

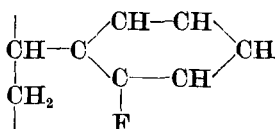
## Crystal Structure of Poly-ortho-Fluorostyrene.

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(ricevuto il 26 Giugno 1959)

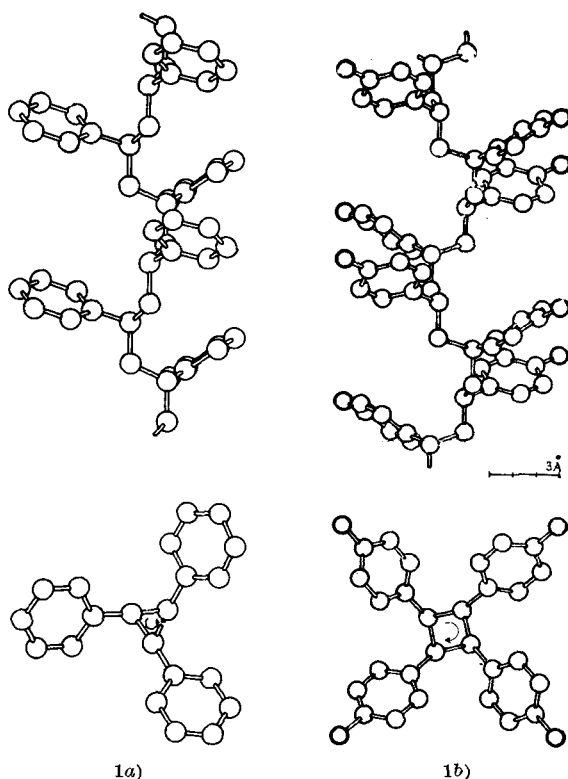
Through processes of stereospecific catalysis, an isotactic crystalline [1] polymer of ortho-fluorostyrene [2]



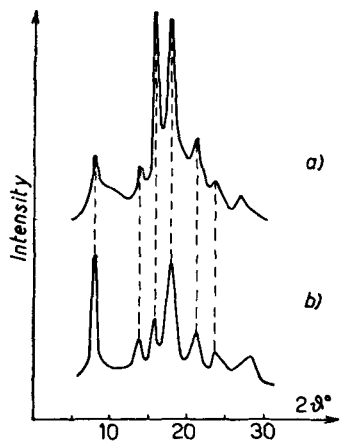
was first synthesized at the Institute of Industrial Chemistry of the Milan Polytechnic.

We shall report, in the present work, the results of our roentgenographic researches carried on in view of establishing the mutual structure relations between this new polymer and the isotactic polystyrene previously studied by us [3].

Fig. 1. - Conformation of the macromolecular chains of isotactic polystyrene (left) and of poly-para-fluorostyrene (right).



In a preceding work, it has been observed that, in the case of a *p*-substitution of a hydrogen atom of polystyrene by a fluorine atom, the form of the chain changed from that of threefold helix to that of a fourfold helix (Fig. 1) [4].



We shall see how the polymer we are considering in this paper has a structure strongly similar to that of isotactic polystyrene. Even an examination of the powder spectra of the two polymers, in fact, emphasizes the close analogy between them, at least as far as the form and dimensions of the unit cell are concerned (Fig. 2).

Fig. 2. - Comparison between the powder spectra (Cu,  $K\alpha$ ) registered with Geiger counter of isotactic polystyrene (a) and poly-ortho-fluorostyrene (b).

## 1. - Experimental.

Samples able to supply oriented crystalline fibers were prepared by extruding a thin cylinder of polymer from the melt. Such a cylinder was submitted to unidirectional hot stretching and was annealed under tension at a temperature of about 150 °C. The specimen so obtained, examined by X-rays, gives fiber photographs with many well oriented reflections such as to allow a good structural investigation.

The indexing of the reflections by reciprocal lattice methods, was made on the basis, as for isotactic polystyrene, of a rhombohedral unit cell.

Referring the constants of this unit cell to hexagonal axes, we obtain:

$$a = b = (22.15 \pm 0.10) \text{ \AA} \quad c = (6.63 \pm 0.05) \text{ \AA} .$$

The *c* direction is coincident with the stretching axis and thus with the axis of the polymeric chain.

The density which may be calculated by assuming that 18 monomeric units are contained in the unit cell is 1.29 g/cm<sup>3</sup>.

The corresponding data for isotactic polystyrene are:

$$a = b = (21.9 \pm 0.1) \text{ \AA} , \quad c = (6.65 \pm 0.05) \text{ \AA} , \quad \rho = 1.12 \text{ g/cm}^3 .$$

In Table I are given the observed and calculated values of the Bragg distances for a cell having these unit translations.

TABLE I. Comparison between calculated and observed Bragg distances for poly-ortho-fluorostyrene.

