Crystal Structure of Poly-ortho-Methylstyrene.

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In precedent papers [1] evidence was given which enabled us to establish the helix chain conformation of many isotactic polymers. The crystal structure of some polymers was studied with more detail, whose chain shows a three-fold helix conformation as that of polypropylene, poly-alpha-butene and polystyrene [2]. Other forms of chain were qualitatively discussed in terms of Fourier transforms [3]. Aim of this work is the determination of the structure of an isotactic polymer, prepared by means of highly stereospecific catalysts obtained reacting titanium halides with alkylaluminum compounds [4], the poly-ortho-methylstyrene, whose chain conformation is that of a fourfold helix.

1. – Experimental.

Oriented fibers were obtained, according to methods similar to those used for polystyrene [5], hot-annealing under tension a small cylinder of poly-ortho-methylstyrene extruded from the melt. The fiber spectra that we have obtained show many reflections. The orientation of the crystals is however worse than that which may be obtained for the other polymers previously studied by us. By reciprocal lattice methods [6] it was possible to reconstruct the unit cell of the polymer under examination. All the reflections may be readily indexed for a tetragonal unit cell with $a = b = 19.01$ Å; $c = 8.1$ Å (within $\pm 1\%$). Owing to the systematic absence of the reflections hkl with $h + k + l = 2n + 1$, $0kl$ with $l = 2n + 1$, hhl with $2h + l = 4n + 2$, we were able to conclude that the space group is $I4_1cd$.

To make an example, the agreement between the observed and calculated Bragg distances for $hk0$ reflections is shown in Table I.

TABLE I. — *Comparison between the observed and calculated Bragg distances* $d(hk0)$ *of poly-ortho-methylstyrene.* (Cu, Kα)

2θ	$hk0$	d_o	d_c
9.3	200	9.500	9.505
13.00	220	6.815	6.720
14.80	310	5.990	6.010
20.80	420	4.270	4.250
24.00	510	3.710	3.730
28.10	600	3.170	3.170
33.40	640	2.683	2.688
36.10	730	2.488	2.496
42.60	840	2.122	2.125
47.90	10 00–860	1.899	1.901

The space group allows the presence of 16 equi-valent structural units in the unit cell, and in fact, should we assume that 16 monomeric units are contained in the unit cell, the density is calculated to be 1.07 g/cm³, in good agreement with the experimental value. The chain is necessarily expected to assume a fourfold helix conformation; the macromolecules are isoclined and, through the operation of glide planes with translation parallel to c, each right handed helical chain is surrounded by four left-handed chains and viceversa.

2. – Chain shape and crystal structure.

The first trials, which aimed at establishing the structure, were made by utilizing the principles that we summarized in a preceding work of ours [7]. The identity period along the fourfold screw axis (8.1 Å) allows, by itself, to fancy the most probable conformation of the chain if for the length of the C—C bond the value of 1.54 Å and for the $\widehat{CCC}$ angles tetrahedral values are assumed (Figs. 1 and 2).
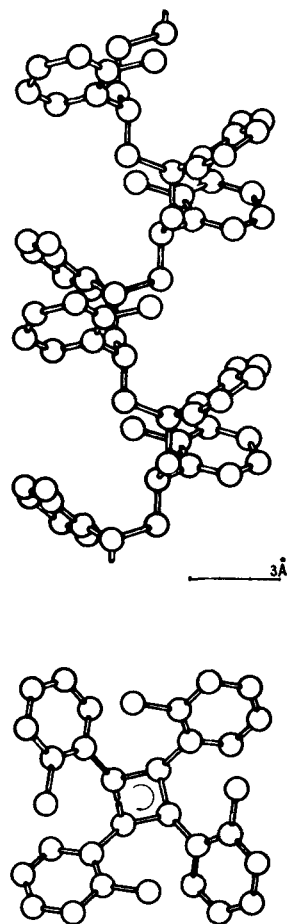
Fig. 1. – Conformation of the poly-ortho-methylstyrene macromolecule in the crystal state (side and end views).

