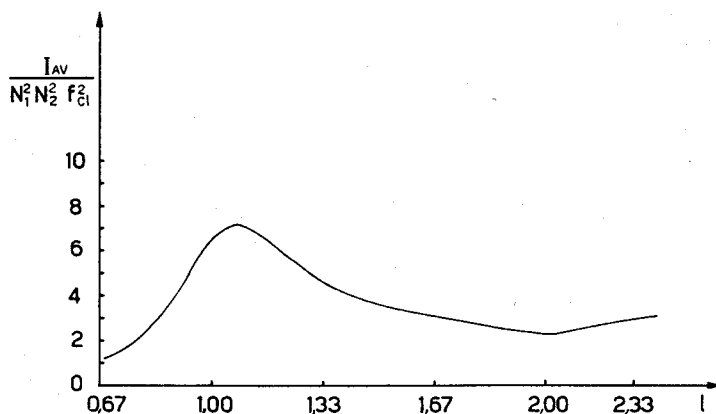


Fig. 5. Diagram showing the variation of I_{av} against l along the reciprocal ($1/l$) line in δ - TiCl_3 , assuming the second statistical model ($\alpha = 0.50$).

model described can undoubtedly be considered in disagreement with experience.

CONCLUSIONS

We have, therefore, definitely considered that the statistical disposition of the structural layers found in δ - TiCl_3 is satisfactorily described by the first model postulated by us. In fact, it seems to be very reasonable, from the type of treatment a α - or γ - TiCl_3 crystal has been subjected to in order to obtain the δ -modification (prolonged grinding), that a certain monodimensional disorder could be caused by the displacement by simple gliding of structurally contiguous layers. We have found for p the most frequent value of 0.63 (higher probability of a hexagonal succession rather than of a cubic one among structural layers).

Other TiCl_3 samples examined, obtained from prolonged grinding, both of α - and γ - TiCl_3 , have sometimes given p values higher than 0.63 [the position of the maximum around $2\theta = 33.8^\circ$ ($\text{Cu } K\alpha$) appeared shifted toward lower angular values, showing the tendency to reach the position foreseen for the $2\theta = 32.9^\circ$ reflection of α - TiCl_3]. p values lower than 0.5 have never been observed. This fact is probably connected with a higher thermodynamic stability of the α -modification, in respect to the γ -form, of TiCl_3 .

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Synopsis

Crystalline $TiCl_3$ is the typical solid component of the catalytic system for the stereospecific polymerization of α -olefins; hence a great interest in the knowledge of its crystal structure arises. Four different crystalline modifications of $TiCl_3$ (α , β , γ and δ) are known to date; three (β , γ , and δ) were first described in our laboratory. A preliminary structural distinction among them can be made in terms of fiber-shaped (β) and layer (α , γ , and δ) modifications. The crystal structure of the β -modification can, in fact, be considered as built up by linear macromolecules, while identical bidimensional (planar) macro molecules, packing with different sequences of shifts, between themselves, can originate an α -, or γ -, or δ - $TiCl_3$ crystal. This close structural analogy explains the great similarity in physical and chemical properties of the last three modifications. In the first part of this paper, the most important structural features of α , β , and γ -modifications are described; in the second, the structure of the most recently discovered δ - $TiCl_3$ is more deeply analyzed. The presence of diffuse halos instead of sharp reflections in its Debye spectra clearly indicates the presence of a certain structural disorder; mathematical calculations (not fully reported here), based on the alternative assumption of two different statistical models of shift successions between structural layers, have led us to find the most probable succession type. As the possible shifts between adjacent structural layers cannot be different in type, in δ - $TiCl_3$, from those which take place in the ordered α - or γ -modifications, we can say that, in δ - $TiCl_3$, the intervention of disorder in shift successions leads to something intermediate (in a statistical sense) between the two stated structures.

