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## Crystal Structure of Isotactic Poly-alpha-Butene

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## Crystal Structure of Isotactic Poly-alpha-Butene.

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In these last years crystalline polymers of alpha-olefins were synthesized in the laboratory of Industrial Chemistry of the Milan Polytechnic. Many of them, such as polypropylene and poly-alpha-butene, are expected to increase their importance because of the excellent physical properties they possess, the low cost and the many foreseeable industrial applications. Their structure has been, therefore, the object of a broad investigation.

We shall refer, in this paper, on the results of our structure studies related to poly-alpha-butene. Preliminary results are outlined in a preceding letter to the Editor [1] of *Makromolekulare Chemie*.

*Unit cell.* - The isotactic polymers of alpha-butene insoluble in ethyl ether prepared by the methods of stereospecific catalysis of co-ordinated anionic type ( $\text{TiCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$ ) have a degree of crystallinity measured by X-ray methods [2] of the order of 60%.

Isotactic poly-alpha-butene shows two crystalline modifications [3]. One of them (modification 1), whose structure is the object of this paper, appears the most stable one at room temperature; the other one (modification 2) is that occurring first, at the moment of crystallization, both from the melt and from solutions. The modification 2 is able to evolve in the most stable modification, at

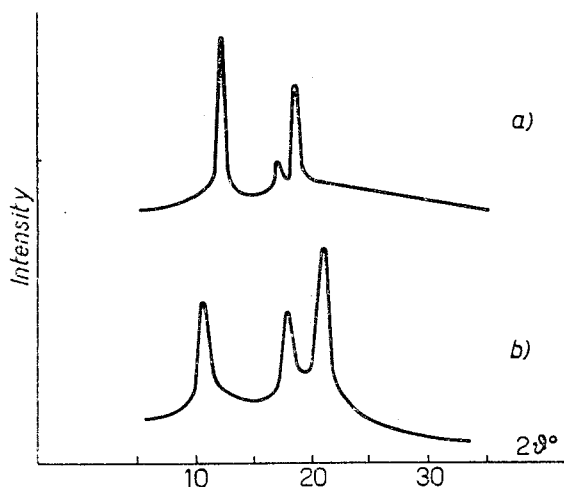


Fig. 1. - Powder spectra of crystalline poly-alpha-butene registered with a Geiger counter (Cu,  $\text{K}\alpha$ ): a) modification 2; b) modification 1.

a more or less high rate, according to the preceding history of the sample and to the thermal or mechanical treatments it undergoes (pressure, unidirectional stretching). The two forms are characterized by a different identity period and, thus, by a different symmetry of the chain. In Fig. 1 is shown, as an example, the X-ray powder spectrum, registered with a Geiger counter, of a sample of poly-alpha-butene cooled from the melted state

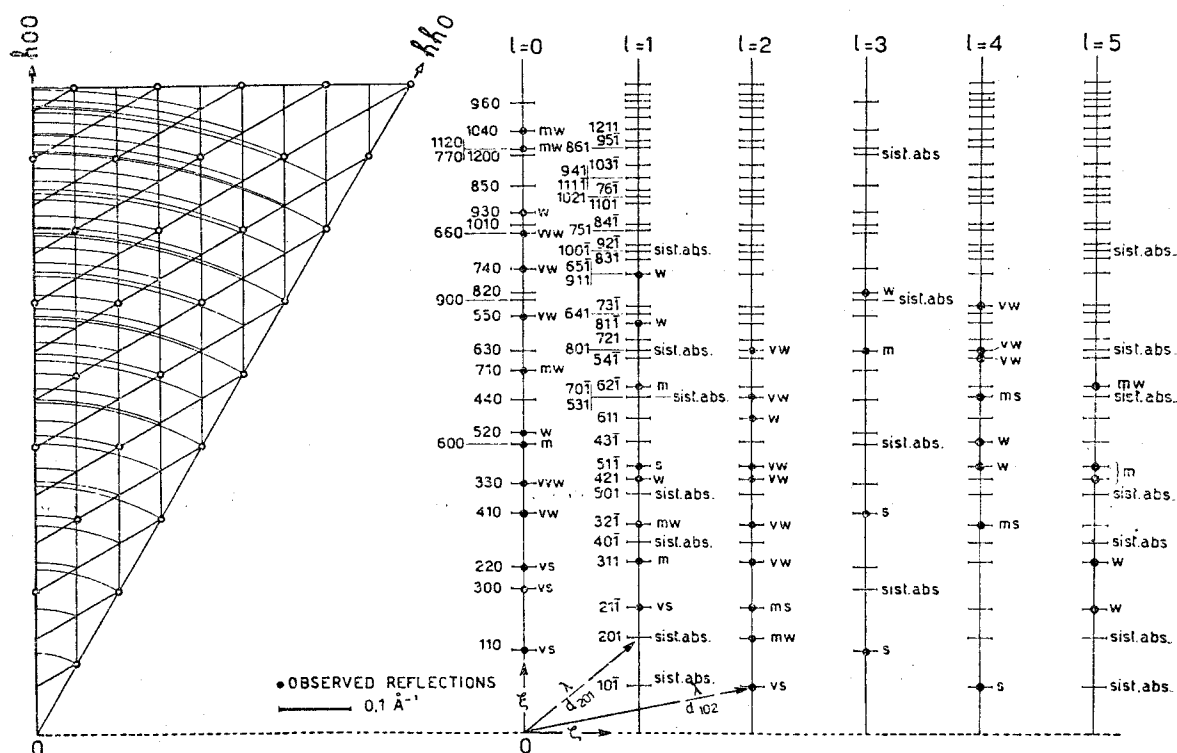


Fig. 3. - Reciprocal lattice of poly-alpha-butene (interpretation of an electron diffraction spectrum of a drawn film of polymer).

without pressure *a*), (modification 2), and the powder spectrum of the same specimen after submitting it, at room temperature, to a pressure of 100 atm, for a few seconds *b*), (modification 1).

In the present study, only the most stable modification will be considered.

Fiber spectra have been taken in a cylindrical camera by Cu, K  $\alpha$  radiation. The identity period along the axis of the chain is  $6.50 \pm 0.05 \text{ \AA}$ .

The photographs show numerous, sharp and, therefore, well resolved reflections (Fig. 2).

It was possible to index all reflections by the reciprocal lattice method (Fig. 3), on the basis of a rhombohedral unit cell whose identity period *a*, referred to hexagonal axes, is  $(17.7 \pm 0.1) \text{ \AA}$ . The (*hkl*) reflections are present only when  $-h + k + l = 3n$ .

