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Structure and Properties of Isotactic Polypropylene.

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1. - Generalities.

In 1954 we announced the main structural characteristics of the isotactic crystalline polymers of alpha-olefins synthesized first at the laboratory of Industrial Chemistry of the Milan Polytechnic [1].

Many of them, such as polypropylene and poly-alpha-butene, seem to be destined to increase even more their importance as raw materials for the production of plastics and textile fibers in consequence of their excellent thermal and mechanical properties, of their low cost and the versatility of uses.

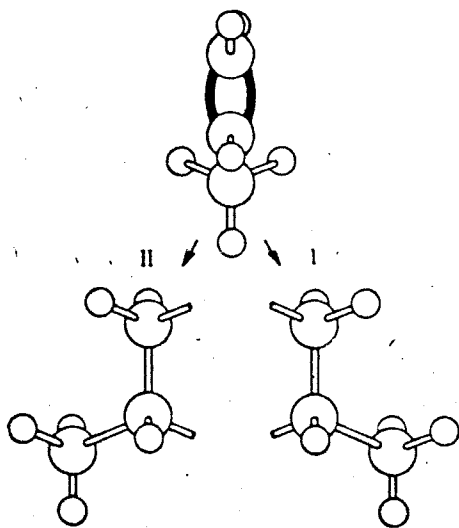


Fig. 1. - Possible configurations that the monomeric unit of propylene may assume.

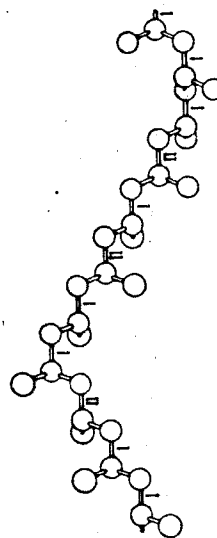


Fig. 2. - Possible conformation of an atactic chain of polypropylene.

2. - Mode of crystallization of polypropylene.

The crystallinity, determined by a method performed in this Institute [5], of samples of polypropylene insoluble in boiling octane having a high sterical regularity, reaches high values for a polymer (until 85%). These samples appear under the microscope, completely spherulitized (Fig. 5).

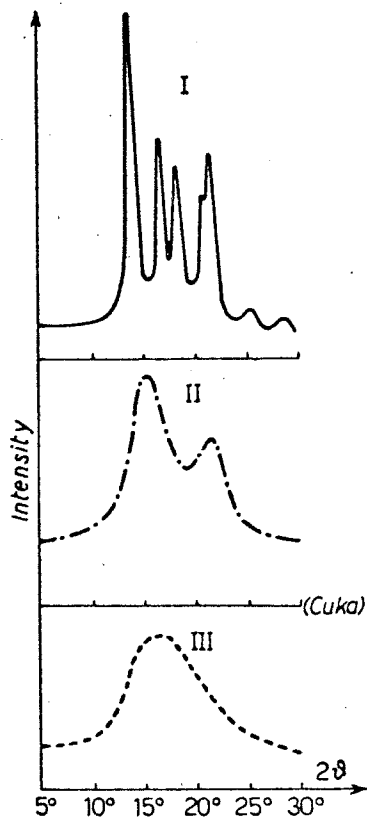


Fig. 4. - Comparison between the X-ray Geiger spectra ($\text{Cu, K}\alpha$) of a sample of crystalline isotactic polypropylene (I), a sample of mesomorphous smectic isotactic polypropylene (II), a sample of amorphous atactic polypropylene (III).

Each spherulite, in analogy with the results obtained by other authors for many polymers, seems to be formed by small fibrils which irradiate themselves from the spherulite center. The cohesion among these fibrils is lower than within the fibrils, and the studies we have performed by X-ray diffraction [6], show that these fibrils are composed by crystal aggregates, all having the a axis (see paragraph on unit cell dimensions) parallel to the spherulite radius. The a axis should be thus coincident with the direction of the highest growing rate and in fact it corresponds to the shortest periodicity of the crystal in a direction different from that of the chain axis (c).

It is again the a axis which happens to be oriented along the axis of extruded, non stretched, filaments [6].

It is interesting to observe that if a sample of isotactic polypropylene is melted and then suddenly cooled in water, it gives an X-ray photograph different from the normal one. It has been assumed by us that a different modification of the polymer, with smectic character is reached; in fact the chains have still a threefold screw conformation as shown by the infrared spectrum, but a disorder exists in the packing of the chains perpendicularly to their axes (Fig. 4) [7].

3. - Stereoblock polymers.