In analogy to what we found for polystyrene, the plane of the benzene ring was placed first to bisect the $\widehat{C_1'C_2C_1'}$ angle. However, as we shall further see, the best agreement between experimental and calculated intensities was obtained for the conformation drawn in Fig. 2, in which the benzene plane forms an angle of 8° with the plane which bisects the $\widehat{C_1'C_2C_1'}$ angle. The C_9 methyl group was bound to C_8 instead of C_4 in order to get better intramolecular Van der Waals contacts; actually, should it be bound to C_4, we would have had a C_9—C_1 contact shorter than 3.0 Å, which is most unlike from a stereochemical viewpoint.
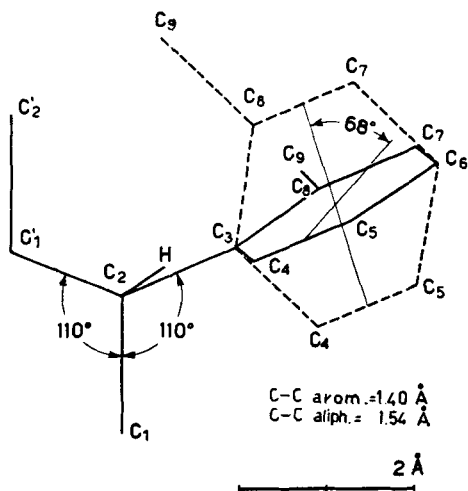
The problem of determining the structure was faced, still with reference to the preliminary conformation, taking into accoun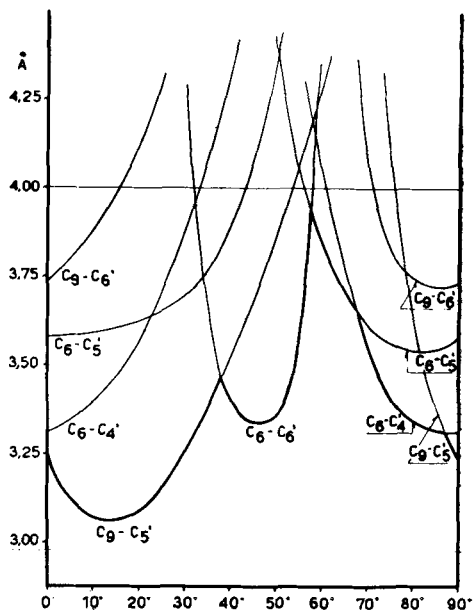t stereochemical considerations concerning the mode of packing between neighbouring macromolecules, and examining the value of some appropriately chosen structure factors.

Fig. 2. – Model of a monomeric unit with specified angles and distances.

C–C arom. = 1.40 Å
C–C aliph. = 1.54 Å
2 Å

In the diagram of Fig. 3 the course of the closest Van der Waals contacts is sketched as a function of the angle φ that may be assumed by the macromolecule, supposed to rotate around the fourfold screw axis. (The value of φ is referred to the angle formed by the axis b with the line joining the center of the chain to C_6). As it may be observed from this diagram, for $\varphi = 57°.5$ a position exists in which the best packing contacts with neighbouring

Fig. 3. – Van der Waals contacts between neighbouring molecules, according to the position φ which could be assumed by the molecule around the four-fold screw axis.

« symmetry-related » macromolecules are obtained. In fact the lowest distances between aromatic carbon atoms, recorded in literature, are comprised within 3.4 and 3.7 Å; for $\varphi = 57°.5$ the values of the observed contacts are all greater than 3.8 Å and suggest that for this position one can obtain the best filling of space.

This result has been further confirmed by a study of the behaviour of the values of the structure factors of the most important reflections ever plotted as a function of the angle φ. A very good agreement between calculated (F_c) and observed (F_o) does exist for φ values of about 57°. As an example we report in Fig. 4 a diagram illustrating the calculated behaviour of the expressions

$$\frac{F_c(h\,k\,0)}{F_c(h'k'0)} \cdot \frac{F_o(h'k'0)}{F_o(h\,k\,0)} \ .$$

Fig. 4. – Values of the ratios $(F_c(h\,k\,0)/F_c(h'k'0)) \cdot (F_o(h'k'0)/F_o(h\,k\,0))$ according to the position φ which could be assumed by the molecule around the four-fold screw axis.