Résumé

$TiCl_3$ cristallin est le composant solide typique du système catalytique pour la polymérisation stéréospécifique des α -oléfines; d'où le grand intérêt de connaître sa structure. Quatre variétés cristallines différentes de $TiCl_3$ (α , β , γ , et δ) ont été décrites en premier lieu dans notre laboratoire. Une différence structurale préliminaire consiste à parler de variété fibreuse (β) et variétés en couches. La structure cristalline de la variété β doit en fait être considérée comme formée de macromolécules linéaires, tandis que l'empilement de macromolécules identiques bidimensionnelles (planaires) avec un glissement variable des séquences entr'elles est à la base des cristaux $TiCl_3$ α -, γ - ou δ . Cette grande analogie structurale explique la grande similarité des propriétés physiques et chimiques des 3 dernières variétés. Dans la première partie de cet article, on décrit les faits structuraux les plus importants pour les variétés α , β et γ . Dans la seconde partie, on donne une analyse détaillée de la structure du $TiCl_3$ - δ , très récemment découverte. La présence de halos diffus au lieu de réflexions nettes dans le spectre de Debye indique clairement la présence d'un certain désordre structural; les calculs mathématiques, non entièrement rapportés ici, basés sur l'hypothèse de deux modèles statistiques différents de succession de glissement entre les couches structurales ont permis d'établir le type de succession le plus probable. Les glissements possibles entre les couches structurales

adjacentes ne peuvent être différents dans le TiCl_3 - δ , de ceux qui ont lieu dans les variétés α ou γ ; en conséquence dans le TiCl_3 - δ l'intervention d'un désordre dans les successions de glissement amène à un état intermédiaire (dans le sens statistique) entre les structures précitées.

Zusammenfassung

Kristallines TiCl_3 ist die typische feste Komponente des katalytischen Systems für die stereospezifische Polymerisation von α -Olefinen: daher besteht ein grosses Interesse an der Kenntnis ihrer Struktur. Derzeit kennt man vier verschiedene kristalline Modifikationen von TiCl_3 (α , β , γ und δ); drei von ihnen (β , γ und δ) wurden in unserem Laboratorium zum ersten Mal beschrieben. Eine vorläufige strukturelle Unterscheidung zwischen ihnen kann als faserartige (β) und schichtartige (α , γ und δ) Modifikationen gemacht werden. Die Kristallstruktur der β -Modifikation kann tatsächlich als aus linearen Makromolekülen aufgebaut angesehen werden, während identische zweidimensionale (ebene) Makromoleküle, die mit verschiedenen, gegenseitigen Verschiebungssequenzen gepackt sind, einen α -, γ - oder δ - TiCl_3 -Kristall ergeben können. Diese enge strukturelle Analogie erklärt die starke Ähnlichkeit in den physikalischen und chemischen Eigenschaften der drei letzten Modifikationen. Im ersten Teil der Arbeit werden die wichtigsten Strukturmerkmale der α -, β - und γ -Modifikation beschrieben; im zweiten Teil wird die Struktur des am spätesten entdeckten δ - TiCl_3 gründlicher analysiert. Das Auftreten diffuser Höfe anstatt scharfer Reflexe in ihren Debye-Spektren spricht deutlich für das Vorhandensein einer gewissen strukturellen Unordnung; mathematische Berechnungen (hier nicht vollständig wiedergegeben), die sich auf der Alternativannahme zweier verschiedener statistischer Modelle für die Verschiebungsfolge zwischen den strukturellen Schichten gründen, führten zu der Auffindung des wahrscheinlichsten Typs für diese Folge. Da die möglichen Verschiebungen zwischen benachbarten Strukturschichten bei δ - TiCl_3 sich von denen in den geordneten α oder γ -Modifikationen nicht grundsätzlich unterscheiden können, kann man sagen, dass im δ - TiCl_3 das Auftreten einer Unordnung in den Verschiebungsfolgen zu einem Zwischenzustand (im statistischen Sinn) zwischen den beiden angeführten Strukturen führt.

Received April 26, 1961