G. NATTA, etc.
1960
N. 1 del *Supplemento* al Vol. **15**, Serie X,
del *Nuovo Cimento* - pag. 68-82

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BOLOGNA
TIPOGRAFIA COMPOSITORI
1960

Crystal Structure of Isotactic Polystyrene.

G. NATTA, P. CORRADINI and I. W. BASSI

Istituto di Chimica Industriale del Politecnico - Milano

(ricevuto il 26 Giugno 1959)

The investigation by X-rays [1] and by electron beams [2] of the styrene polymers, obtained with stereospecific catalysts [3], was made at the Institute of Industrial Chemistry of the Milan Polytechnic, as part of our research work on the crystal structure of isotactic polymers. The results issued from a preliminary examination have been outlined in a preceding Letter to the Editor of *Makromolekulare Chemie* [4].

1. – Experimental.

The isotactic polymers of styrene display at X-ray examination a crystallinity of (40 ÷ 45) % [5]. They show a very high melting point (up to 240 °C) [6], and, therefore, substantially differ from styrene polymers precedently known, which are amorphous and possess a softening point (II order transition) which is not higher than 90 °C.

The crystallization of high molecular weight isotactic polystyrene occurs very slowly; quenching the polymer from the melted state down to room temperature it does not crystallize. The so treated amorphous isotactic polymers of styrene become soluble in ketonic solvents *i.e.* methylethylketone in which the atactic polymers with the same molecular weight are soluble and, heated, they soften at 90 °C. Above this temperature, they can crystallize and become insoluble in the above mentioned solvents. For example, some characteristic kinetic curves of crystallization, obtained by a special apparatus that we have designed [7], are reported in Fig. 1. The fractions in weight of the crystallized polymer are plotted therein against time, for various tempe-

ratures [8]. The crystallization rate is strongly dependent on the molecular weight, and it reaches its highest degree at temperatures of about 180 °C.

Oriented crystalline fibers of polystyrene, allowing to perform a roentgenographic examination of the structure of the polymer, could be obtained in the following way.

The polymer is extruded at 250 °C, in order to obtain a small cylinder.

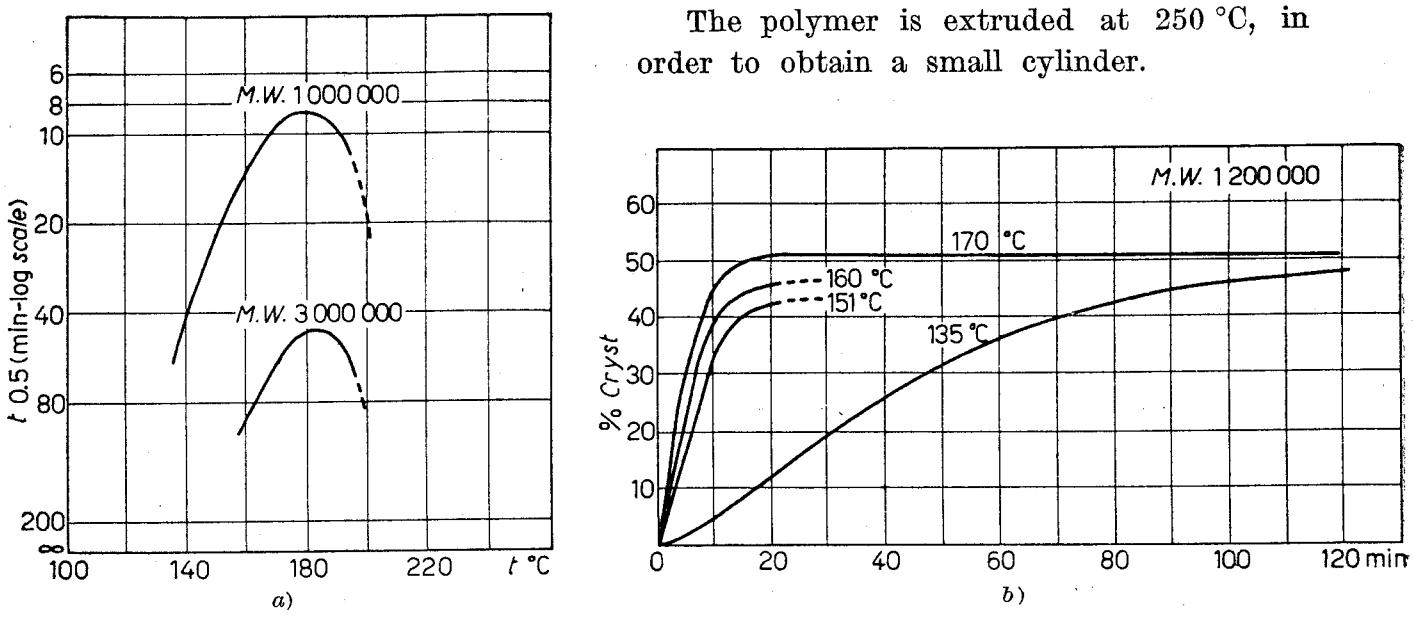

Fig. 1. – Crystallization kinetics curves of different samples of isotactic polystyrene (the molecular weight here reported is that measured before performing the experiences).

When quickly cooled down to room temperature, it results amorphous owing to the low crystallization rate. The extruded filament is then stretched at a temperature (about 100 °C) slightly higher than the softening temperature of the amorphous polymer and allowed to crystallize under tension at 150 °C during $(2 \div 3)$ hours.

The fiber obtained by this method gives an X-ray spectrum, very rich of well oriented reflections (Fig. 2). The spectrum may be readily interpreted by reciprocal lattice methods on the basis of a rhombohedral unit cell (only reflections with $-h+k+l = 3n$ are present) whose identity periods referred to hexagonal axes are: $a = b = (21.9 \pm 0.1)$ Å and $c = (6.65 \pm 0.05)$ Å (c is the axis of the polymeric chain and coincides with the stretching direction).

Should one assume that the number of monomeric units contained in the unit cell is 18, the calculated density ($d_{\text{calc.}} = 1.126$ g/cm^3) is in accordance with the experimental datum ($d_{\text{exp.}} = 1.08$ g/cm^3). From the further systematical absence of reflections $(h\,0\,l)$ with $l = 2n+1$, the choice of the space group is restricted to the $R\bar{3}c$ space group or to its subgroup $R3c$.

The measurement of the reflection intensities was carried out by the multiple film method, and it was possible, in a quantitative way, only for the zero and the 1st layer lines of the fiber photograph.

For the 2nd and 3rd layer lines, which show much enlarged spots with intensities which are thus rather difficult to be evaluated quantitatively, we shall outline only the qualitative course of the diffracted intensities (see below).