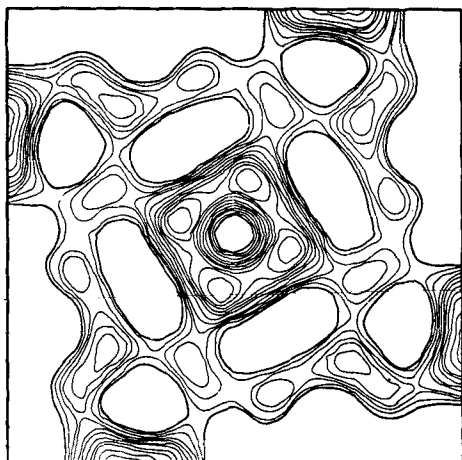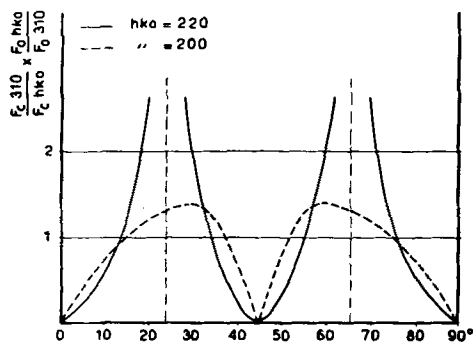for three typical $h\,k\,0$ reflections. The chosen reflections correspond to high Bragg distances so that they are sensitive to the orientation of the macromolecule but not to small variations of its conformation. Since the above reported expression needs to be equal to 1 in a ideally perfect structure, the positions which may be assumed are very limited, and one among these falls at $\approx 57°$.

It was possible to obtain a further improvement of the structure by searching for the model that might better correspond to the image given by a Fourier projection of the electronic density (Fig. 5) whose phases resulted univocally determined from the choice of the approximate orientation of the macromolecule.

For instance a clear evidence was obtained, that the plane of the ben-

2 Å

Fig. 5. – Fourier projection of the electron density on the (0 0 1) plane (arbitrary units).

TABLE II. – *Co-ordinates of the independent structural unit of poly-ortho-methylstyrene.*

	x/a	x/b	z/c
C_1	.197	.270	.810
C_2	.197	.270	.000
C_3	.136	.314	.066
C_4	.133	.383	.042
C_5	.077	.423	.100
C_6	.024	.395	.184
C_7	.027	.325	.205
C_8	.083	.285	.146
C_9	.086	.209	.174

TABLE III. – *Comparison between the observed and calculated structure factors of poly-ortho-methylstyrene.*

The F_o values correspond to the square root of the total intensity diffracted by the general $(h\,k\,l)$ lattice plane after effecting the corrections for the usual angular factors. In order to take into account the different multiplicity of the reflections, the $F(h\,h\,0)$ and $F(h\,0\,0)$ calculated structure factors were divided by $\sqrt{2}$:

$h\,k\,0$	F_c	F_o	$h\,k\,1$	F_c	F_o	$h\,k\,2$	F_c	F_o
2 0 0	150	181	2 1 1	239	206	1 1 2	183	not meas.
2 2 0	85	96	3 2 1	99	148	2 0 2	211	194
3 1 0	201	175	4 1 1	191	201	3 1 2	99	97
4 0 0	49	—	4 3 1	91	163	4 0 2	77	—
4 2 0	99	86	5 2 1	65	73	3 3 2 }	171	171
5 1 0	33	74	6 1 1	40	—	4 2 2 }		
4 4 0	2	—	5 4 1	11	—	5 1 2	90	103
5 3 0	11	—	6 3 1	92	83	5 3 2 }	87	113
6 0 0	91	95	7 2 1	11	—	6 0 2 }		
6 2 0	34	—	6 5 1	39	79	6 2 2	106	118
7 1 0	93	113	8 1 1 }	71	88	7 1 2 }	38	—
6 4 0	60	—	7 4 1 }			5 5 2 }		
7 3 0	128	134	8 3 1	41	—	6 4 2	95	135
8 0 0	57	—	9 2 1 }	121	101	7 3 2	86	—
8 2 0	10	—	7 6 1 }			8 0 2	73	—
6 6 0	55	—	8 5 1	73	—	8 2 2	30	—
7 5 0	25	—	9 4 1	93	—	7 5 2	86	—
8 4 0	100	131	10 1 1	27	—	8 4 2	48	—
9 1 0	27	—	10 3 1	61	—	9 1 2	24	—
9 3 0	52	—	8 7 1	27	—	9 3 2	34	—
10 0 0 }	207	169	9 6 1	61	—	7 7 2	52	—
8 6 0 }			11 2 1 }	82	82	10 0 2 }	86	96
10 2 0	13	—	10 5 1 }			8 6 2 }		
9 5 0	68	—	11 4 1	41	—	10 2 2	55	—