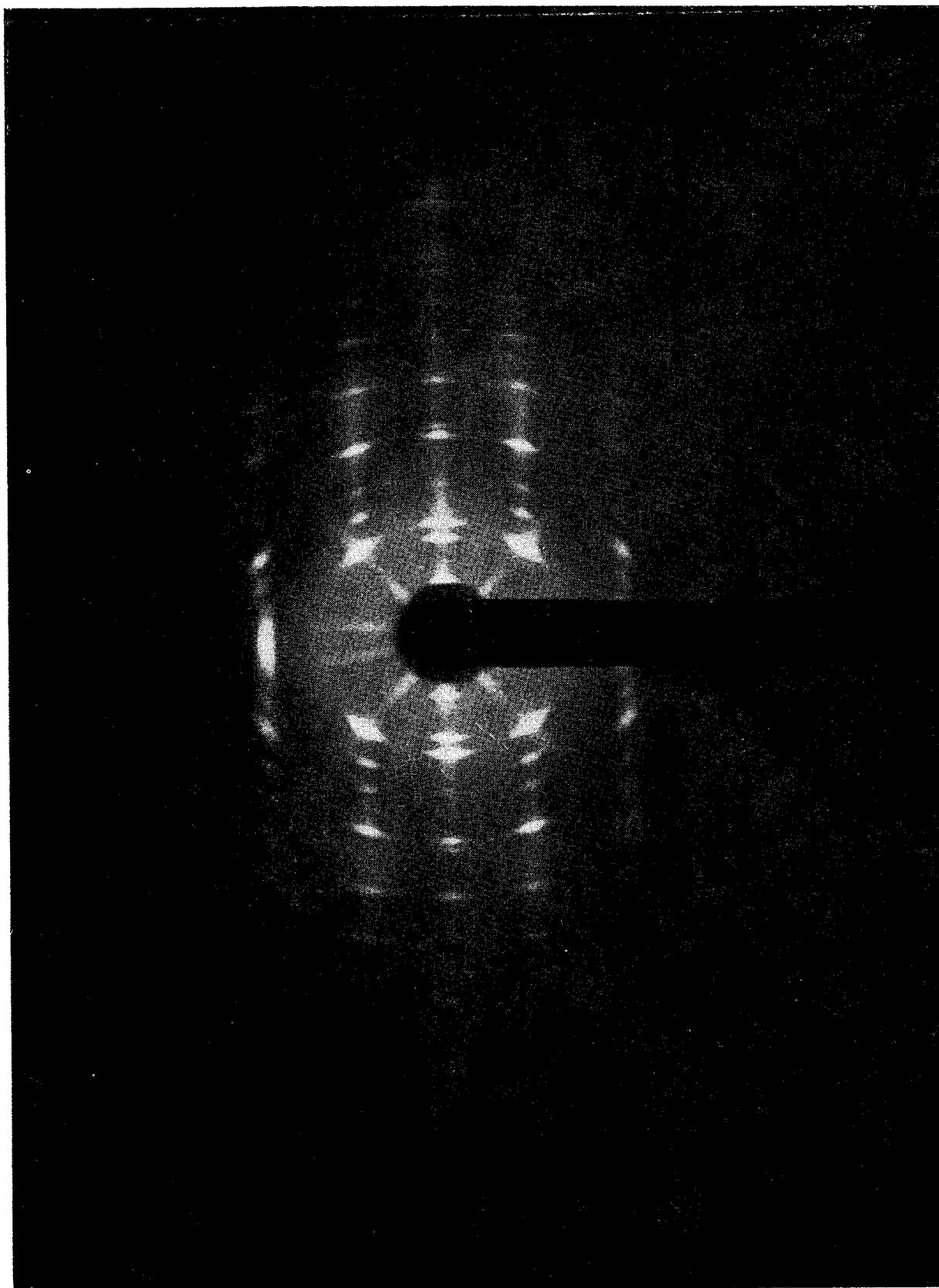


Fig. 2. - Fiber photograph of poly-alpha-butene.

The choice of the possible space groups, from the systematic absence of ( $h0l$ ) reflections with  $l = 2n + 1$ , is restricted to  $R3c$  and  $R\bar{3}c$  groups.

The experimental density is that expected if 18 monomeric units are present per unit cell. The  $R3c$  space group has just 18 equivalent points in general position, whilst 36 are those foreseen for the  $R\bar{3}c$  space group. The two space groups differ one from another according to the presence or to the absence of symmetry centers.

The  $R\bar{3}c$  space group may occur only if chains, with different polar orientation, (anticlinal), isomorphous to each other [4] are able to vicariate in a statistical way around the same threefold screw axis, whereas the  $R3c$  space group is possible only if the chains are able to arrange themselves in the crystal lattice, all having the same polar orientation (isoclinal).

Anyway, only chains with threefold helical symmetry are allowed to be present in the unit cell; each right-handed polymer chain is surrounded by three left-handed chains and viceversa.

The monomeric units following one to another along the threefold helix must obviously have the same sterical conformation.

We have demonstrated that a regular helix type succession in a crystalline vinyl polymer is possible only when the polymer is isotactic [5, 6].

*Structure.* The shape of the main chain of the polymer can be deduced from its threefold helical symmetry and from the knowledge of accepted data, concerning angles and distances between carbon-carbon single bonds. It corresponds to a succession of bonds alternately with trans and gauche conformations. The gauche conformations may be either right or left handed, thus generating, following the terminology introduced by BUNN,  $(AB)_3$  or  $(AC)_3$  enantiomorphous helical chains [7]. The angle between carbon-carbon bonds of the main chain, which may be deduced directly from the value of the identity period  $c$ , differs remarkably from the tetrahedral value and reaches  $114^\circ$ .

The position of the ethyl side group was foreseen in such a way as to satisfy the principle of staggered bonds, and in order to realize suitable Van der Waals distances between different atoms of the same chain.

On the basis of these principles the shape of the chain of poly-alpha-butene remains univocally determined and is shown in Fig. 4.

The problem of determining the way of packing of the macromolecules between themselves has been faced by us both (I) through the consideration of significantly intense ( $hk0$ ) reflections and (II) taking into account the principle that Van der Waals contacts between neighbouring carbon atoms of different chains should not be lower than  $4 \text{ \AA}$ , in accordance with the current data of the most recent literature [8].

An outstanding equatorial reflection is that observed at a Bragg distance  $d = 1.27 \text{ \AA}$ . It corresponds, however, to the possible superposition of two

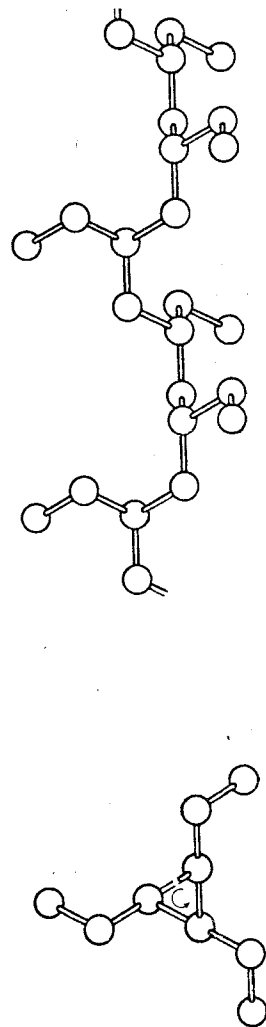
reflections, the (11 2 0) and the (7 7 0) ones, which cannot be distinguished in a fiber diagram.

Making a fiber undergo a strong pressure in a direction normal to its axis (crushing it under the wheels of a tramway car), it was possible to achieve a further orientation of the crystallites.

The  $a$  axis becomes oriented perpendicularly both to the direction of the fiber axis  $c$  and to the direction along which the pressure was applied. The double orientation is so good that the X-ray spectrum given by the sample resembles that given by a single crystal. Thus, it has been possible to us to assign the (7 7 0) indices to the outstanding reflection with  $d = 1.27 \text{ \AA}$ .