The synthesis of isotactic polymers having a high crystallinity degree is generally accompanied by the formation of a certain amount of atactic polymers and of polymers having, in respect of isotactic polymers, lower degree

In previous works we have demonstrated that the molecules of these crystalline polymers show a high regularity of structure [2], allowed by the peculiar anionic co-ordinated mechanism of the stereospecific polymerization reaction of α -olefins. This reaction goes on through successive additions of monomeric units to metal-carbon bonds of complexes formed on the surface of a crystal having a layer lattice, generally the chloride of a transition element (*e.g.* α -TiCl₃), by the action of a metal-alkyl (*e.g.* Al(C₂H₅)₃).

Usually in a head-to-tail but not stereospecific polymerization, for instance in a polymerization with amorphous catalysts and anionic co-ordinated mechanism, the propylene monomeric units may assume two equivalent specular conformations that cannot in any way be superposed (Fig. 1). The resulting polymer is formed by an unordered succession of monomeric units of the two types and the chain has therefore a random steric structure (Fig. 2).

In the above-mentioned reaction conditions of heterogeneous stereospecific catalysis propylene is first assumed to co-ordinate through a π -bond with the transition element of the catalytic complex, and, therefore, when the polarized olefin molecule is added up to the growing chain, becoming a monomeric unit of the polymer, it can assume only one of the two configurations illustrated in Fig. 1 [3].

Under these conditions the successive monomeric units along the chain assume the same sterical configuration (Fig. 3). We called « isotactic » [4], from the Greek word *ἴσος*, similar and *τάττω*, to settle, those vinyl polymers whose monomeric units, which follow one another head-to-tail along the chain, are able to assume by rotation around single carbon-carbon bonds, sterically equal configurations, that is of repeating themselves by simple operations of translation and rotation along an axis.

We were able to demonstrate the high regularity of the polymers prepared with the catalytic systems above described, through a detailed investigation of their crystalline structure.

In the present note we will relate on the results of a complete structural study concerning the isotactic polypropylene.

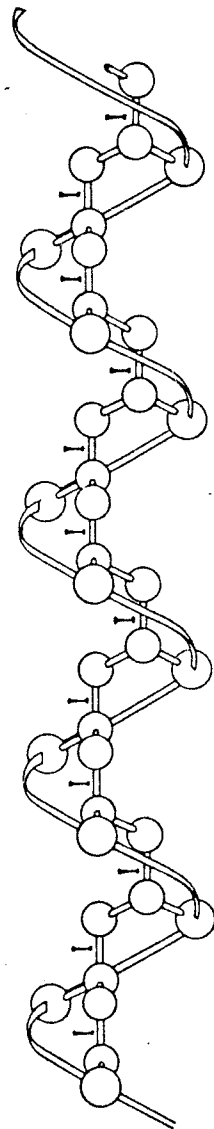


Fig. 3. - Conformation of an isotactic chain of polypropylene in the crystalline state.

of crystallinity, greater solubility into hydrocarbon solvents and lower melting point [8, 9] (Fig. 6).

In Fig. 7 there are shown some X-ray photographs of polymers extracted

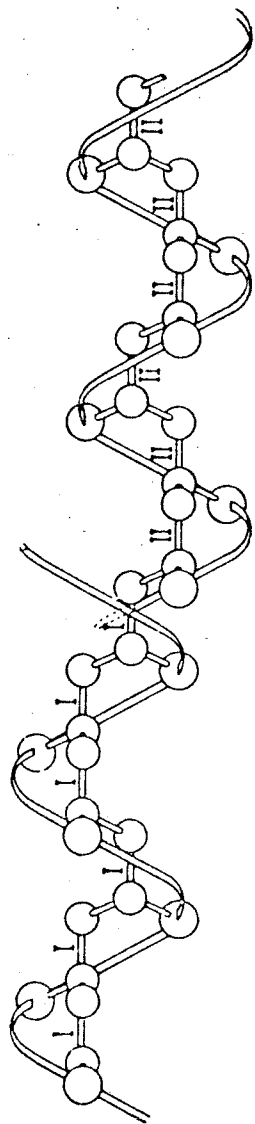


Fig. 6. - Possible model of a chain of stereoblock polypropylene.