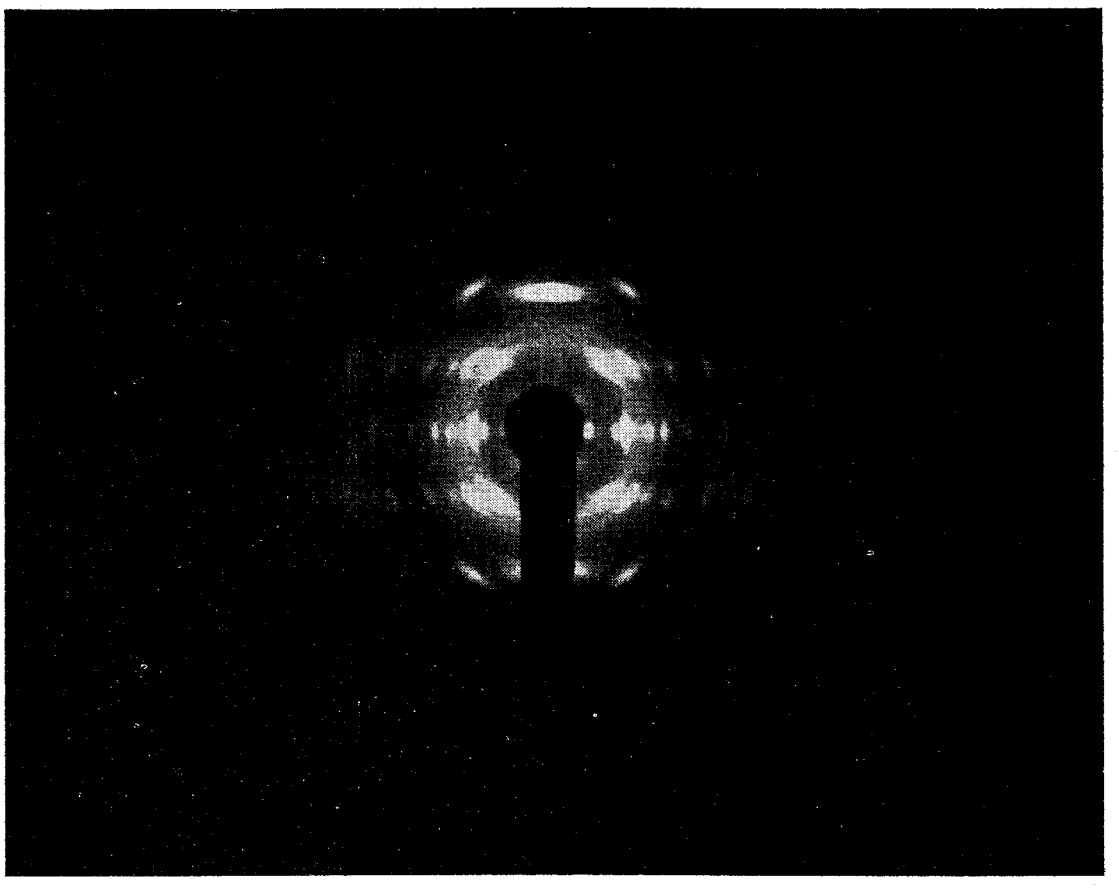

Fig. 2. – Fiber photograph of isotactic polystyrene.

2. – Considerations on the structure.

The monomeric units, according to reasons analogous to those illustrated for poly-alpha-butene [9], must necessarily follow one another along a three-fold screw axis. It is possible, therefore, to construct a model of the chain even when only the identity period along the chain axis is known (6.65 Å), keeping into account the principles summarized in a previous work of ours [10].

Such a model is shown in Fig. 3. In Fig. 4, a small portion of the chain itself is sketched. If one wishes that the atoms of the chain obey the principle of staggered bonds, the $C_1\widehat{C_2}C_{1'}$ and $C_2\widehat{C_1}C_{2''}$ angles must be equal to 116°. The most probable position of the plane on which the benzene ring lies, is that in which the plane bisects the $C_1\widehat{C_2}C_{1'}$ angle [11].

In such a way, unsuitable Van der Waals contacts between carbon atoms

belonging to the same chain, are minimized; in particular C_4 and C_5 have respectively the same distance from $C_{1'}$ and C_1.

In a first instance, the tetrahedral value (109° 28′) has been assumed for the $C_{1'}\widehat{C_2}C_3$ and $C_1\widehat{C_2}C_3$ angles analogously to what we found for poly-alpha-butene. Successively, these angles have been slightly modified in order to obtain the best accordance between observed and calculated structure factors. Such values, reported in Fig. 4, are respectively 108° ($C_1\widehat{C_2}C_3$) and 111° ($C_{1'}\widehat{C_2}C_3$).

The determination of the co-ordinates of the independent structural unit, was performed by us, keeping into account the particular intensity of some equatorial reflections by means of structure factor graphs [12] and by assuming that the Van der Waals contacts between the atoms of neighbouring macromolecules, should be in reasonable accordance with those given in the literature for low molecular weight compounds.

The determination of the probable orientation of the macromolecules around the threefold screw axes of the crystal lattice was facilitated when the (2 2 0)

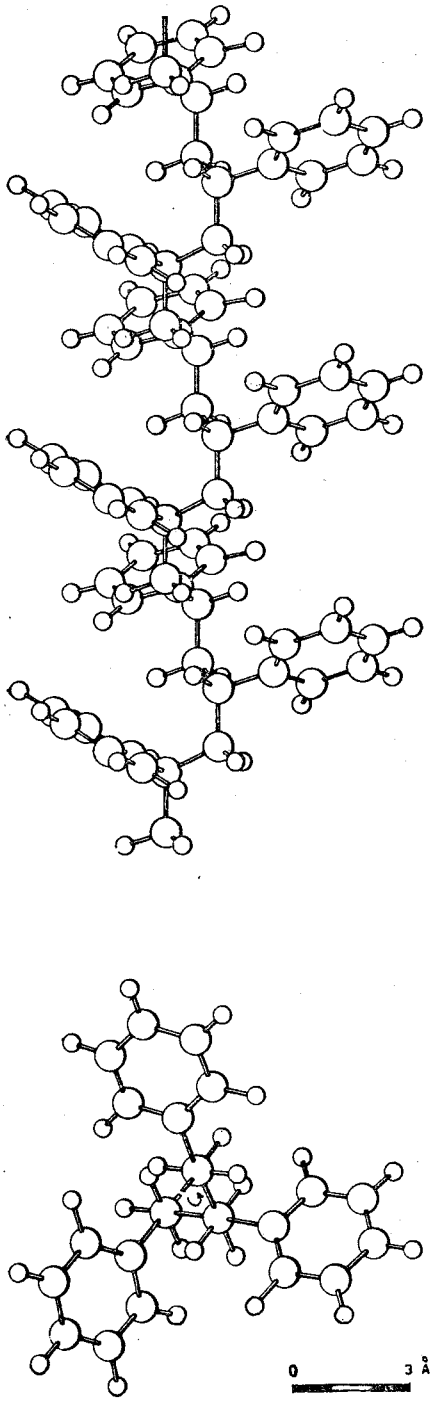

Fig. 3. – Conformation of the isotactic polystyrene macromolecule in the crystalline state (side and end views).