The (7 7 0) structure factor (which has the same analytical expression for the possible space groups  $R3c$  or  $R\bar{3}c$ ) is so high, that it demands that all the atoms of the independent structural unit scatter nearly in phase. The (7 7 0) structure-factor graph is shown in Fig. 5 [9]. The molecule, keeping into consideration also the Van der Waals contacts with the neighbouring molecules, remains compelled to assume the position drawn in the graph itself. It is worth noticing, at this point, that the position held in the space by the independent structural unit is such that the Van der Waals contacts between different molecules are good even if we assume that statistical vicariance of up and down molecules, around the same threefold screw axis, occurs, as needed by the  $R\bar{3}c$  space group. In fact, after suitably choosing the origin of  $z$  coordinates for the independent structural unit, values of Van der Waals contacts between neighbouring molecules, packed according to the  $R\bar{3}c$  space group, are obtained, all of them being greater than  $4 \text{ \AA}$  and quite similar to those realized also in the  $R3c$  space group (Fig. 6). For the latter space group the mode of packing results independent of the choice of the origin along  $c$ .

As shown in Fig. 7 if the space group is  $R3c$ , the macromolecules are isoclined and each of them is surrounded by three enantiomorphous macromolecules and viceversa. On the other hand, should the space group be  $R\bar{3}c$  (Fig. 8) each macromolecule is still surrounded by three enantiomorphous molecules and, furthermore, reciprocally anticlined macromolecules may vicariate in



1 Å

Fig. 4. - Conformation of poly-alpha-butene macromolecule in the crystalline state.

a statistical way around each threefold screw axis. The foreseeable statistical vicariance of anticlined macromolecules removes any polarity from the  $c$  axis.

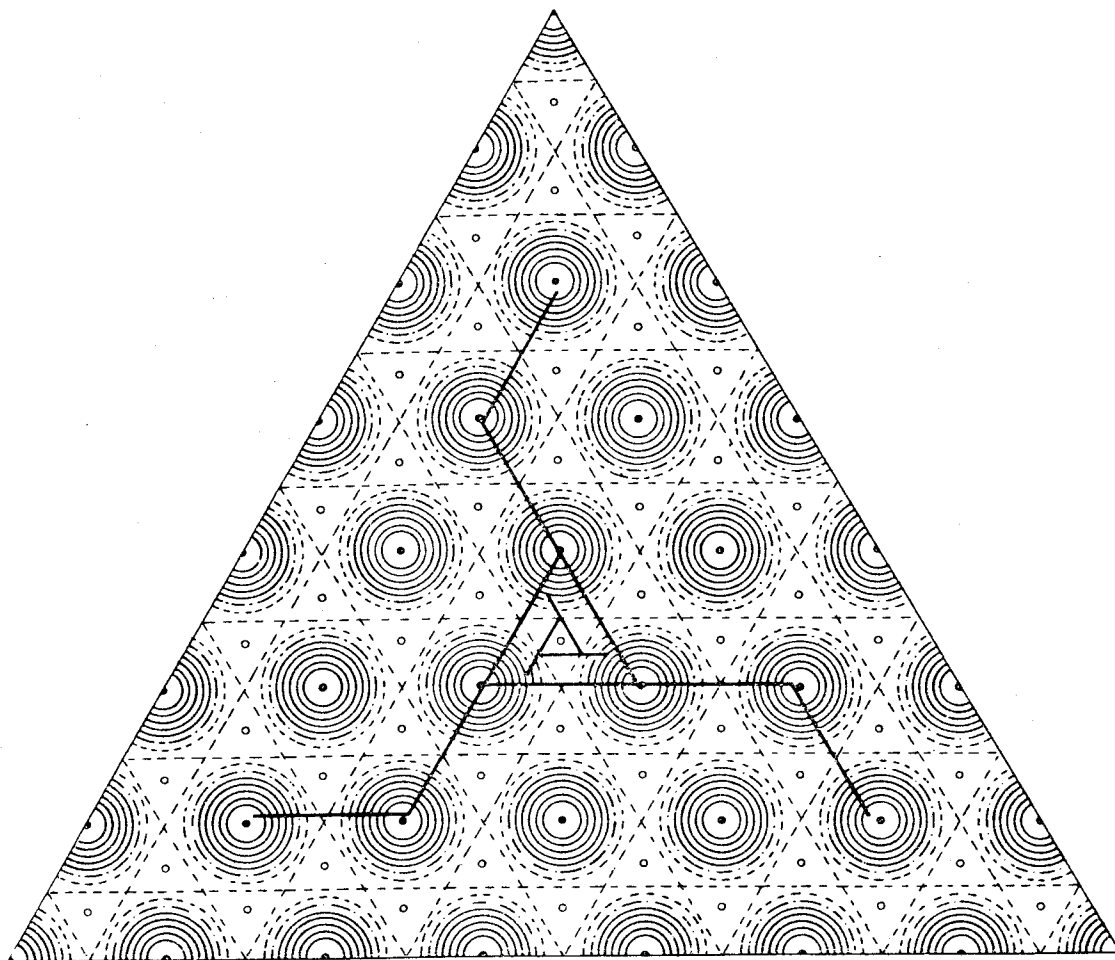


Fig. 5. - (770) structure factor graph of poly-alpha-butene, showing the position of the macromolecule (contours drawn at regular intervals: positive lines ———, zero lines - - - - - , negative lines ······).

A preliminary calculation of the structure factors was performed for both space groups.

The agreement between calculated and observed structure-factors results much better for the centrosymmetrical space group  $R\bar{3}c$ .

It is possible to explain this result by the assumption that the single crystals of the polymer are composed of small blocks, each of them being formed by reciprocally isoclined macromolecules, and thus with a symmetry corresponding to the  $R3c$  space group. These blocks, closely superposed in an anticlined way, would simulate, as far as the global diffraction effects are con-

cerned, the statistical situation foreseeable on the basis of the  $R\bar{3}c$  space group. A choice between the two space groups is thus very difficult and would be critically determined by the dimensions of the blocks.

By the signs resulting from the calculation of the structure factors of  $(hk0)$  reflections it was possible to obtain a Fourier projection of the electron density (Fig. 9) which, though on one side confirming the substantial correctness of the assumed structure, on the other hand pointed out the fact that the

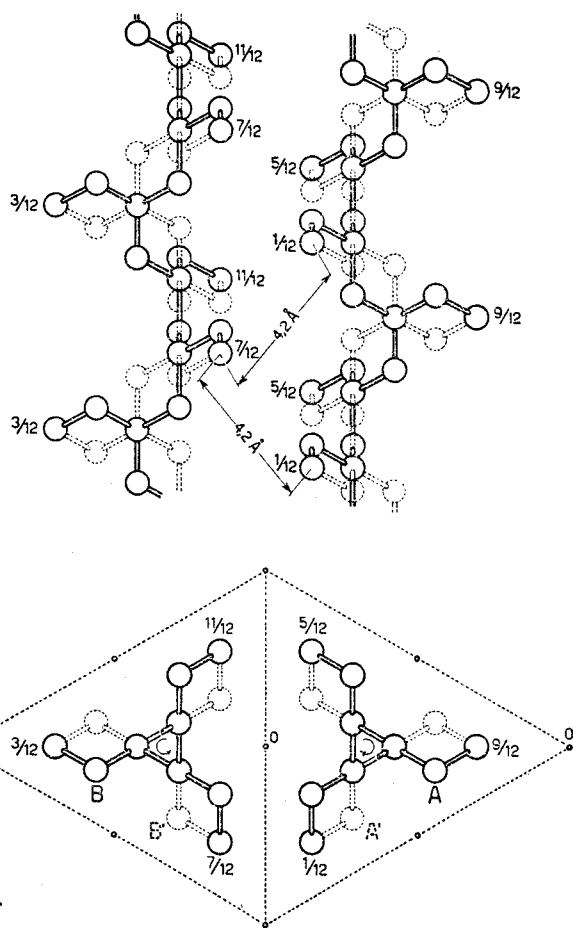


Fig. 6. - Model showing isosterism of antilined isomorphous macromolecules of poly-alpha-butene in the crystal.