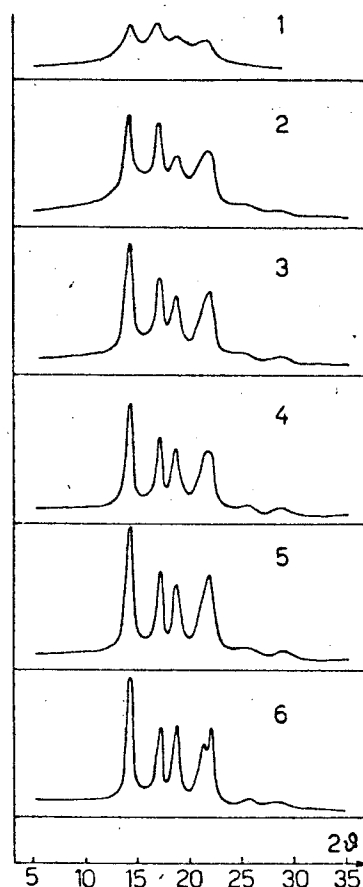


Fig. 7. - Geiger spectra (Cu, $K\alpha$) of stereoblock polymers of propylene. (1. Boiling pentane extracted fraction; Crystallinity: 27%; Melting point: 115 °C. 2. Boiling hexane extracted fraction; Cryst. 36%; M.P. 130 °C. 3. Boiling heptane extracted fraction: Cryst. 52%; M.P. 160 °C. 4. Boiling 2-ethylhexane extracted fraction; Cryst. 62%; M.P. 170 °C. 5. Boiling octane extracted fraction: Cryst. 64%; M.P. 174 °C. 6. Octane non extractible fraction: Cryst. 66%; M.P. 175 °C).

with different hydrocarbon solvents. The polymer crystallinity generally increases with the increase of its melting point.

This fact may be justified by assuming that these polymers have a less regular structure, *e.g.* more or less frequent inversions of the isotactic order exist along the chain.

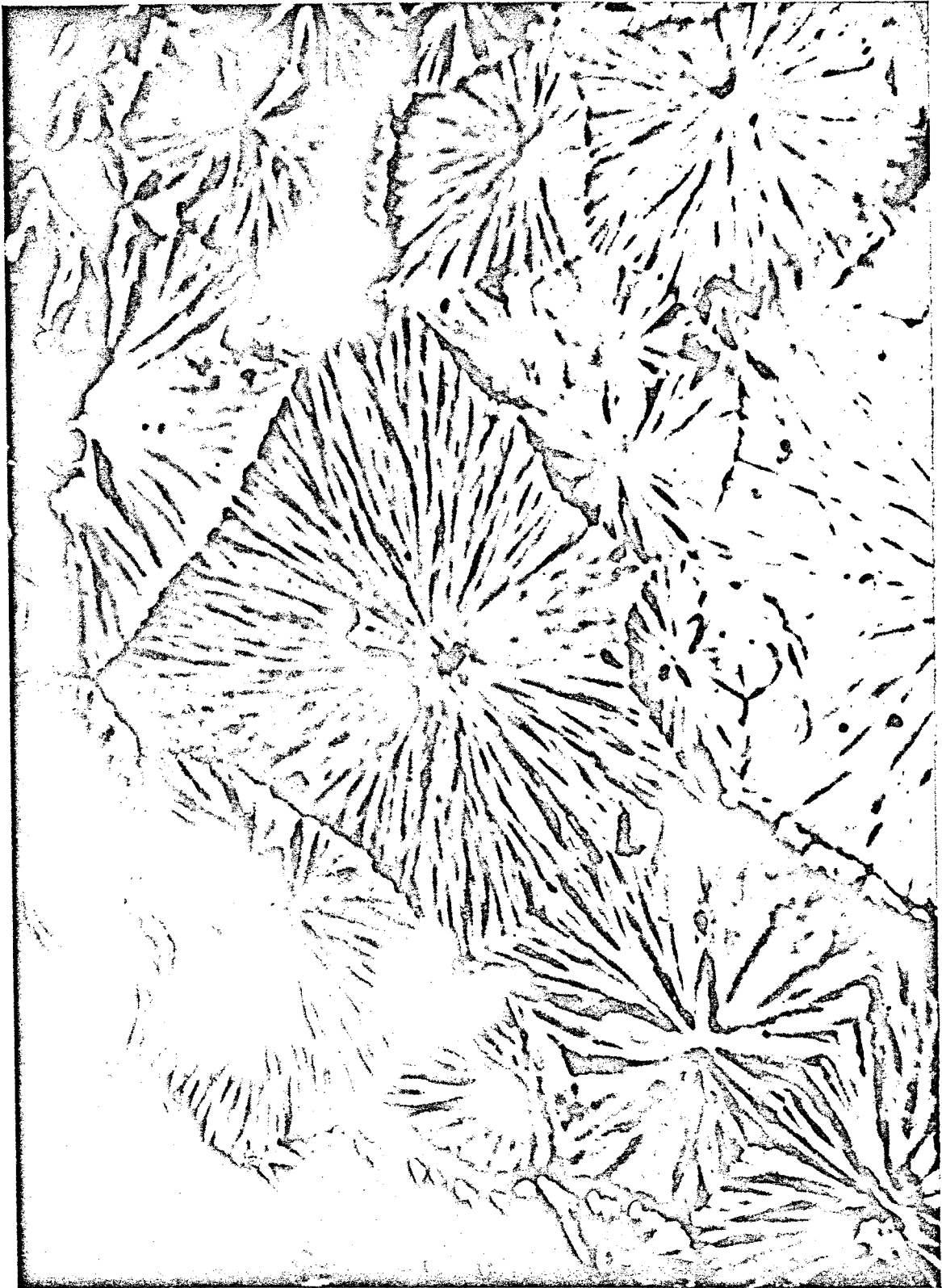


Fig. 5. - Film of polypropylene showing spherulites under the microscope ($\times 100$).