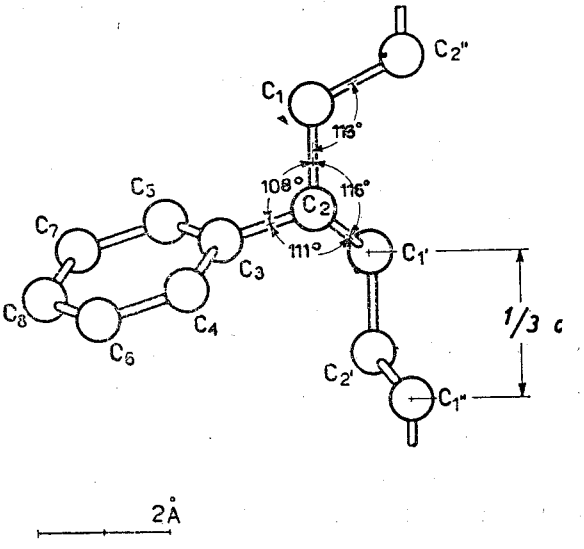

Fig. 4. – Conformation of the independent structural unit of isotactic polystyrene. (C–C = 1.54 Å, $(C—C)_{bz}$ = 1.40 Å).

and (6 6 0) reflections, both particularly intense, were considered. Their structure factors do not vary in respect to the choice of the space group ($R3c$ or $R\bar{3}c$) [13] which choice, in the first phase of researches, did not seem possible to be done.

The structure factor graphs of the (2 2 0) and (6 6 0) reflections are shown in Fig. 5 and 6, together with the position which the independent structural

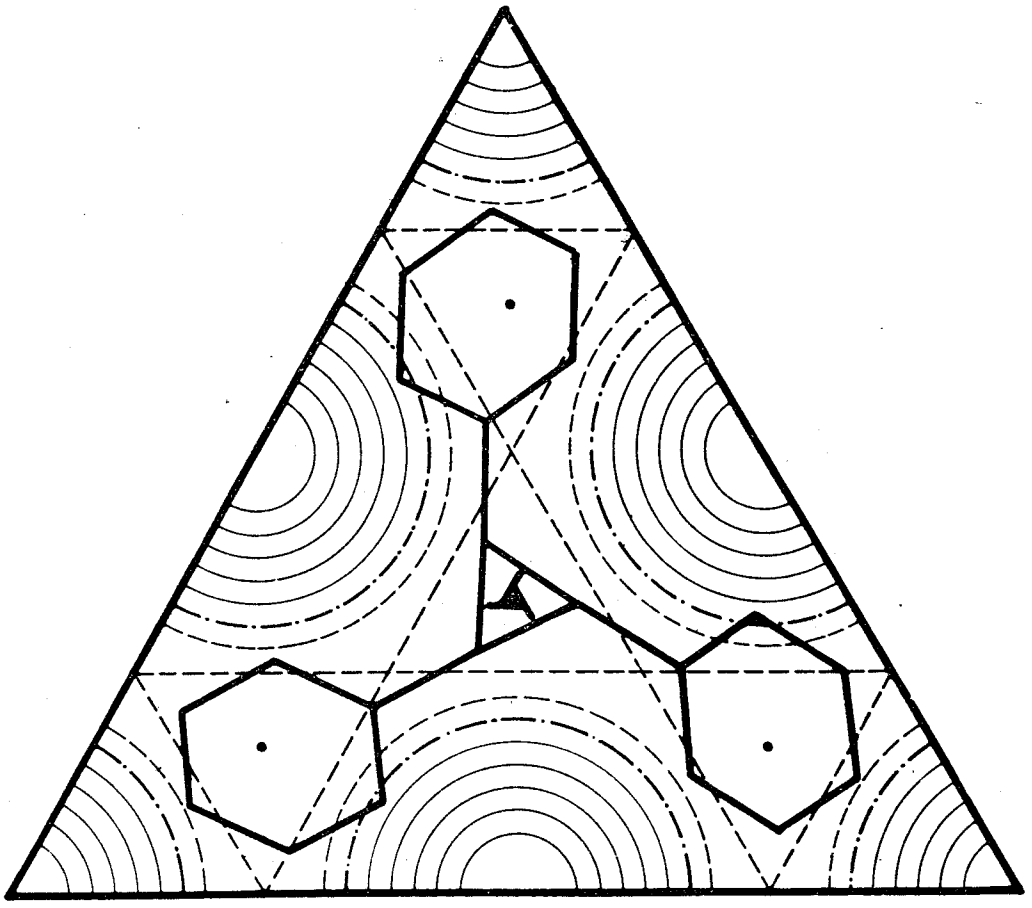

Fig. 5. – (2 2 0) structure factor graph, showing the position assumed by the macromolecule (contours are drawn at regular intervals: ——— positive lines; –·–·–·– zero lines; – – – – negative lines).

unit is approximately expected to assume, in order to get these reflections to have high intensity. The effective co-ordinates of the independent structural unit have been then more rigorously determined, considering the Van der Waals contacts occurring, by rotation of the macromolecule in a narrow range around its threefold screw axis. According to what required by the $R3c$ space group, we analysed first the contacts between macromolecules facing each other through glide planes with translation along c. The attention was retained first on the $R3c$ space group since it is a subgroup of the other possible space group, $R\bar{3}c$. In Fig. 7 is shown the position of the structural

unit (A), which minimizes the Van der Waals contacts between carbon atoms of adjacent macromolecules. By rotating the independent unit by 2° either clockwise or anticlockwise, the Van der Waals contacts become already re-