$hkl$	$d_c$	$d_o$	$hkl$	$d_c$	$d_o$
1 1 0	11.08	11.08	3 2 1	3.67	3.66
3 0 0	6.38	6.41	4 2 $\bar{1}$	3.18	3.19
2 2 0	5.52	5.53	5 1 1	3.06	3.04
4 1 0	4.19	4.17	4 3 1	2.85	2.83
3 3 0	3.69	3.69	6 1 $\bar{1}$	2.68	2.68
6 0 0	3.20	3.20	5 3 $\bar{1}$	2.53	2.54
5 2 0	3.07	3.06	6 2 1	2.47	—
4 4 0	2.77	2.77	5 4 1	2.30	2.31
7 1 0	2.54	2.55	7 2 $\bar{1}$	2.21	2.21
6 3 0	2.42	2.41	8 1 1	2.13	2.16
5 5 0	2.22	2.22	6 4 $\bar{1}$	2.09	—
9 0 0	2.14	2.13	7 3 1	2.05	2.06
8 2 0	2.09	2.08	6 5 1}	1.92	1.93
7 4 0	1.99	1.99	9 1 $\bar{1}$ }		
6 6 0	1.85	1.85	8 3 $\bar{1}$	1.87	1.88
10 1 0	1.82	—	9 2 1	1.82	—
9 3 0	1.78	—	7 5 $\bar{1}$	1.77	1.78
8 5 0	1.69	1.69	8 4 1	1.75	—
12 0 0	1.60	—	10 2 $\bar{1}$	1.67	—
11 2 0}	1.59	1.59	7 6 1	1.65	—
7 7 0}			11 1 1}	1.61	1.63
10 4 0	1.54	—	9 4 $\bar{1}$ }		
9 6 0	1.47	—	10 3 1	1.58	—
13 1 0	1.42	—	8 6 $\bar{1}$	1.53	—
12 3 0	1.40	—	9 5 1	1.52	—
8 8 0	1.38	—	12 1 $\bar{1}$	1.49	1.49
11 5 0	1.35	—	11 3 $\bar{1}$	1.47	—
10 7 0	1.30	—	8 7 1	1.44	—
15 0 0	1.28	1.28	12 2 1	1.43	—
14 2 0	1.27	—	10 5 $\bar{1}$	1.42	—
13 4 0	1.25	—	11 4 1	1.40	—
9 9 0	1.23	—			
12 6 0	1.21	—	1 0 $\bar{2}$	3.27	not meas.
16 1 0}	1.16	1.16	2 0 2	3.12	3.13
11 8 0}			2 1 $\bar{2}$	3.01	—
15 3 0	1.15	—	3 1 2	2.81	2.81
14 5 0	1.12	—	4 0 $\bar{2}$	2.72	—
10 10 0	1.11	—	3 2 $\bar{2}$	2.64	—
13 7 0	1.09	—	5 0 2	2.49	2.50
18 0 0	1.07	1.06	4 2 2	2.43	—
17 2 0	1.06	—	5 1 $\bar{2}$	2.38	—
12 9 0	1.05	—	4 3 $\bar{2}$	2.27	—
			6 1 2	2.22	2.20
2 1 1	4.89	4.88	7 0 $\bar{2}$ }	2.10	2.10
3 1 $\bar{1}$	4.15	4.11	5 3 2}		

TABLE I (continued).

$h k l$	$d_c$	$d_o$	$h k l$	$d_c$	$d_o$
6 2 $\bar{2}$	2.06	—	12 2 $\bar{2}$	1.33	—
5 4 $\bar{2}$	1.95	—	10 5 2	1.32	—
8 0 2	1.93	—	11 4 $\bar{2}$	1.30	—
7 2 2	1.90	—			
8 1 $\bar{2}$	1.85	—	1 1 3	2.17	not meas.
6 4 2	1.82	—	2 2 3	2.05	not meas.
7 3 $\bar{2}$	1.79	—	4 1 3	1.95	1.94
6 5 $\bar{2}$ }			3 3 3	1.89	1.87
9 1 2 } }	1.71	1.73	5 2 3	1.79	1.77
8 3 2	1.67	1.66	4 4 3	1.72	—
10 0 $\bar{2}$	1.65	1.66	7 1 3	1.66	1.67
9 2 $\bar{2}$	1.63	—	6 3 3	1.63	1.62
7 5 2	1.59	—	5 5 3	1.56	—
8 4 $\bar{2}$	1.58	—	8 2 3	1.51	—
11 0 2	1.53	—	7 4 3	1.47	—
10 2 2	1.51	—	6 6 3	1.41	—
7 6 $\bar{2}$	1.50	—	10 1 3	1.40	—
11 1 $\bar{2}$ }			9 3 3	1.38	—
9 4 2 } }	1.47	—	8 5 3	1.34	—
10 3 $\bar{2}$	1.45	—	11 2 3 } }		
8 6 2	1.41	—	7 7 3 } }	1.28	—
9 5 $\bar{2}$	1.40	—	10 4 3	1.25	—
12 1 2	1.38	—	9 6 3	1.21	—
11 3 2	1.36	—	13 1 3	1.19	—
13 0 $\bar{2}$ }			12 3 3	1.17	—
8 7 2 } }	1.34	—			

The  $(hkl)$  reflections with  $-h+k+l \neq 3n$  and the reflections  $(h0l)$  with  $l \neq 2n$  being systematically absent, the choice of the space group is restricted to the  $R\bar{3}c$  group or to its polar  $R3c$  subgroup.