Should we consider the stereoblock polymers as copolymers of monomeric units with a given configuration with a small number of monomeric units having reversed configuration, we could expect that the melting point decreases. In a first approximation and for low n values [9], where n is the fraction of wrong monomeric units along the chain, it results:

$$T^0 - T = \frac{RT^0T}{\Delta H_{u.m.}} \ln(1 - n),$$

where $T^0 = 448^\circ \text{K}$, T the melting point of the considered stereoblock sample, $\Delta H_{u.m.}$ the melting heat for monomeric unit (2400 cal) [10]. An increase of the solubility and a decrease of the crystallinity correspond to a decrease of the melting point, which may be determined, like crystallinity, by roentgenographic methods [5]. The formation of stereoblock polymers may be also connected with chain transfer processes [11]. It can be shown that an equation like the one previously proposed for the lowering of the melting point would still hold.

4. - Unit cell.

The determination of the unit cell was effected directly from fiber photographs taken from a specimen having a high isotacticity degree, with the methods of the reciprocal lattice [12].

The identity period along the axis of the chain results to be $(6.50 \pm 0.05) \text{ \AA}$. The reciprocal lattice net of the equatorial reflections is rectangular with axes $a^* = 0.1524$ and $b^* = 0.0477$ (in $1/d$ units). The $hk0$ reflections with $h+k = 2n+1$ are systematically absent. This immediately suggests an orthorhombic or monoclinic symmetry for the unit cell and a centred unit cell, at least in projection on the a - b plane, is expected. Then we also tried to index the reflections for which l is different from zero. The indexing does not seem possible on the basis of an orthorhombic unit cell, *e.g.* with interaxial angles all measuring 90° , since there are few coincidences between the ξ values of reflections belonging to different layer lines [13]. In fact, assuming that c^* is inclined by $80^\circ 40'$ on the a^* axis, it is possible to index all (hkl) reflections. The values of the unit cell constants are:

$$a = (6.65 \pm 0.05) \text{ \AA},$$

$$b = (20.96 \pm 0.15) \text{ \AA},$$

$$c = (6.50 \pm 0.05) \text{ \AA},$$

$$\beta = 99^\circ 20' \pm 1^\circ.$$

Only hkl reflections with $h+k=2n$ are present; this confirms that the whole crystal lattice is centered. Possible space groups are at this point $C2$, Cm , Cc , $C2/m$, $C2/c$.

The lack of $h0l$ reflections with $l=2n+1$ enables us to retain the space group $C2/c$ or its subgroup Cc as the most probable space groups.

The $C2$ space group may be rejected also on the basis of the fact (less probable) that it does not allow the presence of enantiomorphous macromolecules in the unit cell.

In the unit cell 12 monomeric units are contained ($d_{\text{calc}} = 0,936$, $d_{\text{exp}} = 0.92$) and therefore four chain portions containing 3 monomeric units are present. The Cc space group has just 4 general positions while the equivalent general positions of the $C2/c$ space group are 8; thus, unless a phenomenon of statistical vicariance is assumed, the most probable space group is the Cc space group.

5. - Structural considerations.

The independent structural unit of the crystal is formed, as we have seen above, by a portion of chain containing three monomeric units.

The most probable way in which the three monomeric units repeat themselves so that they result equivalent in respect of the chain axis, is that of a helix [14]. By this assumption supported by many considerations [15], the shape of the chain remains determined by its repetition period (6.5 Å) and by the necessity of respecting known values of angles and distances between carbon atoms (Fig. 8). The found shape of the chain satisfies also the principle of the staggered simple bonds [14]. Having known the conformation of the chain, we tried the possible ways of packing according to the Cc space group, so that the distances between the neighbouring carbon atoms of different macromolecules be always higher than 4 Å, as indicated by literature data concerning the structure of low molecular weight compounds [14].