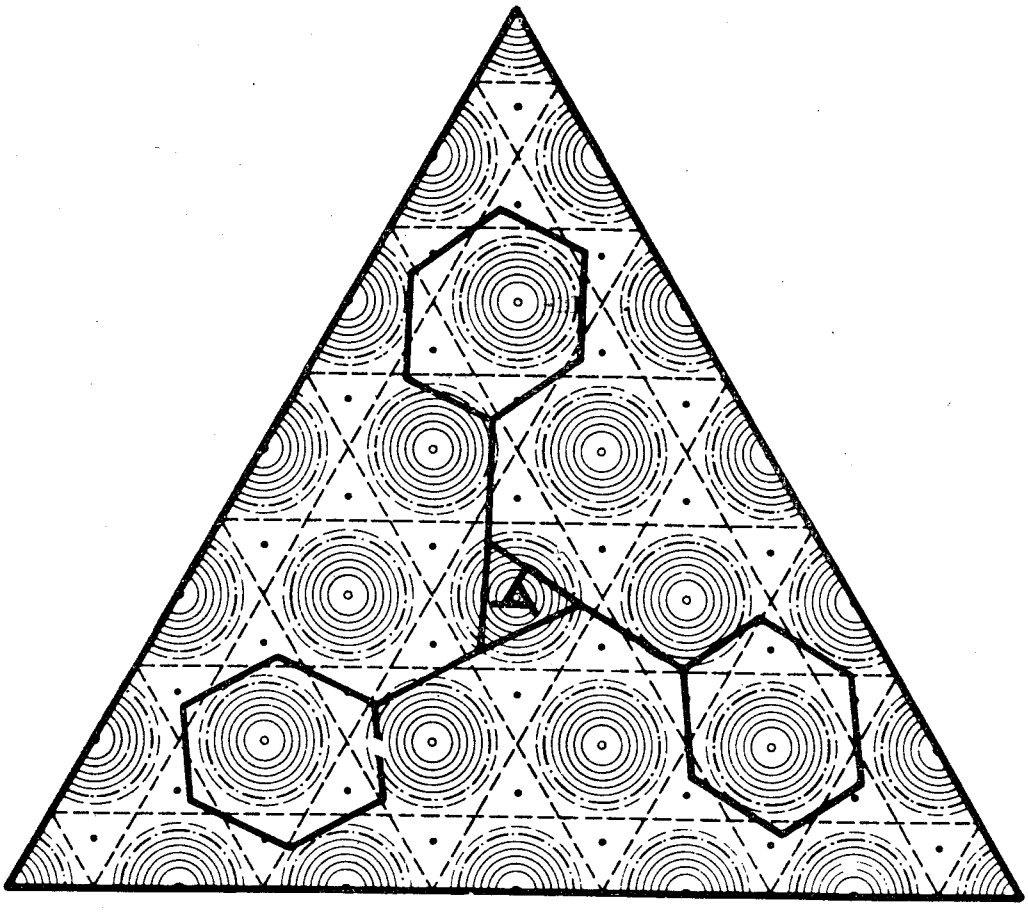

Fig. 6. – (660) structure factor graph.

markably worse (see Table I) and the distances between C atoms of neighbouring chains result lower than the values recorded for other solved structures ((3.4 ÷ 3.7) Å). Because of the frequent occurrence in polymers of phenomena of statistical vicariance [14], the possibility that the space group were $R\bar{3}c$ was also taken into consideration. In fact, the $R\bar{3}c$ space group leads necessarily to the possible statistical presence around the same threefold screw axis of isomorphous anticlined macromolecules, by the addition of a center of symmetry to the symmetry elements of the $R3c$ space group.

A choice is not possible on the basis of Van der Waals contacts between neighbouring molecules. In fact, after choosing, in a suitable way, the origin along the z axis, as indicated in Fig. 7, the macromolecule, isomorphous of A and anticlined to it (dashed in Fig. 7), that may vicariate A around the same threefold screw axis, shows Van der Waals distances in respect of C and B, which are even higher than 3.5 Å.

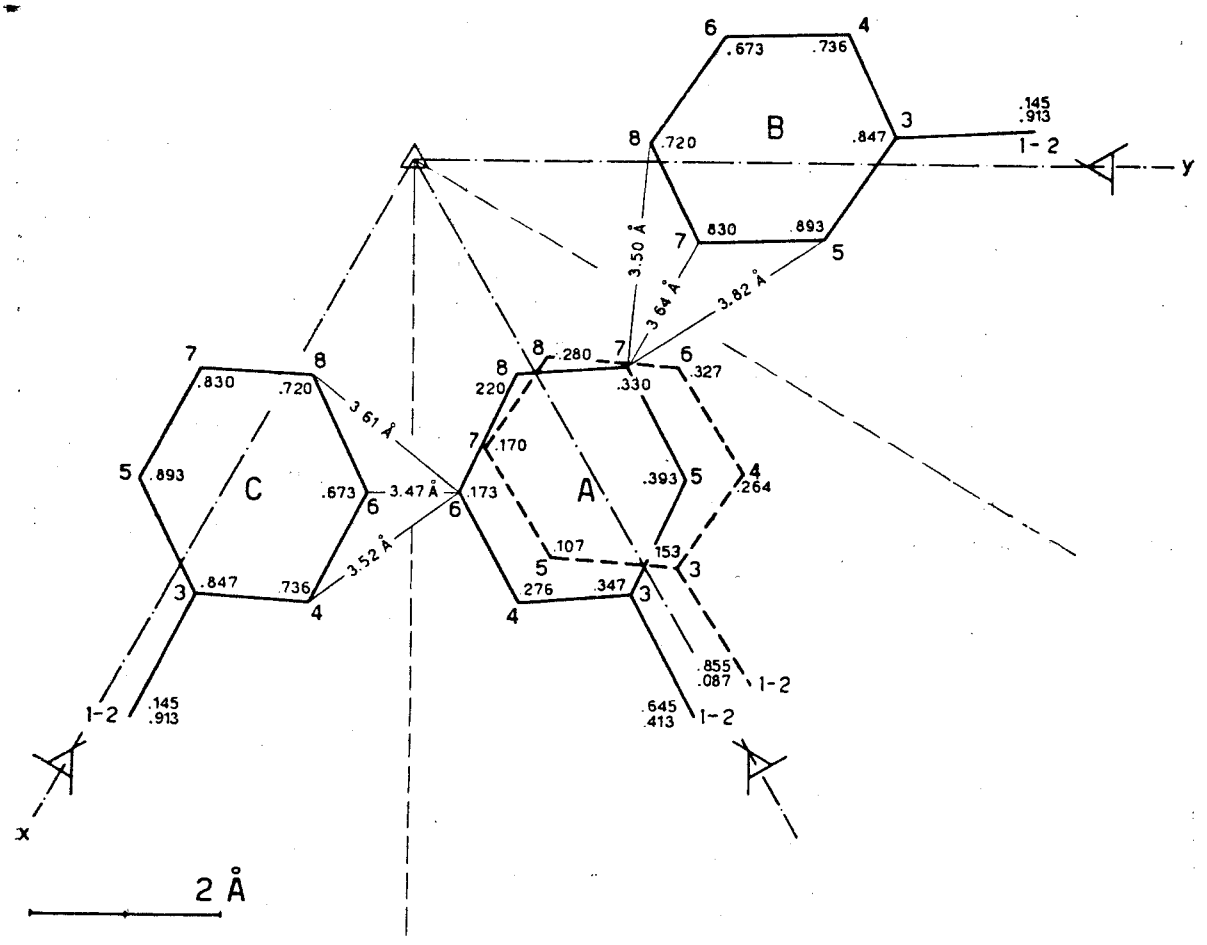

Fig. 7. – Actual position of the independent structural unit (*A*) in the unit cell. The anticlined macromolecule in respect of *A* and possible statistical vicariant of *A* itself, is dashed.

TABLE I. – *Values of the Van der Waals contact distances among atoms of neighbouring macromolecules (only the most significant values are reported).*

I. Values calculated when the position assumed by the macromolecule is that of Fig. 7.
II, III. Values obtained after rotating the macromolecule around its threefold screw axis by 2°, anticlockwise and clockwise respectively.