The intensity measurements were carried out for the zero and the 1st layer lines by the multiple film method; for the higher layer lines, owing to the remarkable enlargement of spots, we limited ourselves to record the qualitative course of the intensities.

## 2. - Structural considerations.

In analogy to what we summarized in the discussion of isotactic poly-alpha-butene and polystyrene structures, the monomeric units must necessarily repeat themselves, three by three, along the six threefold screw axes contained in the unit cell. Keeping into account the principle that the conformation of

a polymeric chain in the crystalline state tends to be that of minimum potential energy which an isolated oriented chain would assume, since the effect of the neighbouring chains is generally small on its conformation, we tried first to build up the most probable model of the polymeric chain (Fig. 3). As second step, we studied the possible way of packing of such macromolecules, keeping into account the restrictions imposed by unit cell symmetry and size.

In Fig. 4 a small portion of the main chain is given, showing the details relative to the construction of the independent structural unit. Angles and bond lengths were deduced from literature data and from what we found in the structural study of analogous crystalline polymers [5]. The  $\widehat{C_1C_2C_1}$ , and  $\widehat{C_2C_1C_1}$  angles were assumed as equal to  $116^\circ$  in order that the main chain atoms satisfy the principle of the staggered bonds.

To the  $\widehat{C_1C_2C_3}$  and  $\widehat{C_1C_2C_3}$  angles was ascribed the tetrahedral value analogously with what we found for poly-alpha-butene [6]. In order to minimize the intramolecular contacts between the carbon atoms of the benzene ring and those of the polymeric chain, the most probable position of the benzene ring should be that in which the plane it defines bisects the  $\widehat{C_1C_2C_1}$  angle, at least until no consideration is taken of contacts due to fluorine atoms. As far as the independent structural unit is concerned there are two ortho non-equivalent positions, both possible

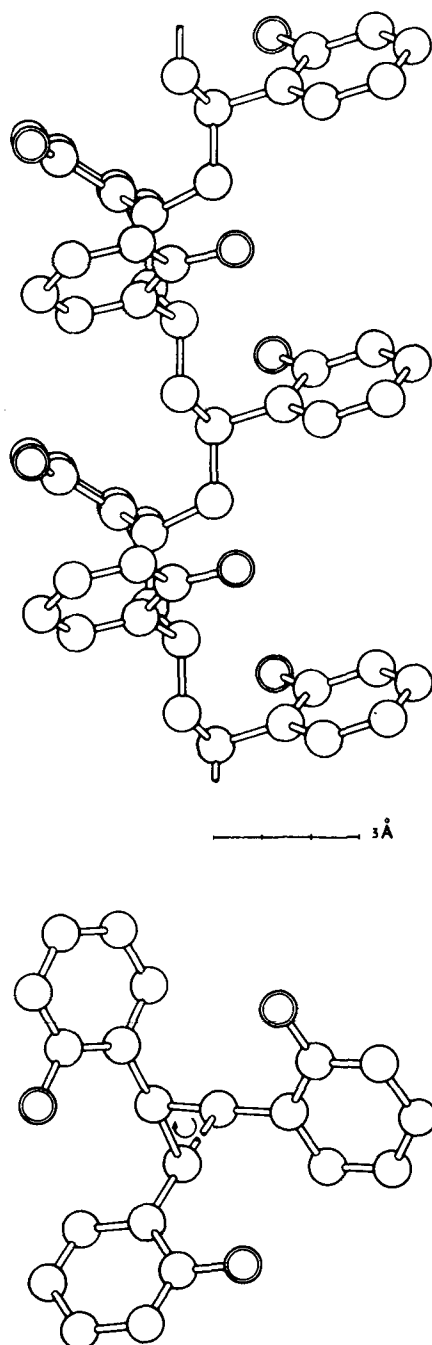


Fig. 3. - Conformation of the poly-ortho-fluorostyrene macromolecule (side and end views).

for the fluorine atom, say  $F_4$  or  $F_5$  (the index refers to the carbon atom to which the fluorine atom is linked).