Considering that the Cc space group is: a) a centered space group; b) it shows symmetry planes with translation parallel to the axis of the chain in $y=0$, $y=\frac{1}{2}$, the most probable model results the one

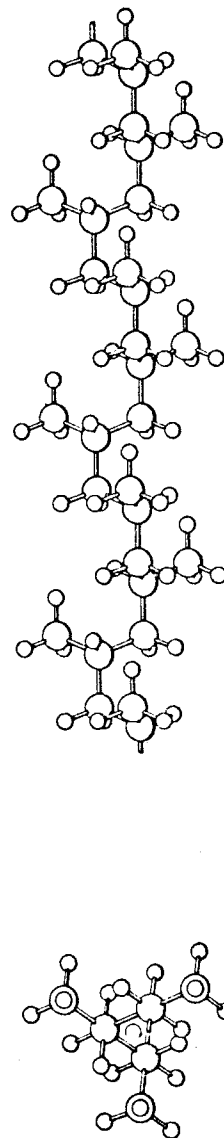


Fig. 8. - Conformation of a macromolecule of polypropylene (side and end views).

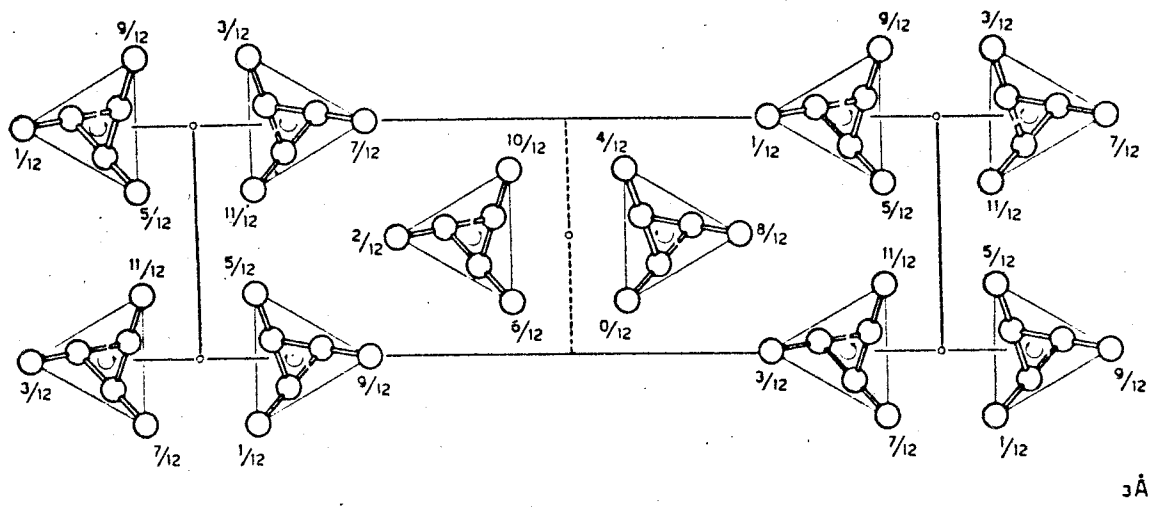


Fig. 9. - Projection on (001) of the structure of polypropylene for the C_c space group.