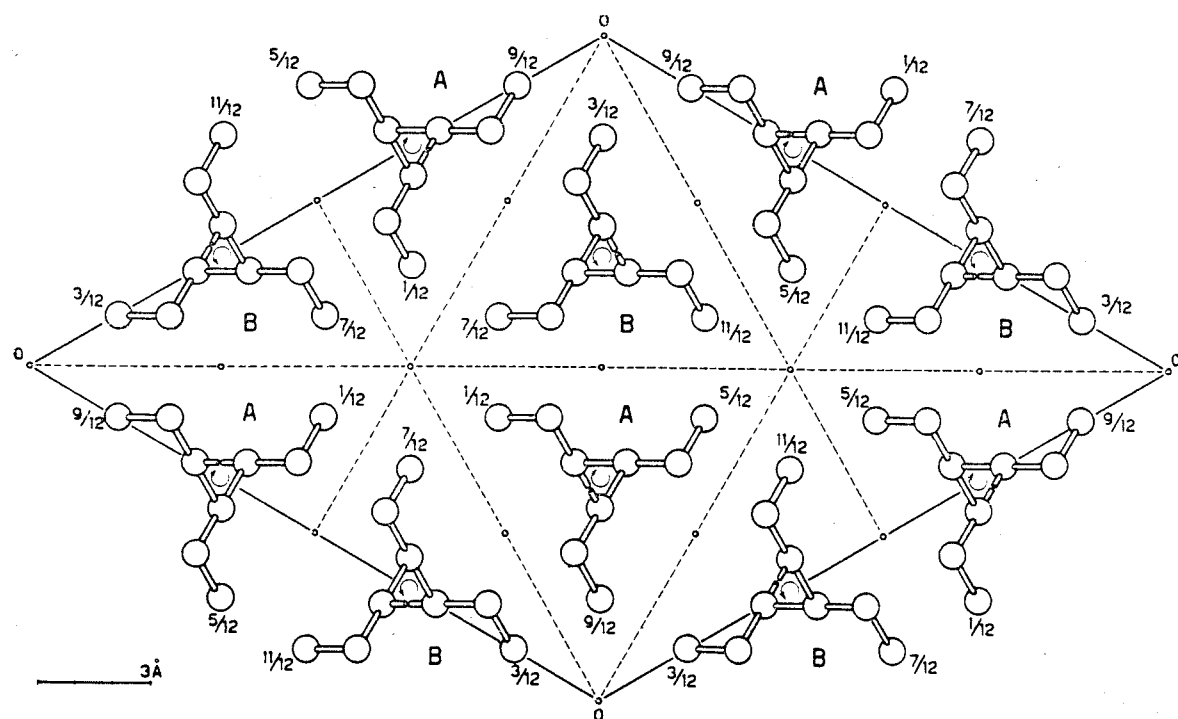


Fig. 7. - Projection of the structure of poly-alpha-butene on  $(001)$  for the  $R3c$  space group.



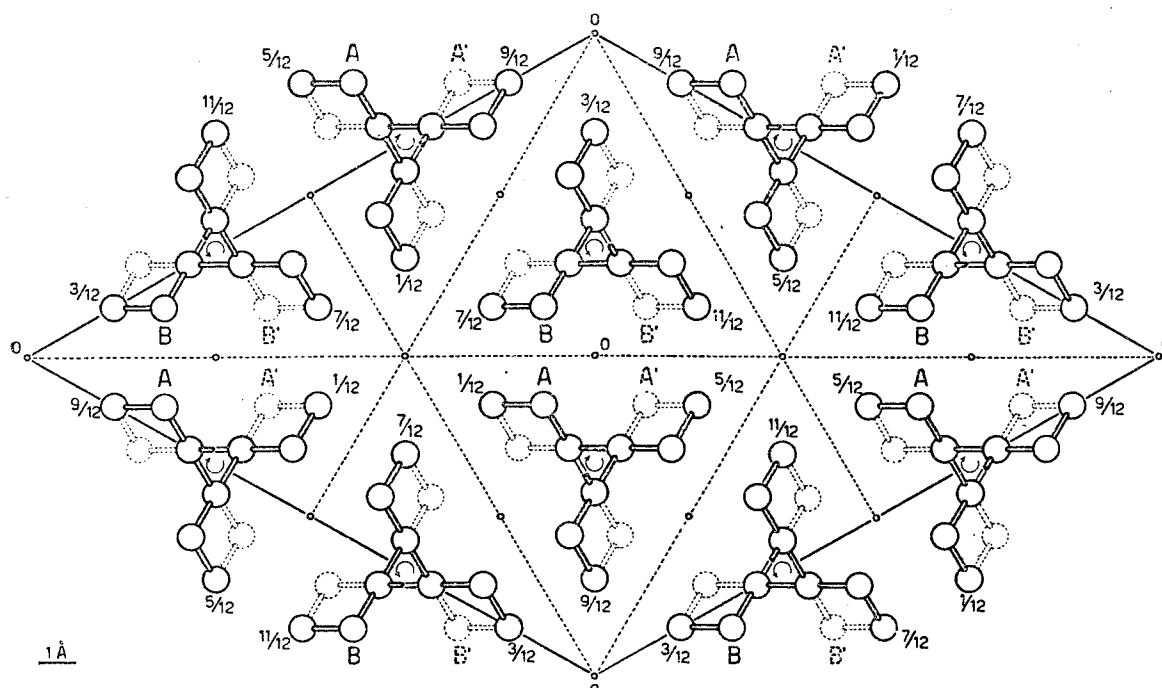


Fig. 8. — Projection of the structure of poly-alpha-butene on (001) for the  $R\bar{3}c$  space group.

methylene carbon atom of the ethyl group ( $C_3$  in Fig. 10) does not lay on the same plane on which 4 by 4 the carbon atoms of the main chain (say for instance, as in Fig. 10,  $C_{1a} C_{2a} C_1 C_2$ ) lay along the helix.