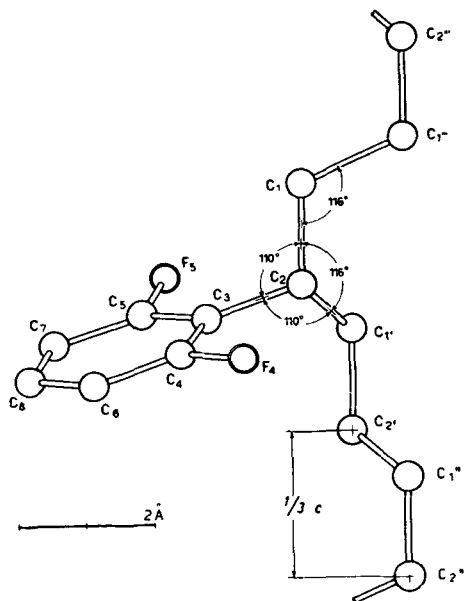


Fig. 4. - Conformation of the independent structural unit of poly-ortho-fluorostyrene ( $C-C = 1.54 \text{ \AA}$ ,  $(C-C)_{\text{ortho}} = 1.40 \text{ \AA}$ ,  $C-F = 1.35 \text{ \AA}$ ,  $CCF = 120^\circ$ ).

polystyrene, because of their outstanding intensity and because their structure factors do not vary with respect to the choice of the space group ( $R3c$  or  $R\bar{3}c$ ).

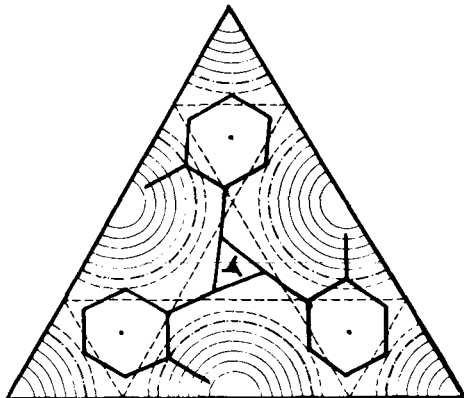
From Figs. 5, 6 it is possible to observe the position which must be given to the macromolecule in respect of the  $x$  and  $y$  axes, so as to justify the different ratio of intensity existing between the two reflections in the case of poly-ortho-fluorostyrene and polystyrene. In fact supposing that carbon atoms in poly-ortho-fluorostyrene have nearly equal positions in

Fig. 5. -  $(220)$  structure factor graph, showing the position assumed by the macromolecule (contours are drawn at regular intervals: — positive lines; - - - - zero lines; - - - - negative lines).

Assuming as carbon-fluorine bond distance the value of literature [7], *i.e.*  $1.35 \text{ \AA}$ , the Van der Waals contacts between fluorine atoms and the main chain carbon atoms result worse for the  $F_5$  than for the  $F_4$  position. Thus the position  $F_5$  has to be rejected. The determination of the position assumed by the independent structural unit inside the unit cell, owing to the great structural analogy existing between poly-ortho-fluorostyrene and isotactic polystyrene, was made as for this latter, taking account of the particularly significant intensity of some equatorial reflections by means of structure factors graphs [8].

Moreover, we tried to have everywhere analogous Van der Waals contacts between the atoms of the neighbouring macromolecules.

The  $(220)$  and  $(660)$  reflections were first investigated, as for isotactic



respect of the  $x$  and  $y$  axes, as in polystyrene, the fluorine atoms are in phase discordance with the carbon atoms for the (220) reflection and in accordance for the (660) reflection. Hence, it may be calculated, as found also experimentally, that  $F(660)/F(220)$  for poly-ortho-fluorostyrene is greater than the corresponding ratio for isotactic polystyrene.

Assuming the approximate position postulated for the macromolecule in order to satisfy the above assumptions, we have more precisely defined the coordinates of the independent structural unit taking into account the intermolecular contacts generated by rotating the macromolecule around its threefold screw axis. The calculations have been made first for the crystalline lattice defined by the  $R3c$  space group, for which the packing of the macromolecules is independent of the choice of the origin in respect of the  $z$  axis.

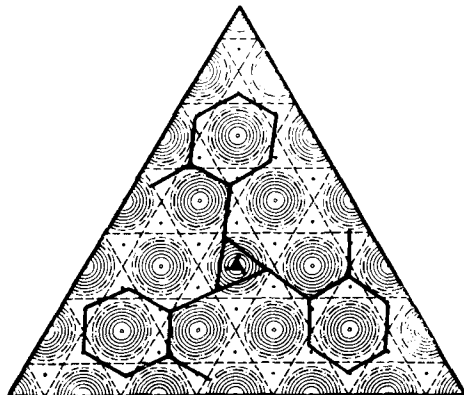


Fig. 6. — (660) structure factor graph.

In Fig. 7 is reported the position which gives the best packing contacts between neighbouring macromolecules. For this position the contacts between carbon atoms are all in good accordance with the literature data and are homogeneous in all directions [9].

By rotating clockwise and anticlockwise the macromolecule by  $2^\circ$ , the contacts become fairly worse as it results from Table II. In the same table we

TABLE II. — Values of Van der Waals contacts between atoms of neighbouring macromolecules of poly-ortho-fluorostyrene. (Only the most significant values are reported).

(I): values calculated when the position assumed by the independent structural unit is that of Fig. 7. (II) and (III): values calculated by rotating the macromolecule by  $2^\circ$  anticlockwise and clockwise respectively.