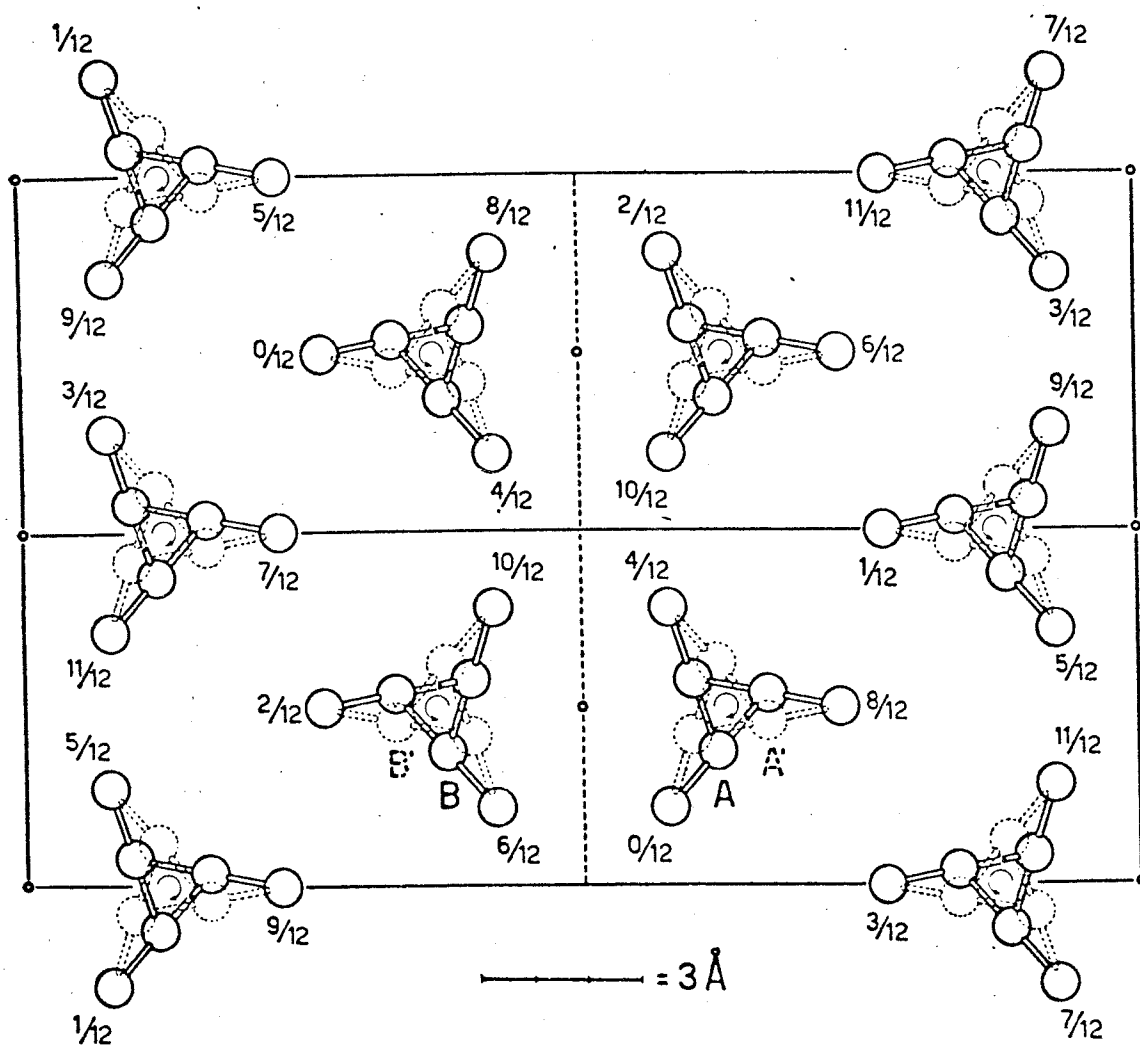


Fig. 10. - Projection on (001) of the structure of polypropylene for the $C^{2/c}$ space group.

sketched in Fig. 9. The contact distances between methyl groups of different molecules are, according to this model, all higher than 4.2 Å, while the distances between methyl and methylenic groups are all higher than 4.0 Å.

It is interesting to note at this point that the packing results good even if one substitutes an up molecule (full drawn in Fig. 9) with an isomorphous molecule, centrosymmetric in respect of the molecule which lies in front of it and therefore with the methyl group turned down (dashed in Fig. 9).

Should one assume that in each site isomorphous anticlinal macromolecules can statistically be substituted, the new situation, that cannot be excluded on the basis of the contacts, corresponds to the $C2/c$ space group of which Cc is a subgroup (Fig. 10).

Therefore in the following calculations even the possibility was taken into consideration that the space group is $C2/c$, taking account also of the fact that phenomena of statistical vicariance were previously observed in other polymers [16].

6. - Calculation of the structure.

The results of the calculation plotted in Table II have been obtained with the co-ordinates of the atoms supplied in Table I. They correspond to a shape

TABLE I. - *Co-ordinates of the independent structural unit of polypropylene.*

Carbon atoms	Co-ordinates of the atoms in the unit cell (Sp. Gr. $C2/c$)		
	x	y	z
C ₁709	.075	.035
C ₂924	.100	.151
C ₃924	.100	.388
C ₄290	.075	.465
C ₅121	.119	.519
C ₆121	.119	.756
C ₇000	.233	.750
C ₈967	.164	.826
C ₉967	.164	.063

of the chain in which the distances between singly linked carbon atoms have been assumed as equal to 1.54 Å, the angle C—C—C along the chain, inferable directly from the identity period, is of 114°, the two angles CH₃—C—C have been assumed as equal to 110°.

This last position leads to a slight displacement from the coplanarity of

TABLE II. - Comparison between the observed and calculated structure factors of polypropylene. The F_0 values correspond to the square root of the total intensity diffracted by the general (hkl) lattice plane after effecting the corrections for the usual angular factors. The temperature factor is $B=7.5 \text{ \AA}^2$ for the $C2/c$ and $B=8.5 \text{ \AA}^2$ for the C/c space group. In order to take into account the different multiplicities of the reflections the $F(h0l)$ and $F(0k0)$ calculated structure factors were divided by $\sqrt{2}$.