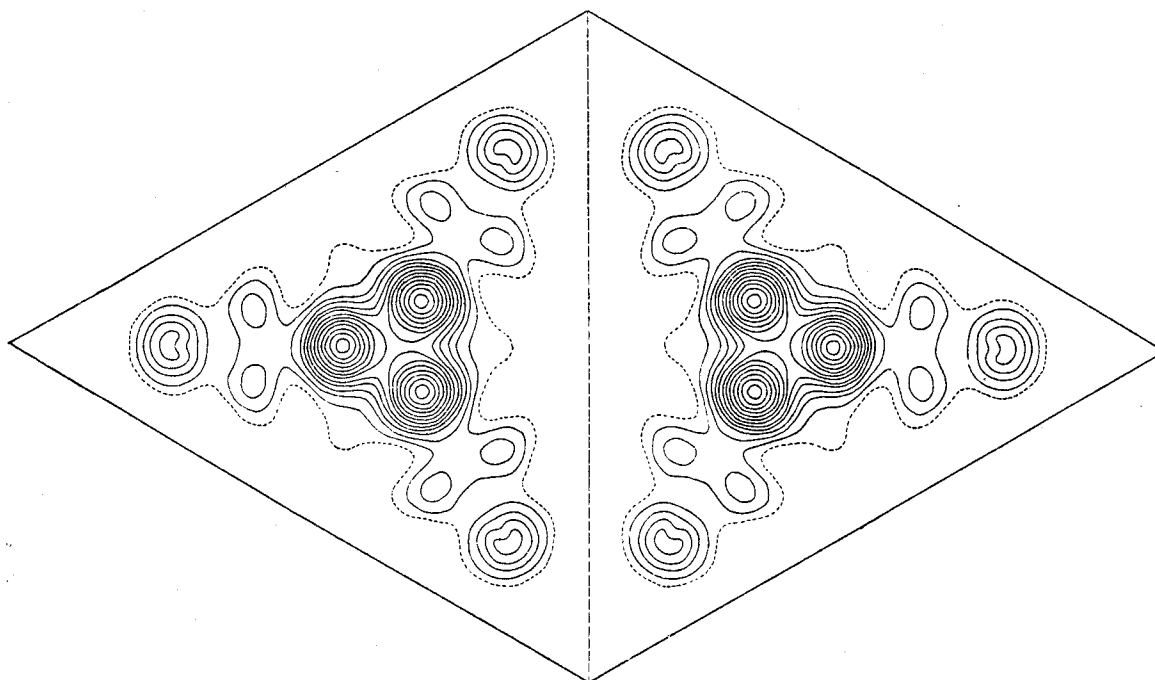


Fig. 9. — Poly-alpha-butene electron density projection on (001), calculated according to the  $R\bar{3}c$  space group (contours at intervals of  $0.5e \text{ \AA}^2$ , the broken line is the  $2e/\text{\AA}^2$  level).

In the original model, on the contrary, the carbon atoms were arranged staggered on the same plane 5 by 5 (Fig. 4).

In fact, as it comes out from Fig. 10, should one assume that the  $\widehat{C_1C_2C_{1b}}$  and  $\widehat{C_2C_1C_{2a}}$  angles are  $114^\circ$  and that the  $\widehat{C_1C_2C_3}$  and  $\widehat{C_{1b}C_2C_3}$  angles cannot go down to values below the tetrahedral ones ( $109^\circ 28'$ ) the discussed displacement can be justified at once (Fig. 11).

This displacement will generally occur in each isotactic polymer with threefold helix, given that the  $\widehat{C_1C_2C_{1b}}$  and  $\widehat{C_2C_1C_{2a}}$  angles, Fig. 10, along the chain, which may be calculated from

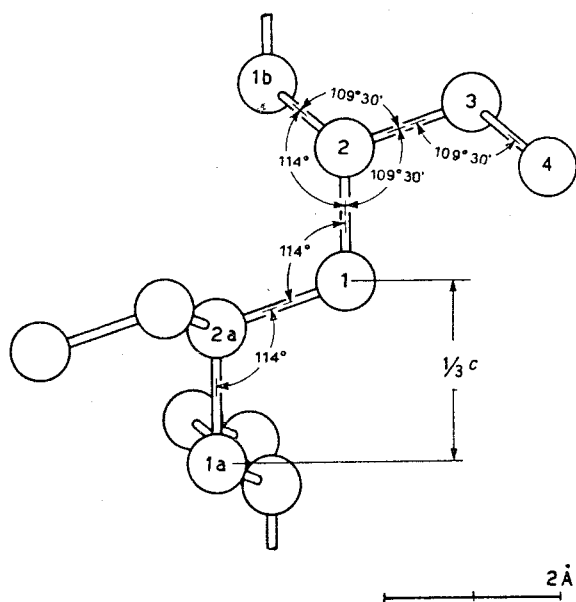


Fig. 10. - Model of the independent structural unit of poly-alpha-butene showing angles and distances between atoms ( $C-C = 1.54 \text{ \AA}$ ).

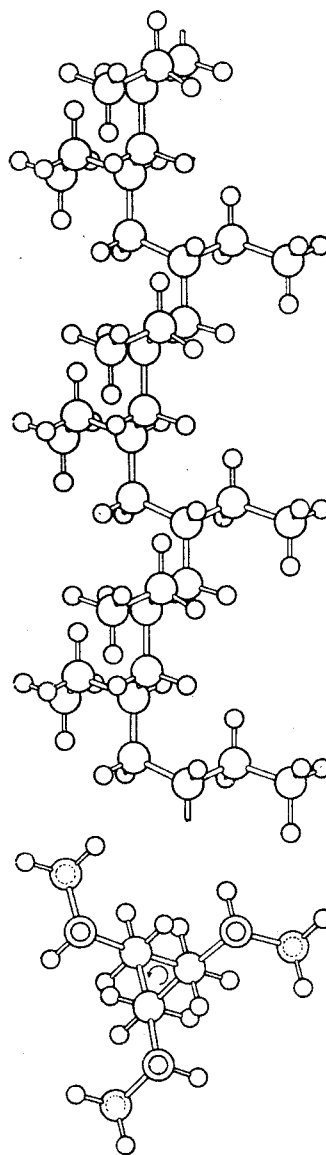


Fig. 11. - Actual conformation of the poly-alpha-butene macromolecule in the crystalline state (side and end views).

the observed identity periods, overcome in any case the tetrahedral values.

A recalculation of the structure factors was effected and showed a remarkable improvement in the accordance.

The best atomic co-ordinates found by us are plotted in Table I, and the results of the calculation, including also hydrogen atoms, supposing the temperature factor to be  $B = 8.9 \text{ \AA}^2$  are plotted in Table II. The introduction

TABLE I. - *Co-ordinates of the atoms of the independent structural unit.*  
 (The atoms are marked according to Fig. 10; the hydrogen atoms index refers to the carbon atom to which they are linked).

	$x/a$	$y/b$	$z/c$
C <sub>1</sub>	0.288	0.288	0.015
C <sub>2</sub>	0.288	0.288	0.250
C <sub>3</sub>	0.232	0.192	0.330
C <sub>4</sub>	0.136	0.143	0.250
H <sub>1</sub>	0.322	0.254	0.960
H <sub>1'</sub>	0.220	0.254	0.960
H <sub>2</sub>	0.253	0.320	0.304
H <sub>3</sub>	0.233	0.191	0.496
H <sub>3'</sub>	0.265	0.157	0.271
H <sub>4</sub>	0.136	0.143	0.082
H <sub>4'</sub>	0.101	0.176	0.304
H <sub>4''</sub>	0.101	0.074	0.304

into the calculation of the contribution of the hydrogen atoms caused a true improvement for some reflections (*e.g.* (330), (321), (40 $\bar{2}$ ), (502)), whose calculated structure factors deviated a little from the observed value.