Atoms of isoclined molecules (Full drawn in Fig. 7)		II Å	I Å	III Å	Atoms of anticlined molecules		I Å
C_{7A}	C_{7B}	3.76	3.64	3.57	C_{6A}	C_{7B}	3.56
C_{7A}	C_{5B}	3.95	3.82	3.72	C_{6A}	C_{8B}	3.52
C_{7A}	C_{8B}	3.68	3.50	3.36	C_{6A}	C_{5B}	3.54
C_{6A}	C_{6C}	3.42	3.47	3.54	C_{8A}	C_{7B}	3.59
C_{6A}	C_{8C}	3.54	3.61	3.75	C_{8A}	C_{8B}	3.85
C_{6A}	C_{4C}	3.44	3.52	3.62	C_{4A}	C_{5B}	3.60
					C_{4A}	C_{7B}	3.81

3. – Calculation of the structure factors.

We found it advisable to make the calculations of the structure factors for both space groups, owing to the above seen impossibility of choosing between them on the basis of possible unsuitable Van der Waals contacts. The calculation of the structure factors comprising also the contribution of hydrogen atoms, was performed for the previously suggested model and for some different models in which the independent structural unit was allowed to slightly rotate around its threefold screw axis or in which the benzene ring was allowed to slightly rotate around the C_2—C_3 bond (Fig. 7 and Fig. 4).

The best results were obtained just for the model sketched in Fig. 4 which was most convincing from a stereochemical viewpoint, and by the co-ordinates plotted in Table II.

Table II. – *Coordinates of the independent structural unit.*
(The index of the hydrogen atoms refers to the carbon atoms they are linked to, the carbon atoms are marked as in Fig. 4).

	x/a	y/b	z/c
C_1	0.308	0.290	0.645
C_2	0.308	0.290	0.413
C_3	0.240	0.226	0.347
C_4	0.245	0.173	0.236
C_5	0.176	0.219	0.393
C_6	0.184	0.114	0.173
C_7	0.114	0.160	0.330
C_8	0.118	0.108	0.220
H_1	0.304	0.241	0.700
H_1'	0.263	0.294	0.700
H_2	0.354	0.287	0.358
H_4	0.296	0.178	0.200
H_5	0.174	0.261	0.479
H_6	0.187	0.074	0.086
H_7	0.062	0.154	0.367
H_8	0.071	0.063	0.170

The accordance is good as well, either by assuming that the space group is $R\bar{3}c$, or that it is $R3c$ (Tables III and IV).

It must be noticed that, owing to the difficulty of the visual measurement of intensities, the values of F_o may be affected by absolute errors fairly appreciable. Fortunately there is evidence to believe that such errors are monotonous functions of the diffraction angle and thus, in making the accordance, are compensated through the thermal factor applied to the calculated structure

TABLE III. – *Comparison between the observed and calculated structure factors for the* $R\bar{3}c$ *space group.* $B = 11$ Å^2.

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 the different multiplicity of the reflections into account, all the calculated structure factors except the ($h\,0\,0$) and ($h\,h\,0$) ones, were multiplied by $\sqrt{2}$. (Cu, K α).

$h\,k\,l$	2 sin ϑ	F_c.	F_o.
1 1 0	0.141	− 36	33
3 0 0	0.245	+ 53	67
2 2 0	0.282	−177	182
4 1 0	0.373	− 40	43
3 3 0	0.425	+ 53	59
6 0 0	0.487	+ 13	—
5 2 0	0.508	− 34	33
4 4 0	0.564	+ 22	21
7 1 0	0.614	− 1	—
6 3 0	0.645	+ 40	53
5 5 0	0.704	− 30	33
9 0 0	0.732	+ 7	—
8 2 0	0.746	+ 28	34
7 4 0	0.784	− 13	—
6 6 0	0.845	− 53	66
10 1 0	0.856	+ 7	—
9 3 0	0.880	− 6	—
8 5 0	0.923	+ 1	—
12 0 0	0.976	− 1	—
11 2 0 / 7 7 0	0.986	+ / + 10	17
10 4 0	1.016	+ 13	17
9 6 0	1.062	− 4	—
13 1 0	1.099	− 3	—
12 3 0	1.118	− 12	15
8 8 0	1.127	+ 3	—
11 5 0	1.153	+ 2	—
10 7 0	1.204	+ 4	—
15 0 0	1.221	− 14	17
14 2 0	1.227	− 3	—
13 4 0	1.252	+ 12	12
9 9 0	1.267	− 1	—
12 6 0	1.290	− 4	—
16 1 0 / 11 8 0	1.343	+ / − 14	15
15 3 0	1.358	− 8	—
14 5 0	1.387	− 3	—
1010 0	1.408	+ 3	—
2 1 1	0.318	+224	249
3 1 $\bar{1}$	0.374	−135	128
3 2 1	0.423	+ 56	67
4 2 $\bar{1}$	0.489	− 89	71
5 1 1	0.508	− 50	39
4 3 1	0.546	− 4	—
6 1 $\bar{1}$	0.581	+ 16	—
5 3 $\bar{1}$	0.614	− 84	83
6 2 1	0.630	+ 4	—
5 4 1	0.675	+ 33	40
7 2 $\bar{1}$	0.704	+ 27	34
8 1 1	0.731	− 31	—
6 4 $\bar{1}$	0.745	− 43	43
7 3 1	0.759	− 59	75
6 5 1 / 9 1 $\bar{1}$	0.809	+ / + 34	45
8 3 $\bar{1}$	0.833	+ 1	—
9 2 1	0.857	− 4	—
7 5 $\bar{1}$	0.879	− 3	—
8 4 1	0.891	+ 9	—
10 2 $\bar{1}$	0.917	− 8	—
7 6 1	0.944	− 10	—
11 1 1 / 9 4 $\bar{1}$	0.965	+ / + 6	—
10 3 1	0.985	− 3	—
8 6 $\bar{1}$	1.018	− 10	—
9 5 1	1.024	+ 16	27
12 1 $\bar{1}$	1.042	+ 15	
11 3 $\bar{1}$	1.062	− 1	—
8 7 1	1.081	− 15	—
12 2 1	1.089	+ 23	23
10 5 $\bar{1}$	1.098	− 7	—
11 4 1	1.117	+ 5	—
9 7 $\bar{1}$	1.154	+ 9	—

$h\,k\,l$	2 sin ϑ	Int.$_c$.	Int.$_o$.
1 0 $\bar{2}$	0.471	not calc.	vs
2 0 2	0.493	2118	m
2 1 $\bar{2}$	0.512	795	mw
3 1 2	0.548	7862	ms
4 0 $\bar{2}$	0.566	1453	m
3 2 $\bar{2}$	0.583	83	—

TABLE III (*continued*).