Atoms of isoclinal molecules		II Å	I Å	III Å	Atoms of antiinclined molecules		I Å
$C_{6A}$	$C_{6C}$	3.45	3.54	3.60	$C_{4A}$	$C_{5C}$	3.44
$C_{6A}$	$C_{4C}$	3.46	3.56	3.64	$C_{4A}$	$C_{7C}$	3.51
$C_{6A}$	$F_C$	3.86	3.88	3.93	$F_A$	$C_{5C}$	3.28
$C_{7A}$	$C_{7B}$	3.58	3.50	3.43	$F_A$	$C_{7C}$	3.87
$C_{7A}$	$C_{5B}$	3.71	3.55	3.49	$C_{5A}$	$F_B$	3.25
$C_{7A}$	$C_{8B}$	3.58	3.45	3.34	$C_{5A}$	$C_{4B}$	3.40
$F_A$	$F_C$	3.43	3.44	3.46	$C_{5A}$	$C_{6B}$	3.56
$F_A$	$C_{4C}$	3.78	3.81	3.84	$C_{8A}$	$C_{6B}$	3.48
$F_A$	$C_{1C}$	3.53	3.58	3.63	$C_{8A}$	$C_B$	3.81

report the values of the intermolecular contacts if the space group were  $R\bar{3}c$  (a suitable choice of the origin in respect of the  $z$  axis is needed). In this case too, as for isotactic polystyrene and poly- $\alpha$ -butene, it is not possible to

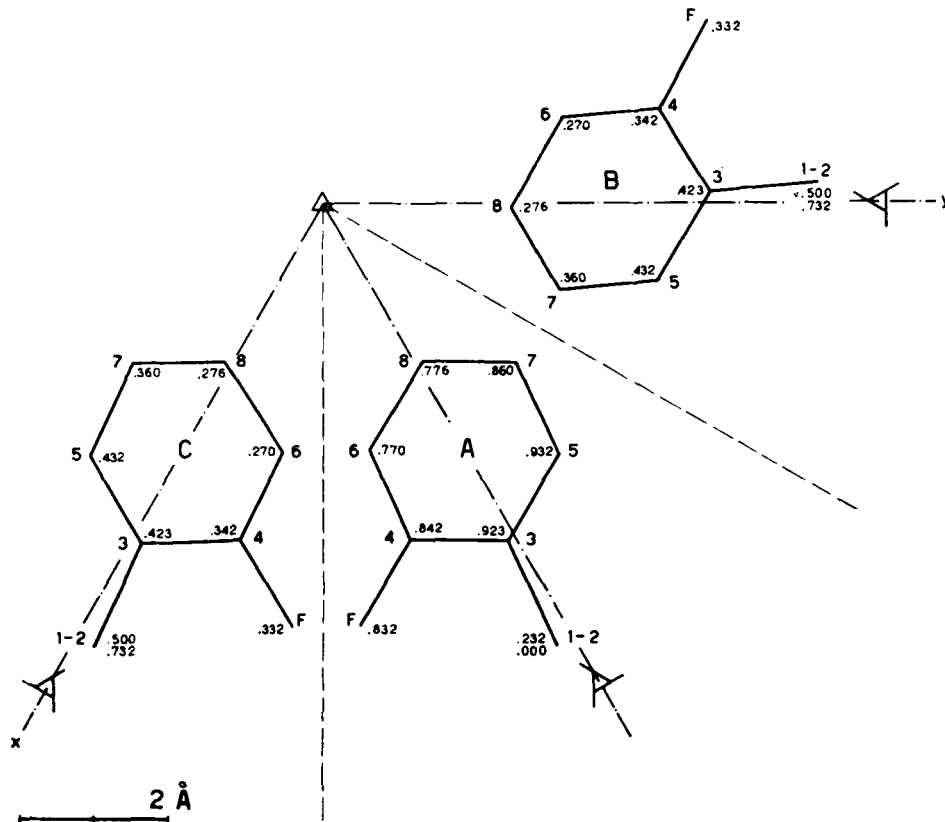


Fig. 7. — Actual position of the poly-ortho-fluorostyrene macromolecule in the unit cell.

choose univocally the true space group, on the basis of the contacts only. It is possible, however, to remark that, although the distances of contacts do not diminish when enantiomorphous antilined macromolecules face one another, the number of contacts increases remarkably.

### 3. — Calculation of structure factors.

We found it advisable also for poly-ortho-fluorostyrene, to make the calculation of the structure factors for both the space groups either according to the suggested model, or according to other trial models in which the mono-



meric unit was slightly rotated around the threefold screw axis or in which the plane of the benzene ring was slightly rotated around the  $C_2C_3$  bond.

The best agreement between the observed and calculated structure factors (Table IV) was obtained for the non-centrosymmetric space group  $R3c$  using the co-ordinates reported in Table III, which nearly correspond to those of

TABLE III. - Co-ordinates of the independent structural unit of poly-ortho-fluorostyrene. (The atoms are marked as in Fig. 7).