The fact that the improvement introduced by the consideration of hydrogen atoms is appreciable only for low angle reflections may be readily understood, because of the very low diffracting power of hydrogen at high  $2\theta$  values. Moreover, the improvement is expected to be appreciable only when almost all hydrogen atoms are in phase coincidence one with another. The reliability index calculated for observed and non-observed reflections up to  $d = 1,0 \text{ \AA}$  for 0, 1, 2, 3 layer lines results to be 0.23 and is one of the best values, until now obtained, for the structure of a polymer. The corresponding Fourier projection of the content of the unit cell, already shown in Fig. 9, presents different maxima of relative weight  $2 : \frac{1}{2} : 1$  in respect of the number of atoms which are truly projected herein. In Table III also the values of the structure factors calculated for the  $R3c$  space group for the same independent unit are given for comparison with the observed ones. According to our opinion, the results are less good ( $R = 0.32$ ).

The structure of poly-alpha-butene shows a remarkable analogy with that of polystyrene on one side and of polypropylene on the other.

In any case, the presence, at the same time, in the unit cell of enantiomorphous molecules is actuated by means of a glide plane with translation along  $c$  (Fig. 12). In the case of poly-alpha-butene and polystyrene, the crystal shows also the threefold symmetry peculiar to the chain, contrary to poly-

TABLE II. — Comparison between calculated and observed structure factors of poly-alpha-butene according to the  $R\bar{3}c$  space group.

The  $F_o$  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. In order to take into account the different multiplicity of reflections, all the calculated structure factors except the  $(h00)$ ,  $(hh0)$  and  $(h0l)$  ones, were multiplied by  $\sqrt{2}$ . The numbers into brackets are the values which the structure factors of non-observed reflections should assume if their intensity were one half of the lowest observed one. (Cu, K  $\alpha$ ).

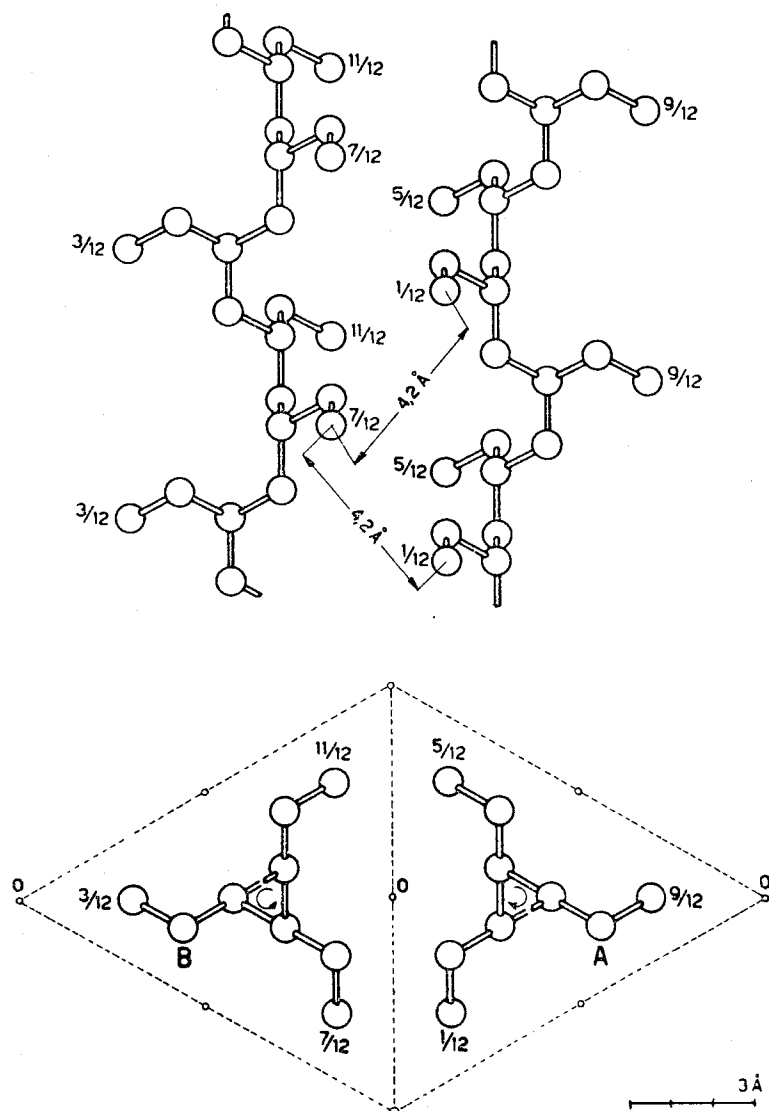
$hkl$	$2 \sin \vartheta$	$F_c.$	$F_o.$	$hkl$	$2 \sin \vartheta$	$F_c.$	$F_o.$
1 1 0	0.174	— 69	92	4 2 $\bar{1}$	0.580	— 18	15
3 0 0	0.301	+ 87	105	5 1 1	0.606	+ 67	70
2 2 0	0.347	—110	127	4 3 1	0.654	+ 8	(3)
4 1 0	0.460	— 14	13	6 1 $\bar{1}$	0.701	— 2	(4)
3 3 0	0.521	— 4	(2)	5 3 $\bar{1}$	0.741	+ 6	(4)
6 0 0	0.602	+ 33	40	6 2 1	0.761	— 41	38
5 2 0	0.626	— 24	23	5 4 1	0.818	— 5	(4)
4 4 0	0.695	+ 1	(3)	7 2 $\bar{1}$	0.854	+ 1	(4)
7 1 0	0.758	+ 33	31	8 1 1	0.889	+ 37	38
6 3 0	0.796	— 2	(3)	6 4 $\bar{1}$	0.905	+ 7	(4)
5 5 0	0.869	— 20	17	7 3 1	0.922	— 5	(4)
9 0 0	0.903	— 2	(3)	6 5 1		— 33	
8 2 0	0.919	+ 1	(3)		0.985	33	28
7 4 0	0.967	+ 17	18	9 1 $\bar{1}$		< +1	
6 6 0	1.042	— 14	16	8 3 $\bar{1}$	1.016	+ 1	(5)
10 1 0	1.057	+ 2	(4)	9 2 1	1.045	—	(5)
9 3 0	1.085	— 22	21	7 5 $\bar{1}$	1.073	+ 1	(5)
8 5 0	1.140	— 11	14	8 4 1	1.087	+ 22	19
12 0 0	1.204	— 8	(4)	10 2 $\bar{1}$	1.140	— 5	(5)
11 2 0		— 2		7 6 1	1.155	+ 3	(5)
	1.216		35	11 1 1		+ 9	
7 7 0		+ 35			1.181		24
10 4 0	1.253	+ 14	17	9 4 $\bar{1}$		— 22	
9 6 0	1.311	— 5	(4)	10 3 1	1.205	+ 6	(5)
13 1 0	1.357	+ 8	< 6	8 6 $\bar{1}$	1.242	+ 2	(5)
12 3 0	1.379	— 1	(4)	9 5 1	1.254	+ 1	(5)
8 8 0	1.390	— 3	(4)	12 1 $\bar{1}$	1.278	+ 11	< 9
11 5 0	1.422	— 11	10	11 3 $\bar{1}$	1.301	— 4	(6)
10 7 0	1.485	+ 8	6	8 7 1	1.325	—	(6)
15 0 0	1.504	+ 2	(4)	12 2 1	1.337	— 1	(6)
14 2 0	1.515	— 1	(4)	10 5 $\bar{1}$	1.347	+ 10	11
13 4 0	1.544	+ 1	(4)	11 4 1	1.369	— 1	(6)
9 9 0	1.564	— 5	(4)	9 7 $\bar{1}$	1.413	+ 1	(6)
				10 6 1	1.424	— 10	
2 1 1	0.355	+152	175				14
3 1 $\bar{1}$	0.432	— 39	40	13 2 $\bar{1}$	1.434	+ 9	15
3 2 1	0.497	+ 32	22	12 4 $\bar{1}$	1.466	< +1	(6)

TABLE II (continued).