zene ring forms an angle of 68° with the $C_1C_2C_3$ plane of Fig. 2. This angle resulted of 60° for polystyrene and in fact the C_4 and C_8 atoms were thus equidistant from C_1 and C_1'. However, with an angle of 60° we would have had a too close contact between C_9 and C_2'. An analogous effect was noticed for poly-ortho-fluorostyrene [8], where the plane of benzene does not bisect the $\widehat{C_1C_2C_1'}$ angle being displaced of about 15° from the bisecting plane.
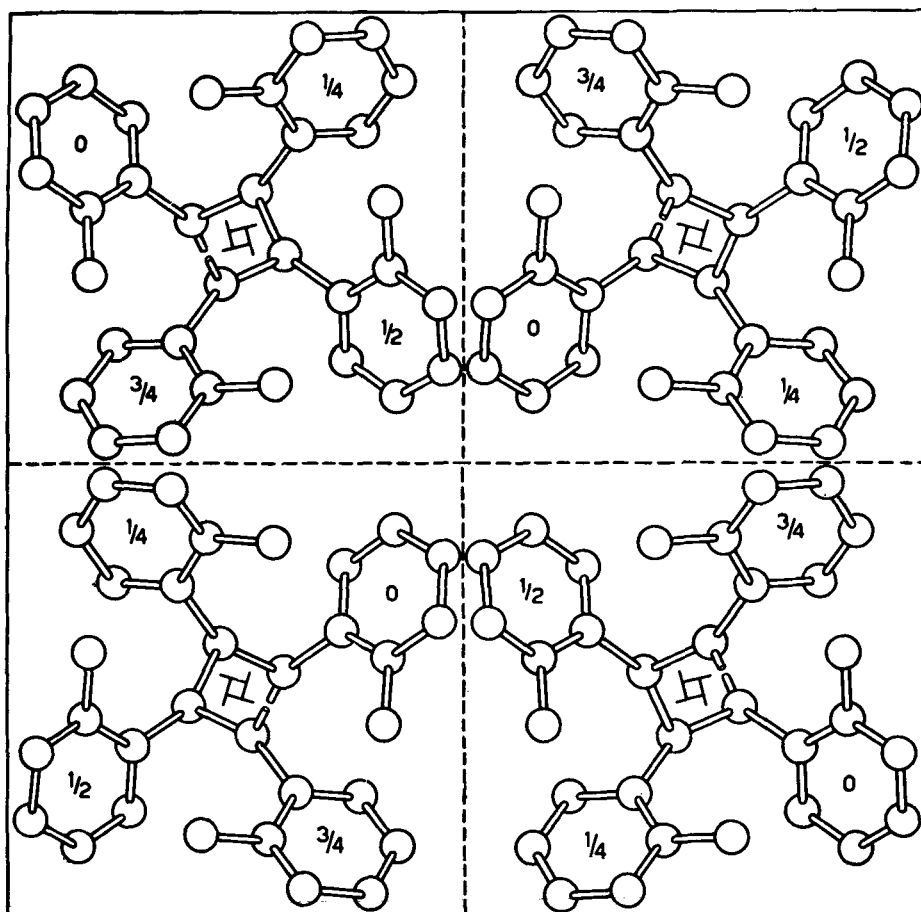

Fig. 6. – Model of the structure of poly-ortho-methylstyrene on (001).

By means of the found co-ordinates, given in Table II, a complete calculation of the structure factors was made, thus finding a good agreement between experimental and calculated structure factors for the $hk0$, $hk1$, $hk2$ reflections (Table III). This enables us to believe that the structure (Fig. 6) is

sufficiently determined, within the limits of the experimental data. For the structure factors of this compound we did not bring any correction due to thermal movements. In fact it was impossible to perform the observation of reflections having values of 2 sin ϑ higher than 1.0, owing to the blackening of the film and the progressive enlargement of diffraction spots. For a structure of this type, characterized by a high degree of order, a relatively low thermal factor may be reasonably expected, probably of the order of 4 Å², and thus practically without affecting the structure factors in the angular region under consideration.

3. – Final considerations.