h k l	2 sin ϑ	Int.$_{c.}$	Int.$_{o.}$	*h k l*	2 sin ϑ	Int$_{c.}$.	Int$_{o.}$.
5 0 2	0.618	470	mw	8 4 $\bar{2}$	0.976	4	—
4 2 2	0.634	174	w	11 0 2	1.007	10	—
5 1 $\bar{2}$	0.648	61	—	10 2 2	1.017	16	—
4 3 $\bar{2}$	0.678	91	w	7 6 $\bar{2}$	1.026	7	—
6 1 2	0.694	65	—	9 4 2 / 11 1 $\bar{2}$	1.045	15	vvw
7 0 $\bar{2}$ / 5 3 2	0.733	437	mw	10 3 $\bar{2}$	1.064	—	—
6 2 $\bar{2}$	0.747	10	—	8 6 2	1.091	1	—
5 4 $\bar{2}$	0.788	61	—				
8 0 2	0.798	50	—	1 1 3 (*)	0.711	not calc.	s
7 2 2	0.810	173	w	2 2 3	0.752	1956	
8 1 $\bar{2}$	0.835	169		4 1 3	0.791	371	w
6 4 2	0.847	2	—	3 3 3	0.816	678	mw
7 3 $\bar{2}$	0.859	5	—	5 2 3	0.862	815	m
6 5 $\bar{2}$ / 9 1 2	0.903	183	w	4 4 3	0.897	101	—
				7 1 3	0.929	33	—
8 3 2	0.925	12	—	6 3 3	0.946	172	vw
10 0 $\bar{2}$	0.936	3	—	5 5 3	0.989	37	—
9 2 $\bar{2}$	0.945	38	vw	8 2 3	1.021	2	—
7 5 2	0.967	26		7 4 3	1.049	11	—

(*) The calculated intensity of *h k* 3 reflections is the sum of the diffracted intensities of both (*h k* 3) and (*h k* $\bar{3}$) lattice planes.

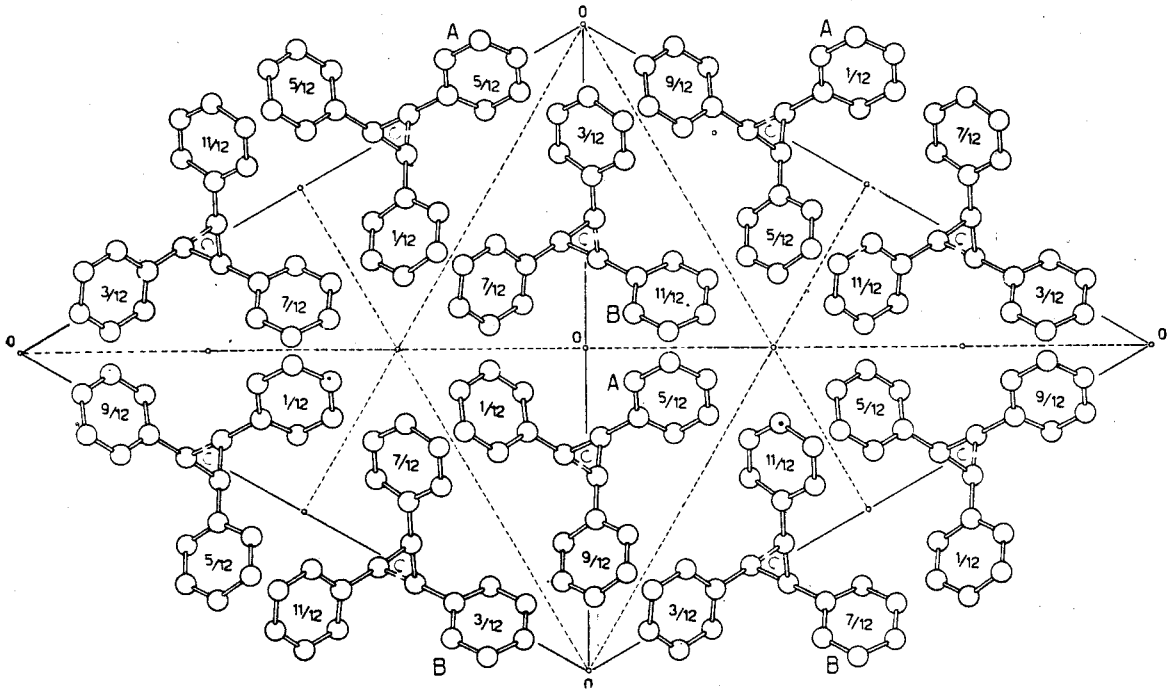

Fig. 8. – Projection on (0 0 1) of the structure of isotactic polystyrene for the *R*3*c* space group.

TABLE IV. – *Comparison between the observed and calculated structure factors for the R3c space group. For the meaning of* F_c. *and* F_o. see Table II. $B = 9.5$ Å^2.

h k l	A	B	F_c.	F_o.	*h k l*	A	B	F_c.	F_o.
1 1 0	— 37	—	37	40	1010 0	+ 4	—	4	—
3 0 0	+ 54	— 53	76	81					
2 2 0	—179	—	179	220	2 1 1	+228	—139	267	301
4 1 0	— 41	+ 25	48	52	3 1 $\bar{1}$	—137	— 38	142	155
3 3 0	+ 55	—	55	71	3 2 1	+ 57	+ 99	114	81
6 0 0	+ 14	— 11	18	—	4 2 $\bar{1}$	— 90	— 37	97	86
5 2 0	— 34	+ 3	34	40	5 1 1	— 51	— 43	67	47
4 4 0	+ 23	—	23	25	4 3 1	— 4	+ 34	34	—
7 1 0	— 1	+ 21	21	—	6 1 $\bar{1}$	+ 16	+ 26	31	—
6 3 0	+ 42	— 49	65	65	5 3 $\bar{1}$	— 87	+ 33	93	100
5 5 0	— 32	—	32	39	6 2 1	+ 4	+ 5	6	—
9 0 0	+ 7	— 4	8	—	5 4 1	+ 35	— 39	52	48
8 2 0	+ 30	— 1	30	41	7 2 $\bar{1}$	+ 28	— 13	31	41
7 4 0	— 14	— 16	21	—	8 1 1	— 32	— 32	45	—
6 6 0	— 59	—	59	79	6 4 $\bar{1}$	— 47	— 10	48	52
10 1 0	+ 8	+ 7	11	—	7 3 1	— 64	+ 30	71	91
9 3 0	— 7	— 22	23	—	6 5 1	+ 19	+ 37	55	54
8 5 0	+ 1	+ 32	32	—	9 1 $\bar{1}$	+ 33	+ 13		
12 0 0	— 2	— 12	12	—	8 3 $\bar{1}$	+ 1	+ 7	7	—
11 2 0	+ 4	+ 22	25	20	9 2 1	— 5	+ 4	6	—
7 7 0	+ 11	—			7 5 $\bar{1}$	— 4	— 38	38	—
10 4 0	+ 16	+ 12	20	20	8 4 1	+ 11	— 13	17	—
9 6 0	— 5	+ 4	6	—	10 2 $\bar{1}$	— 9	+ 10	13	—
13 1 0	— 3	+ 9	10	—	7 6 1	— 12	+ 5	13	—
12 3 0	— 15	— 15	21	18	11 1 1	+ 6	— 7	23	—
8 8 0	+ 4	—	4	—	9 4 $\bar{1}$	+ 3	— 21		
11 5 0	+ 3	$<+1$	3	—	10 3 1	— 4	— 5	6	—
10 7 0	+ 5	+ 2	5	—	8 6 $\bar{1}$	— 12	+ 1	12	—
15 0 0	— 18	— 37	41	21	9 5 1	+ 19	+ 7	20	33
14 2 0	— 4	+ 3	5	—	12 1 $\bar{1}$	+ 19	+ 4	19	
13 4 0	+ 15	+ 4	16	15	11 3 $\bar{1}$	— 1	+ 1	1	—
9 9 0	— 1	—	1	—	8 7 1	— 18	— 9	20	—
12 6 0	— 5	— 3	6	—	12 2 1	+ 27	+ 31	41	28
16 1 0	+ 18	+ 7	19	18	10 5 $\bar{1}$	— 8	— 13	15	—
11 8 0	— 2	<-1			11 4 1	+ 7	+ 5	9	—
15 3 0	— 11	— 1	11	—	9 7 $\bar{1}$	+ 12	+ 8	14	—
14 5 0	— 4	+ 3	5	—					