	$x/a$	$y/b$	$z/c$
$C_1$	0.306	0.293	0.232
$C_2$	0.306	0.293	0.000
$C_3$	0.238	0.231	0.923
$C_4$	0.238	0.173	0.842
$C_5$	0.176	0.233	0.932
$C_6$	0.175	0.116	0.770
$C_7$	0.114	0.176	0.860
$C_8$	0.114	0.118	0.776
F	0.297	0.170	0.832

the model first postulated, with the exception of a rotation by  $15^\circ$  of the plane of the benzene ring around the  $C_2C_3$  bond, from the position in which

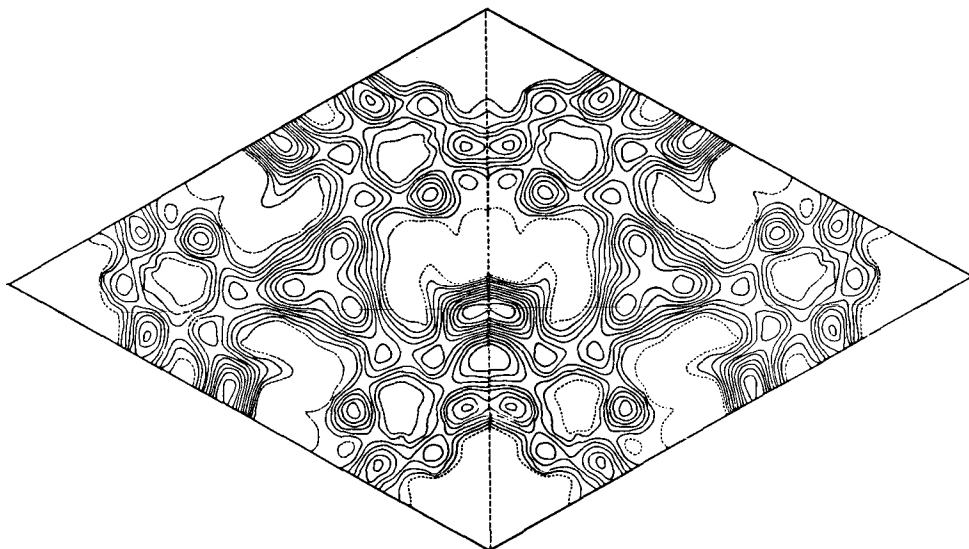


Fig. 8. - Projection on (001) of the electron density for poly-ortho-fluorostyrene, calculated for the  $R3c$  space group (levels in arbitrary units).

TABLE IV. — Comparison between the observed and the calculated structure factors. The  $F_o$  values correspond to the square root of the total intensity diffracted by the  $(hkl)$  lattice plane, after effecting the usual corrections for the angular factors. In order to take into account the different multiplicity of the reflections, all the calculated structure factors, except the  $(h00)$  and  $(hh0)$  ones, were multiplied by  $\sqrt{2}$ ;  $B=6 \text{ \AA}^2$ . (Cu,  $K \alpha$ ).