Apart from the different symmetry of the helix it is evident from Fig.s 6 and 7 that a close analogy exists between the structure and the mode of packing of this compound with the structure and the mode of packing of poly-
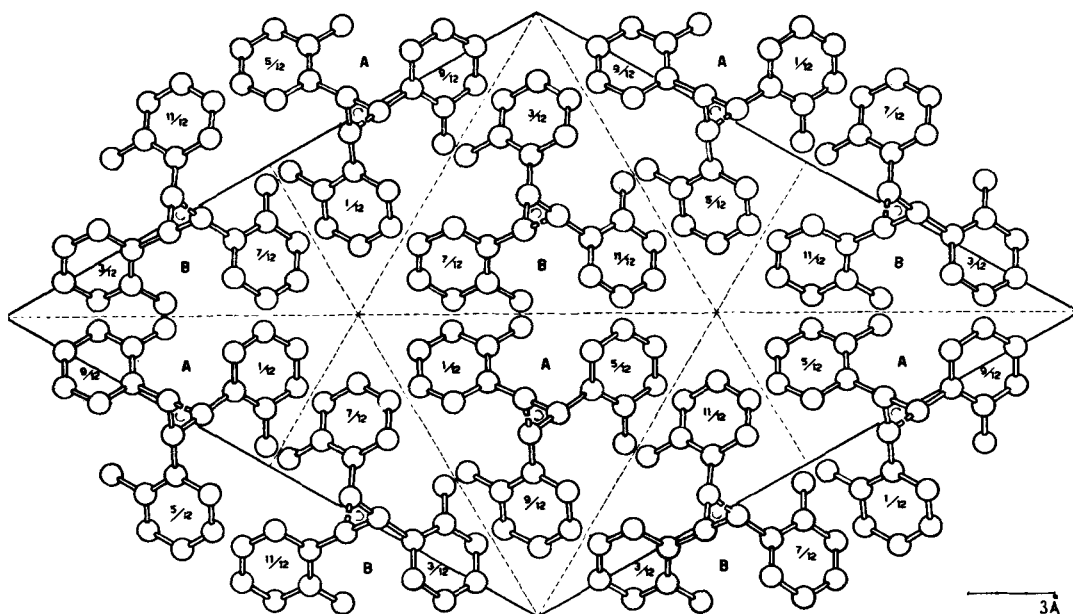

Fig. 7. – Model of the structure of poly-ortho-fluorostyrene on (001).

ortho-fluorostyrene, which belongs to the polar space group of the rhombohedral system ($R3c$), correspondent to the polar space group of the tetragonal system $I4_1cd$.

The typical shape of the chain of poly-ortho-methylstyrene, has been already

discussed by us [3] and corresponds to the ('B'), type, according to the terminology introduced by BUNN, which was slightly modified by us. The angles of internal rotation along carbon-carbon bonds along the chain are alternately of 180° (A) and 90° (B') instead of 180° (A) and 60° (B) as it happens with poly-ortho-fluorostyrene and polystyrene. This fact is due to the bulkiness of the methyl group, in comparison with fluorine or hydrogen atoms.

REFERENCES

[1] See for instance the literature quoted in the second paper of this issue, G. NATTA and P. CORRADINI: *Suppl. Nuovo Cimento*, **15**, 9 (1960).
[2] G. NATTA and P. CORRADINI: *Suppl. Nuovo Cimento*, **15**, 40 (1960); G. NATTA, P. CORRADINI and I. W. BASSI: *Suppl. Nuovo Cimeato*, **15**, 52, 68, 83 (1960).
[3] P. CORRADINI and I. PASQUON: *Rend. Acc. Naz. Lincei*, **19** (8), 453 (1955); G. NATTA, P. CORRADINI and I. W. BASSI: *Gazz. Chim. Ital.*, **89**, 784 (1959).
[4] G. NATTA, F. DANUSSO and D. SIANESI: *Makr. Chem.*, **28**, 253 (1958); D. SIANESI, M. RAMPICHINI and F. DANUSSO: *La Chim. e l'Ind.*, **41**, 287 (1959).
[5] G. NATTA, P. CORRADINI and I. W. BASSI: *Suppl. Nuovo Cimento*, **15**, 68 (1960).
[6] P. CORRADINI and I. W. BASSI: *Ric. Sci.*, **28**, 1435 (1958).
[7] G. NATTA and P. CORRADINI: *Suppl. Nuovo Cimento*, **15**, 9 (1960).
[8] G. NATTA P. CORRADINI and I. W. BASSI: *Suppl. Nuovo Cimento*, **15**, 83 (1960), p. 94.