$hkl$	$2 \sin \vartheta$	$F_c$	$F_o$	$hkl$	$2 \sin \vartheta$	$F_c$	$F_o$
14 1 1	1.477	— 1	(6)	9 5 $\bar{2}$	1.319	— 4	(5)
13 3 1		— 1		12 1 2	1.350	— 3	(6)
9 8 1	1.497		2 (6)				
11 6 $\bar{1}$	1.516	+ 3	(6)	1 1 3	0.731	— 28	39 not calc.
12 5 1	1.536	— 1	(6)	1 1 $\bar{3}$		+ 28	
				2 2 3	0.787	— 7	10 not calc.
1 0 $\bar{2}$	0.481	— 54	not calc.	2 2 $\bar{3}$		+ 7	
2 0 2	0.512	— 20	11	4 1 3	0.843	— 33	34 25
2 1 $\bar{2}$	0.540	+ 28	26	4 1 $\bar{3}$		+ 8	
3 1 2	0.594	+ 17	12	3 3 3	0.878	— 9	13 6
4 0 $\bar{2}$	0.618	+ 12	8	3 3 $\bar{3}$		+ 9	
3 2 $\bar{2}$	0.642	+ 12	14	5 2 3	0.944	— 2	2 7
5 0 2	0.688	— 2	(3)	5 2 $\bar{3}$		< — 1	
4 2 2	0.710	+ 21	17	4 4 3	0.991	+ 3	4 < 6
5 1 $\bar{2}$	0.730	— 12	15	4 4 $\bar{3}$		— 3	
4 3 $\bar{2}$	0.771	+ 3	(3)	7 1 3	1.035	+ 1	1 < 7
6 7 2	0.809	— 29	22	7 1 $\bar{3}$		— 1	
7 0 $\bar{2}$		+ 1		6 3 3	1.064	+ 21	21 19
5 3 2	0.845		17 15	6 3 $\bar{3}$		— 1	
6 2 $\bar{2}$	0.863	— 11	12	5 5 3	1.120	+ 5	7 (4)
5 4 $\bar{2}$	0.914	— 4	(4)	5 5 $\bar{3}$		— 5	
8 0 2	0.930	— 20	22	8 2 3	1.159	— 16	16 15
7 2 2	0.946	— 6	(4)	8 2 $\bar{3}$		— 1	
8 1 $\bar{2}$	0.978	— 9	< 7	7 4 3	1.198	+ 3	3 (4)
6 4 2	0.993	+ 4	(4)	7 4 $\bar{3}$		— 1	
7 3 $\bar{2}$	1.020	+ 1	(4)	6 6 3	1.259	+ 5	7 8
6 5 $\bar{2}$		+ 11		6 6 $\bar{3}$		— 5	
9 1 2	1.066		13 14	10 1 3	1.271	— 6	6 (5)
8 3 2	1.094	+ 5	(5)	10 1 $\bar{3}$		+ 1	
10 0 $\bar{2}$	1.108	— 1	(5)	9 3 3	1.295	— 4	5 (5)
9 2 $\bar{2}$	1.121	+ 1	(5)	9 3 $\bar{3}$		+ 3	
7 5 2	1.148	— 4	10 8				
8 4 $\bar{2}$	1.161	+ 9					
11 0 2	1.200	< +1	(5)				
10 2 2	1.212	+ 5	< 8				
7 6 $\bar{2}$	1.224	— 6	< 8				
9 4 2		+ 5					
11 1 $\bar{2}$	1.248		10 9				
10 3 $\bar{2}$	1.273	< +1	(5)				
8 6 2	1.308	— 9	10				

TABLE II (continued).

$hkl$	$2 \sin \vartheta$	$F_c$	$F_o$	$hkl$	$2 \sin \vartheta$	$F_c$	$F_o$	
$8\ 5\ 3$	1.341	- 8	10	$10\ 4\ 3$	1.438	+ 1	3	
$8\ 5\ \bar{3}$		+ 5		$10\ 4\ \bar{3}$		+ 3		
$11\ 2\ 3$	1.407	- 2	9	$9\ 6\ 3$	1.489	+ 3	7	
$11\ 2\ \bar{3}$		+ 9		$9\ 6\ \bar{3}$		- 6		
$7\ 7\ 3$		< -1						
$7\ 7\ \bar{3}$		< +1						

Fig. 12. - Projection on (001) and on a plane parallel to the  $c$  axis of two facing enantiomorphous macromolecules.

propylene, for which it is impossible to get a good filling of space in this way (Fig. 13).

It is worth noticing that 1,2 isotactic polybutadiene shows a structure closely analogous to that of poly- $\alpha$ -butene, differing only for the orientation of the lateral group and for small differences in the length of the