$hkl$	$2 \sin \theta$	A	B	$F_c$	$F_o$	$hkl$	$2 \sin \theta$	A	B	$F_c$	$F_o$
1 1 0	0.139	— 90	—	90	99	2 1 1	0.315	—194	+220	294	244
3 0 0	0.242	— 3	— 66	66	69	3 1 $\bar{1}$	0.372	+ 99	+ 95	137	152
2 2 0	0.279	— 81	—	81	100	3 2 1	0.420	—120	—113	165	165
4 1 0	0.367	— 64	+ 85	107	95	4 2 $\bar{1}$	0.485	+ 26	+ 43	51	108
3 3 0	0.418	+ 61	—	61	75	5 1 1	0.504	+123	+ 27	126	148
6 0 0	0.483	+ 69	— 26	74	55	4 3 1	0.541	— 73	— 6	74	72
5 2 0	0.502	— 82	— 77	113	86	6 1 $\bar{1}$	0.575	+ 5	— 98	98	101
4 4 0	0.557	+ 57	—	57	60	5 3 $\bar{1}$	0.609	+ 42	+ 49	65	111
7 1 0	0.607	+ 4	+ 44	44	52	6 2 1	0.624	+ 18	— 19	26	—
6 3 0	0.638	+ 61	+ 37	71	84	5 4 1	0.670	— 15	+ 36	39	43
5 5 0	0.696	— 53	—	53	46	7 2 $\bar{1}$	0.698	— 45	— 12	47	37
9 0 0	0.722	— 2	— 56	56	42	8 1 1	0.724	+ 18	+ 37	41	—
8 2 0	0.736	+ 33	— 10	34	—	6 4 $\bar{1}$	0.738	— 60	— 11	61	55
7 4 0	0.775	— 26	— 40	48	50	7 3 1	0.752	+ 94	— 57	110	147
6 6 0	0.835	— 85	—	85	101	6 5 1}	0.803	— 78	— 3	91	105
10 1 0	0.846	+ 14	+ 30	33	—	9 1 $\bar{1}$ }		— 45	+ 15		
9 3 0	0.869	+ 19	— 25	31	—	8 3 $\bar{1}$	0.825	+ 3	— 66	66	43
8 5 0	0.912	+ 11	+ 36	38	54	9 2 1	0.847	— 17	— 30	34	—
12 0 0	0.965	— 1	— 25	25	—	7 5 $\bar{1}$	0.871	— 9	+ 50	51	—
11 2 0}	0.974	— 13	+ 14	41	44	8 4 1	0.881	+ 38	+ 62	73	82
7 7 0}		+ 36	—			10 2 $\bar{1}$	0.923	— 16	+ 13	21	—
10 4 0	1.004	+ 6	— 10	12	—	7 6 1	0.934	+ 11	— 42	44	—
9 6 0	1.050	— 6	— 17	18	—	11 1 1}	0.958	+ 26	— 2	39	46
13 1 0	1.088	+ 8	+ 22	24	—	9 4 $\bar{1}$ }		+ 25	+ 14		
12 3 0	1.105	— 19	— 15	24	—	10 3 1	0.976	— 31	+ 22	38	—
8 8 0	1.114	— 8	—	8	—	8 6 $\bar{1}$	1.008	— 20	+ 1	20	—
11 5 0	1.140	+ 7	— 4	8	—	9 5 1	1.014	— 21	— 8	22	—
10 7 0	1.188	+ 24	+ 13	27	—	12 1 $\bar{1}$	1.035	— 28	— 43	51	51
15 0 0	1.206	— 28	— 21	53	42	11 3 $\bar{1}$	1.049	+ 32	+ 6	32	—
14 2 0	1.213	— 38	+ 13			8 7 1	1.070	+ 16	— 3	16	—
13 4 0	1.238	+ 15	+ 14	20	—	12 2 1	1.079	— 45	— 6	46	vwv
9 9 0	1.252	+ 1	—	1	—	10 5 $\bar{1}$	1.085	+ 5	— 14	15	—
12 6 0	1.275	— 23	— 10	25	—	11 4 1	1.101	+ 2	— 25	25	—
16 1 0}	1.328	+ 70	+ 11	71	44	9 7 $\bar{1}$	1.141	— 13	— 11	17	—
11 8 0}		— 1	+ 8			10 6 1	1.150	+ 45	+ 7	46	—
15 3 0	1.343	— 29	— 28	40	—	13 2 $\bar{1}$	1.159	+ 59	+ 22	63	vwv
14 5 0	1.372	+ 2	+ 4	5	—	12 4 $\bar{1}$	1.184	— 14	+ 10	17	—
10 10 0	1.391	+ 10	—	10	—	14 1 1	1.193	— 49	+ 62	79	vwv
13 7 0	1.413	+ 13	+ 5	14	—	13 3 1}	1.206	— 5	+ 1	14	—
18 0 0	1.447	+ 23	— 18	40	50	9 8 1}		— 12	— 6		
17 2 0	1.453	— 6	+ 27			11 6 $\bar{1}$	1.224	+ 19	+ 13	23	—
						12 5 1	1.233	— 26	— 1	26	—