factors F_c. The thermal factor applied to F_c., determined by studying the behaviour of $\ln F_c/F_o$ as a function of $(\sin\vartheta/\lambda)^2$, has then to be assumed as the product of two terms, say the true thermal factor and a function of the scattering angle, which does compensate eventual errors of evaluation of the inten-

sities (*e.g.* owing to the enlargement of spots on increasing of the scattering angle; owing to the blackening of the film, etc.).

Using the data we disposed of, it did not seem possible to us to choose univocally between the two space groups. It cannot be excluded that, inside

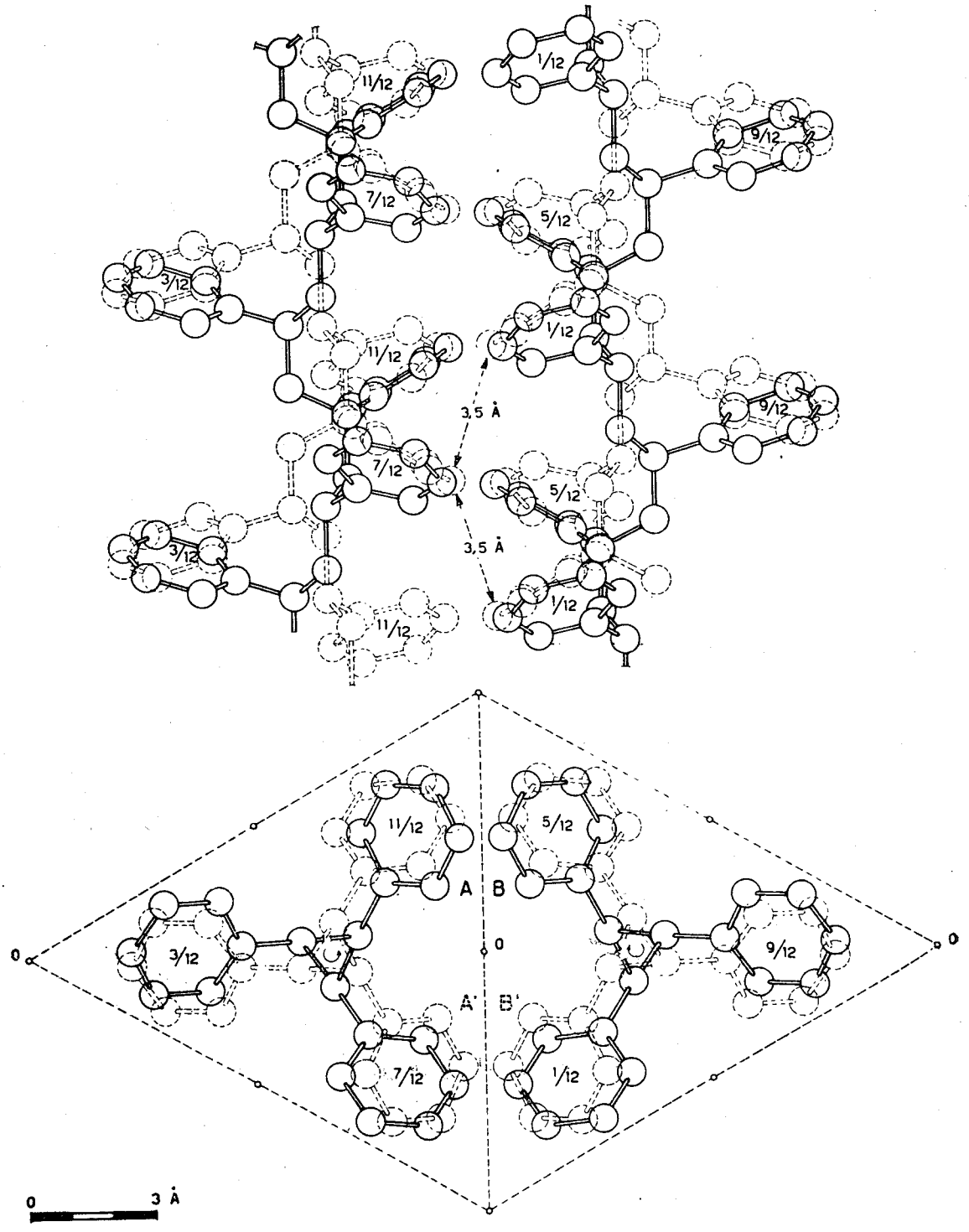

Fig. 9. – Model showing isosterism between anticlined isomorphous macromolecules.

any single crystal, as we supposed for polypropylene and poly-alpha-butene, the macromolecules are locally ranged according to the $R3c$ space group (Fig. 8) forming small blocks with a polar orientation. A larger crystal may be built up by an ensemble of such blocks, neighbouring one another in an anticlined way, in such a way as to keep unaltered the equatorial periodicity at the jointment planes. According to the magnitude of these blocks, the space group, as far as the diffraction effects are concerned, more approaches either the $R\bar{3}c$ or the $R3c$ space group. The assumption that each crystal is formed by small anticlined blocks, each formed by reciprocally isoclined macromolecules, seems to be reasonable when one thinks of the difficulty of separation of reciprocally anticlined macromolecules (which, from a kinetic point of view, should cause the formation of great polar aggregates to be somewhat difficult) and of the nature of the very similar Van der Waals contacts, which occur between enantiomorphous isoclined macromolecules and anticlined enantiomorphous ones (Fig. 9).