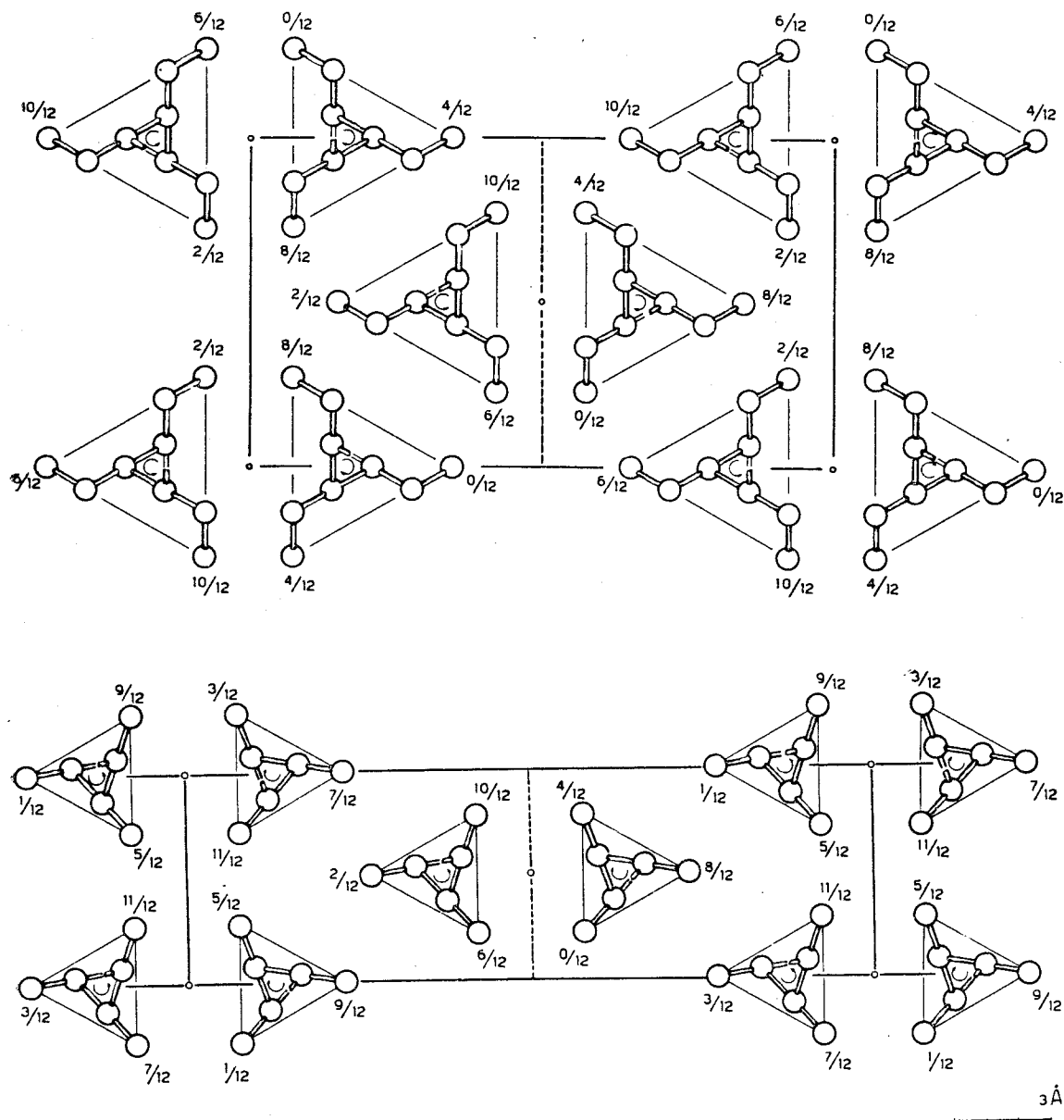


Fig. 13. - Comparison between the packing realized by poly- $\alpha$ -butene and polypropylene macromolecules in the crystals.

$a$  axis [10]. A similar structure is shown by polyvinylmethylether, whose X-ray diagram is closely similar to that of poly- $\alpha$ -butene. May be that in this case the molecules are somewhat more closely assembled since the

TABLE III. - Comparison between calculated and observed structure factors of poly-alpha-butene according to the  $R3c$  space group.  
(For the meaning of  $F_c$  and  $F_o$  see Table II.  $B = 8.2 \text{ \AA}^2$ ).

$hkl$	$F_c$	$F_o$	$hkl$	$F_c$	$F_o$
1 1 0	69	115	7 2 $\bar{1}$	5	(4)
3 0 0	94	131	8 1 1	53	47
2 2 0	106	159	6 4 $\bar{1}$	19	(4)
4 1 0	38	17	7 3 1	6	(4)
3 3 0	4	(2)	6 5 1}	37	35
6 0 0	34	51	9 1 $\bar{1}$ }		
5 2 0	29	29	8 3 $\bar{1}$	11	(5)
4 4 0	1	(3)	9 2 1	1	(5)
7 1 0	44	38	7 5 $\bar{1}$	3	(5)
6 3 0	4	(3)	8 4 1	26	24
5 5 0	21	21	10 2 $\bar{1}$	6	(5)
9 0 0	9	(3)	7 6 1	5	(5)
8 2 0	7	(3)	11 1 1}	27	29
7 4 0	25	25	9 4 $\bar{1}$ }		
6 6 0	15	20	10 3 1	13	(5)
10 1 0	6	(4)	8 6 $\bar{1}$	8	(6)
9 3 0	24	26	9 5 1	4	(6)
8 5 0	14	18	12 1 $\bar{1}$	18	< 11
12 0 0	10	(4)	11 3 $\bar{1}$	5	< 7
11 2 0}	38	35	8 7 1	4	(6)
7 7 0}			12 2 1	4	(6)
10 4 0	16	22	10 5 $\bar{1}$	12	14
9 6 0	7	(4)	11 4 1	4	(6)
13 1 0	9	< 8	9 7 $\bar{1}$	2	(6)
12 3 0	5	< 5	10 6 1}	16	19
8 8 0	3	(4)	13 2 $\bar{1}$ }		
11 5 0	12	13	12 4 $\bar{1}$	2	(6)
10 7 0	10	8	14 1 1	2	(6)
15 0 0	3	(4)	13 3 1}	5	(6)
14 2 0	3	(4)	9 8 1>}		
13 4 0	2	(4)	11 6 $\bar{1}$	5	(6)
9 9 0	7	(4)	12 5 1	2	(6)
2 1 1	155	219	1 0 $\bar{2}$	62	not calc.
3 1 $\bar{1}$	65	50	2 0 2	26	13
3 2 1	34	28	2 1 $\bar{2}$	35	32
4 2 $\bar{1}$	28	19	3 1 2	18	15
5 1 1	99	88	4 0 $\bar{2}$	16	10
4 3 1	10	(3)	3 2 $\bar{2}$	12	17
6 1 $\bar{1}$	8	(4)	5 0 2	2	(3)
5 3 $\bar{1}$	7	(4)	4 2 2	22	21
6 2 1	76	48	5 1 $\bar{2}$	13	19
5 4 1	7	(4)	4 3 $\bar{2}$	21	(3)



TABLE III (continued).

$hkl$	$F_c$	$F_o$	$hkl$	$F_c$	$F_o$
6 1 2	35	28	3 3 3}		
7 0 $\bar{2}$ }			3 3 $\bar{3}$ }	22	8
5 3 2}	20	19	5 2 3}		
6 2 $\bar{2}$	12	15	5 2 $\bar{3}$ }	6	9
5 4 $\bar{2}$	9	(4)	4 4 3}		
8 0 2	24	28	4 4 $\bar{3}$ }	17	< 8
7 2 2	9	(4)	7 1 3}		
8 1 $\bar{2}$	12	< 9	7 1 $\bar{3}$ }	7	< 9
6 4 2	6	(4)	6 3 3}		
7 3 $\bar{2}$	7	(4)	6 3 $\bar{3}$ }	24	24
6 5 $\bar{2}$ }			5 5 3}		
9 1 2}	18	18	5 5 $\bar{3}$ }	8	(4)
8 3 2	6	(5)	8 2 3}		
10 0 $\bar{2}$	6	(5)	8 2 $\bar{3}$ }	17	19
9 2 $\bar{2}$	1	(5)	7 4 3}		
7 5 2}			7 4 $\bar{3}$ }	15	(5)
8 4 $\bar{2}$ }	15	< 10	6 6 3}		
11 0 2	3	(5)	6 6 $\bar{3}$ }	14	10
10 2 2	6	< 10	10 1 3}		
7 6 $\bar{2}$	9	< 10	10 1 $\bar{3}$ }	11	(5)
9 4 2}			9 3 3}		
11 1 $\bar{2}$ }	11	11	9 3 $\bar{3}$ }	6	(5)
10 3 $\bar{2}$	< 1	(5)	8 5 3}		
8 6 2	10	12	8 5 $\bar{3}$ }	19	13
9 5 $\bar{2}$	4	(5)	11 2 3}		
12 1 2	4	(6)	11 2 $\bar{3}$ }		
			7 7 3}	11	< 11
			7 7 $\bar{3}$ }		
1 1 3}			10 4 3}		
1 1 $\bar{3}$ }	71	not calc.	10 4 $\bar{3}$ }	4	(5)
2 2 3}			9 6 3}		
2 2 $\bar{3}$ }	11	not calc.	9 6 $\bar{3}$ }	10	(5)
4 1 3}					
4 1 $\bar{3}$ }	39	31			

allowed Van der Waals contacts between  $\text{CH}_3$  and O are expected to be lower, with regard to the correspondent contacts between methyl and methylene groups.

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