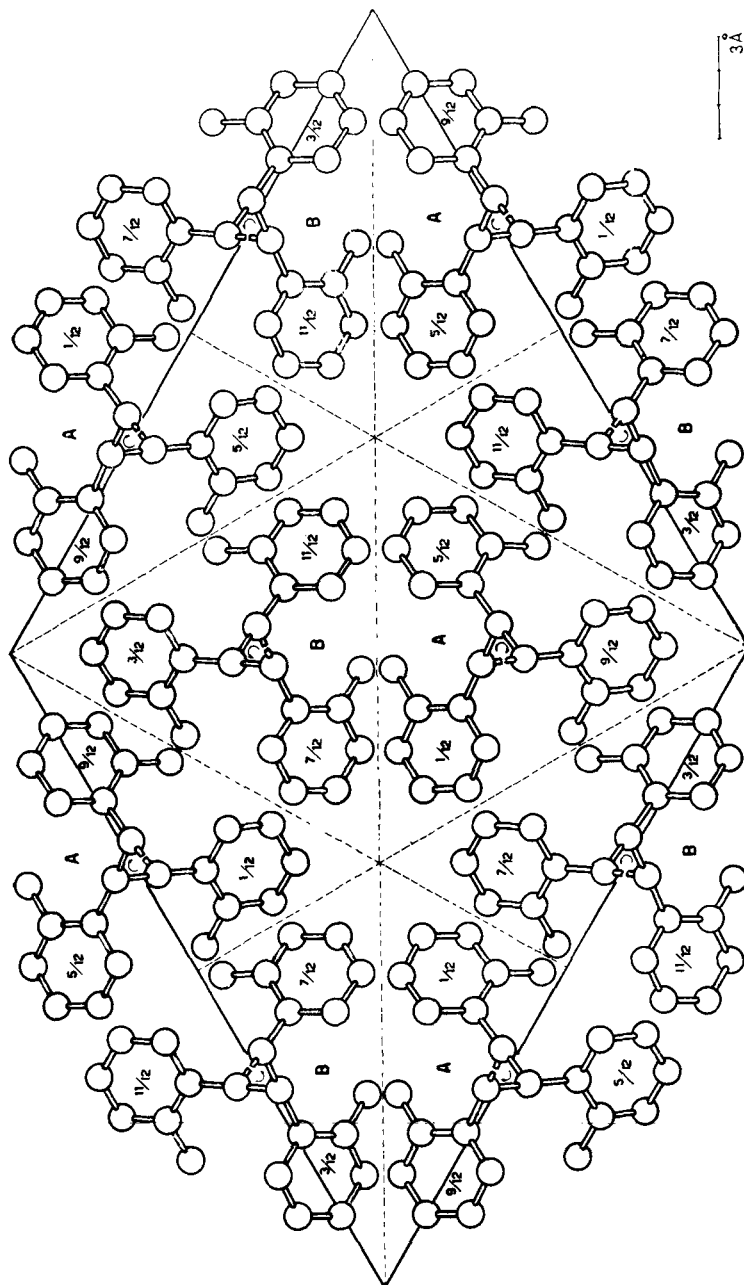


Fig. 9. — Projection on (001) of the unit cell content of poly-ortho-fluorostyrene ( $R3c$  space group).

it bisects the  $C_1\widehat{C}_2C_1$  angle. Following the knowledge of the phase angles of the  $(hk0)$  reflections (the  $R3c$  space group is a non-centrosymmetric one) it was possible to make a Fourier projection of the electron density on the (001)

plane. The Fourier projection has given a good evidence of the rotation of the plane of the benzene ring in respect of the plane which bisects the  $C_1\widehat{C}_2C_1$  angle. The coherent values assumed by the electron density in the points corresponding to the postulated positions of the atoms and the lack of spurious maxima, as given in Fig. 8, enable us to believe in the substantial exactness

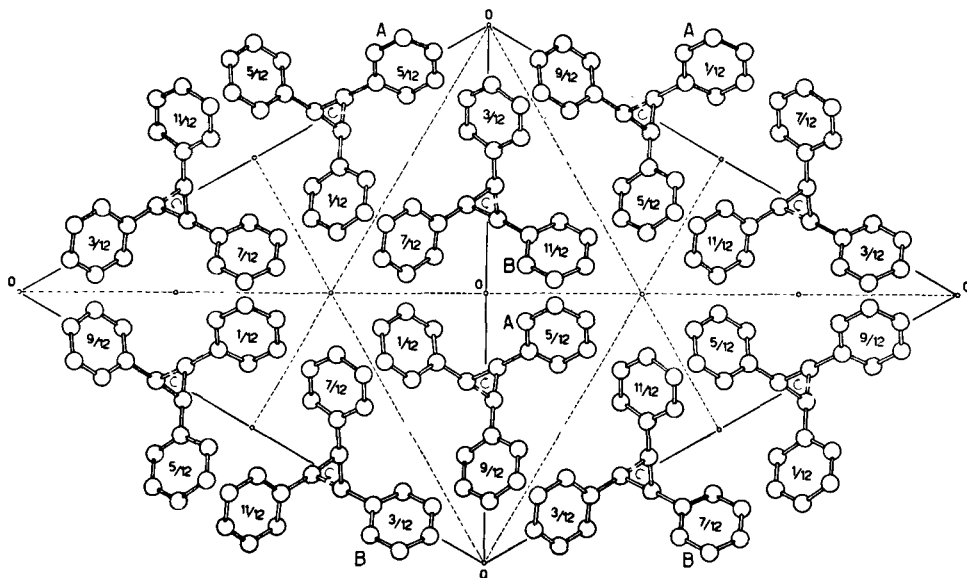


Fig. 10. - Projection on (001) of the structure of isotactic polystyrene for the  $R3c$  space group.

of the suggested model. In Fig. 9 and Fig. 10 a comparison between the structure of the examined polymer and that found for isotactic polystyrene is given.

The analogy results quite fair between the structures of the two polymers, which determines the possibility, experimentally proved by us [10], to obtain crystalline copolymers of styrene and orthofluorostyrene.

The fact that, as reported above, the plane of the benzene ring appears to be rotated by  $15^\circ$  around the  $C_2C_3$  bond, from the position in which it bisects the  $C_1\widehat{C}_2C_1$  angle (as it occurs for polystyrene) may be easily explained in order to diminish the contact between  $F_4$  and  $C_{1'}$  (Fig. 4).

Such a rotation also takes place for other polymers of ortho-substituted styrenes as poly-ortho-methylstyrene, even when the shape of the main chain is slightly different from the threefold helix one.

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