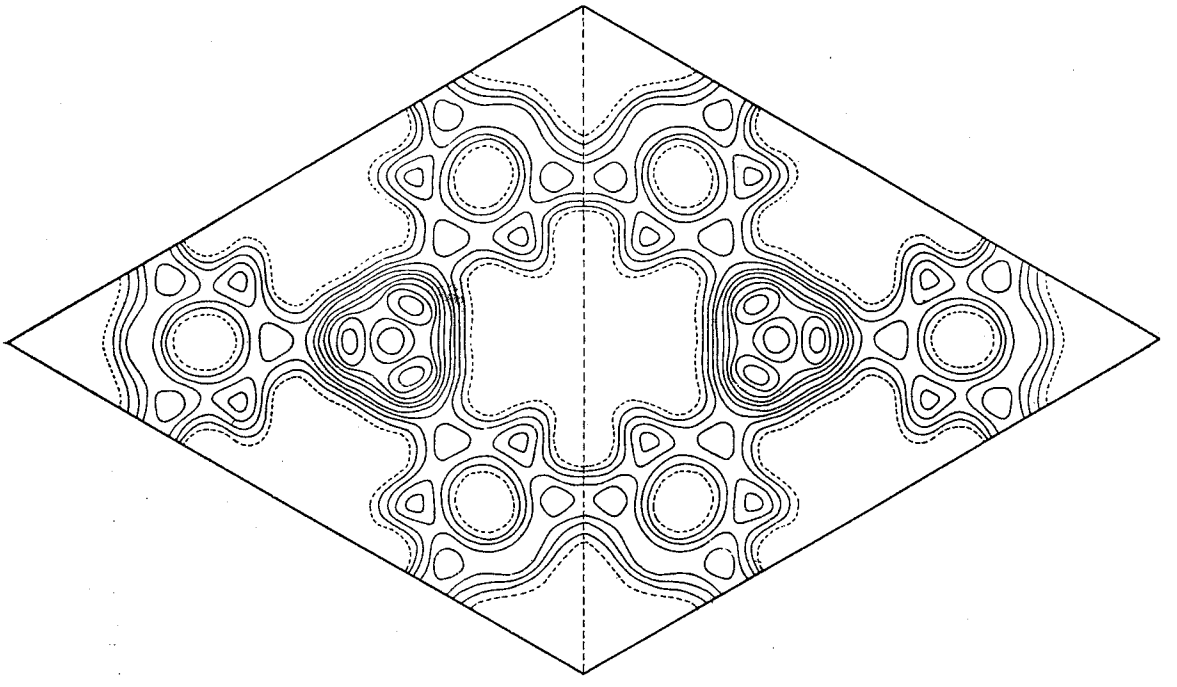

Fig. 10. – Projection on (001) of the electron density calculated according to the $R\bar{3}c$ space group (contours are drawn at 0.5 $e/Å^2$, the broken line is the 2 $e/Å^2$ level).

A similar kind of statistical vicariance was promoted by us in the case of the structure of natural rubber and, most probably, is in connection with the high value of the thermal factor.

With the signs obtained from the calculation of the structure factors according to the $R\bar{3}c$ space group of the equatorial reflections, a Fourier pro-

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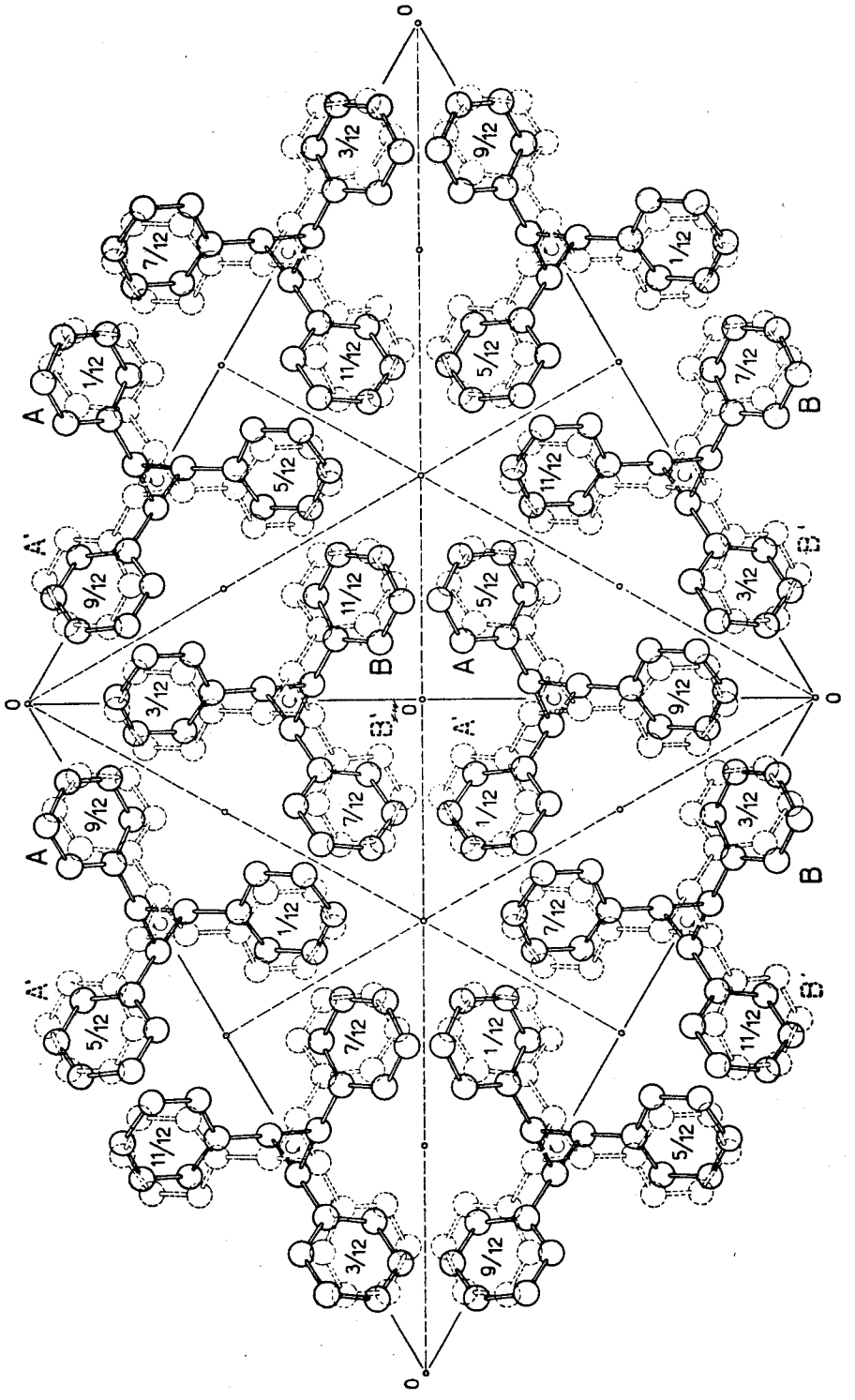

Fig. 11. – Projection on (0 0 1) of isotactic polystyrene structure according to the $R\bar{3}c$ space group. (For this space group, around the same threefold screw axis, isomorphous anticlined macromolecules may statistically vicariate).

jection of the electron density on the (0 0 1) plane has been calculated. As it may be realized from Fig. 10 either the positions of the monomeric units or their weights (see also Fig. 11) are in good accordance with the assumptions we have made.

G. NATTA, etc.
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