hkl	F_0	F_c $C2/c$	F_c Cc	hkl	F_0	F_c $C2/c$	F_c Cc
0 2 0	—	<1	<1	2 16 0	—	6	8
1 1 0	55	62	61	1 17 0	—	5	5
0 4 0	54	55	54	5 7 0}	9	9	9
1 3 0	64	61	60	4 12 0}			
1 5 0}	35	30	30	0 18 0}	7	5	4
0 6 0}				5 9 0}			
2 0 0	18	19	19	4 14 0	—	3	4
2 2 0	34	29	28	2 18 0}	—	7	7
2 4 0	—	6	6	6 0 0}			
1 7 0	12	11	13	1 19 0}	—	3	3
0 8 0	3	5	5	5 11 0			
2 6 0	10	14	14	3 17 0	—	<1	2
1 9 0}	15	17	19	0 2 1	—	1	2
3 1 0}				1 1 $\bar{1}$	3	4	5
0 10 0	—	5	5	1 1 1	47	41	46
3 3 0	—	7	9	1 3 $\bar{1}$ }	67	62	69
2 8 0	12	12	16	0 4 1}			
3 5 0	3	6	6	1 3 1	12	12	14
1 11 0	—	2	7	1 5 $\bar{1}$	7	8	10
2 10 0}	9	9	9	0 6 1	—	2	10
3 7 0}				2 2 $\bar{1}$ }	6	9	20
0 12 0	10	9	9	1 5 1}			
4 0 0}	4	6	11	2 4 $\bar{1}$ }	14	7	30
4 2 0}				1 7 $\bar{1}$			
3 9 0}	12	13	15	1 7 1	—	4	5
1 13 0}	—	3	11	0 8 1}	18	21	25
4 4 0}				2 4 1}			
2 12 0	—	3	11	2 6 1	20	18	22
0 14 0}	7	4	3	3 1 $\bar{1}$ }	13	1	12
4 6 0}				2 6 1}			
3 11 0	—	3	8	1 9 $\bar{1}$ }	21	22	23
4 8 0	7	8	7	3 3 $\bar{1}$ }			
1 15 0}	16	16	14	1 9 1	—	2	2
2 14 0}				2 8 $\bar{1}$ }			
0 16 0}	12	9	10	0 10 1}	17	20	29
5 1 0}				3 1 1}			
3 13 0}	13	13	14	3 5 $\bar{1}$ }	15	24	28
4 10 0}				3 3 1}			
5 3 0}	17	12	11	2 8 1	—	7	7
5 5 0							

TABLE II (continued).

$h k l$	F_o	F_c $C 2/c$	F_c Cc	$h k l$	F_o	F_c $C 2/c$	F_c Cc
$\left. \begin{matrix} 3 & 5 & 1 \\ 1 & 11 & \bar{1} \end{matrix} \right\}$	9	8	19	$\left. \begin{matrix} 4 & 4 & \bar{1} \\ 1 & 13 & \bar{1} \end{matrix} \right\}$	—	6	8
$\left. \begin{matrix} 3 & 7 & \bar{1} \\ 1 & 11 & 1 \\ 2 & 10 & \bar{1} \end{matrix} \right\}$	—	< 1	13	$\left. \begin{matrix} 2 & 12 & \bar{1} \\ 4 & 2 & 1 \end{matrix} \right\}$	16	13	16
$\left. \begin{matrix} 1 & 11 & 1 \\ 2 & 10 & \bar{1} \end{matrix} \right\}$	10	13	16	$\left. \begin{matrix} 1 & 13 & 1 \\ 3 & 9 & 1 \end{matrix} \right\}$	—	5	6
$\left. \begin{matrix} 0 & 12 & 1 \\ 2 & 10 & 1 \end{matrix} \right\}$	—	8	8	$\left. \begin{matrix} 4 & 6 & \bar{1} \\ 2 & 12 & 1 \end{matrix} \right\}$	—	9	8
$\left. \begin{matrix} 3 & 7 & 1 \\ 4 & 2 & \bar{1} \end{matrix} \right\}$	11	14	15	$\left. \begin{matrix} 4 & 6 & \bar{1} \\ 2 & 12 & 1 \end{matrix} \right\}$	—	3	3
$\left. \begin{matrix} 4 & 2 & \bar{1} \\ 3 & 9 & \bar{1} \end{matrix} \right\}$	—	5	6	$\left. \begin{matrix} 2 & 12 & 1 \\ 4 & 4 & 1 \end{matrix} \right\}$	—	5	6
						1	2

the methyl group in respect of one of the three planes in which, four by four, the carbon atoms of the chain are lying.

We shall try to bring experimental evidence which favours this model. The structure factor, in the $C2/c$ space group, is given by the relation (neglecting the hydrogen atoms in the calculation):

$$A = \sum 4f_c \cos^2 2\pi \frac{h+k}{4} \cos 2\pi \left(hx + lz + \frac{l}{4} \right) \cos 2\pi \left(ky - \frac{l}{4} \right),$$

whereas for the Cc space group it is given by the relationship [17]:

$$A = \sum 4f_c \cos^2 2\pi \frac{h+k}{4} \cos 2\pi \left(hx + lz + \frac{l}{4} \right) \cos 2\pi \left(ky - \frac{l}{4} \right),$$

$$B = \sum 4f_c \cos^2 2\pi \frac{h+k}{4} \sin 2\pi \left(hx + lz + \frac{l}{4} \right) \cos 2\pi \left(ky - \frac{l}{4} \right).$$

The structure factors calculated according to the $C2/c$ space group are thus all averagely lower than those calculated according to the Cc space group. This corresponds to the fact that, in structures showing statistical disorder, the mean diffracted intensity by lattice planes is lower than the one diffracted by ordered structures [18].

The mean value of the structure factor is given, in fact, in a non-statistical structure having N equal atoms per unit cell, by the relationship:

$$\bar{I} = \sum f_i^2 = Nf^2,$$

where f is the scattering factor of the considered atom. A statistical structure

with N equal atoms per unit cell, which are able to take two different positions at random, will diffract as if it had $2N$ equal atoms per unit cell, with a scattering factor $\frac{1}{2}f$. Provided that such different positions are not coincident with the possible ones of other atoms, the average scattered intensity is given by

$$\bar{I} = \sum^{2N} (\frac{1}{2}f_i)^2 = \frac{1}{2}Nf^2.$$

In the case of polypropylene, where the methyl groups of molecules vicariant according to $C2/c$ would always have the same position, we have:

$$\bar{I} = \frac{2}{3}Nf^2.$$

In fact, the values calculated for the $(hk0)$ reflections are very similar for the two space groups, but the values calculated for the $(hk1)$ reflections are actually much higher for the Cc space group than for the $C2/c$ space group.

From Table II it may be seen that a better agreement with the experimental values can be obtained for the structure factors calculated according to the $C2/c$ space group. However, the course of the values calculated for the Cc space group is very similar to that calculated for the $C2/c$ space group and, whereas the two calculated values are very different, the observed structure factor often has an intermediate value.

A choice between the two space groups results therefore rather difficult. That probably corresponds to the true situation of the crystal. We believe that the crystalline structure of polypropylene just locally corresponds to the

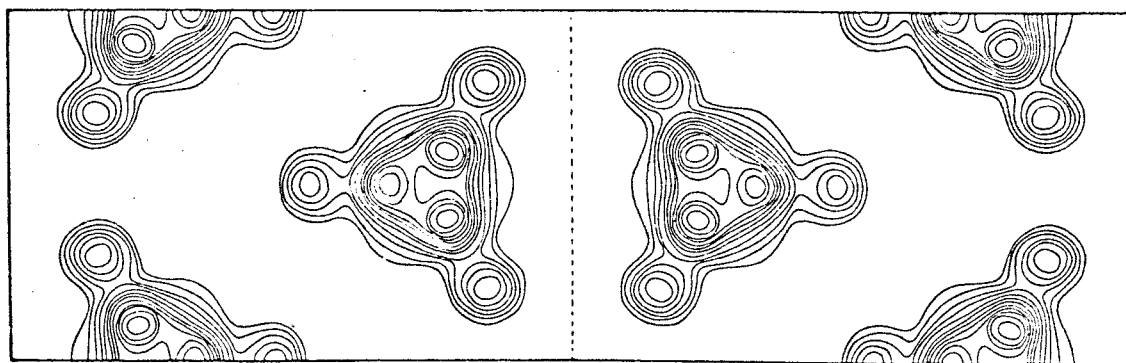


Fig. 11. - Electron density projection on (001) of polypropylene calculated according to the $C2/c$ space group. Contours are drawn every $0.5e/\text{\AA}^2$. The first line corresponds to the $2e/\text{\AA}^2$ level.

Cc space group, *i. e.*, each single crystal should be constituted by an aggregate of small blocks, anticlinal among themselves, of isoclinal macromolecules. Thus, in each block, the structure corresponds to the situation outlined in

Fig. 9, that is to the Cc space group. If the equatorial periodicities are maintained unaltered at the jointment planes between the anticlined blocks, in a generical site of a composite crystal it should be however possible to find almost statistically macromolecules anticlined among themselves. The smaller are the blocks of macromolecules isoclined among them, the more the experimental structure factor disagrees with that calculated for the Cc space group and agrees with the one that may be calculated for the $C2/c$ space group.

A Fourier synthesis of the electronic density was performed along c for this group and enabled us to fix within 0.05 Å the co-ordinates of the atoms.

These co-ordinates are very nearly those given in Table I for the model illustrated at the beginning of this paragraph.

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