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In previous works [1], we announced the identification and discussed the structure of three of the four possible pure stereoisomers of polybutadiene; two with 1,2 enchainment (isotactic and syndiotactic respectively) and the third with trans 1,4 enchainment.

In a letter to the Editor of *Angewandte Chemie* we have given preliminary data concerning the crystal structure of the polymer with cis 1,4 configuration, of which we succeeded in preparing sufficiently long and crystallizable macromolecular chains formed by cis 1,4 units [2].

All the various stereoisomeric polymers we examined, were prepared with different catalysts, all obtained by reaction of metalalkyls on suitable compounds of transition elements [3].

For all these catalysts the mechanism of the polymerization reaction is of the co-ordinated anionic type; the different behavior can be ascribed to the mode of co-ordination of the olefin with the metallorganic complex of the transition metal.

As it is well known, polybutadienes, previously prepared by methods of the radicalic or cationic polymerization type, had always given amorphous products and when examined by infrared methods showed the presence of monomeric units having 1,2 enchainment together with monomeric units having 1,4 enchainment and cis and trans 1,4 configurations, irregularly distributed along the polymeric chain. At first the preparation of polybutadiene having very high cis 1,4 content was realized fractionating a mixture of macromolecules with 1,4 enchainment and different steric composition [4]. Following this method it was possible to obtain fractions having a melting point almost of 0 °C, consisting of macromolecules showing a cis 1,4 configuration for very

long sections of their chains, at least. In fact, the melting point of these fractions is practically the same as that observed in polymers successively prepared with other highly stereospecific catalysts, which give crude products having a content in cis 1,4 units greater than 98%, The melting point of practically pure (> 99% of cis 1,4 units), unstretched, polybutadienes prepared in this Institute is +1°C [5].

In this note we will only report the data which we have obtained on the structure of cis 1,4 polybutadiene, which differs from the other pure stereo-isomeric butadiene polymers for a greater similarity with natural, rubber due to its properties of possessing highly reversible elasticity with low hysteresis and of crystallizing under stretch at room temperature and even at higher temperatures.

In Table I, to make an example, we give some mechanical properties measured for a sample of our polymer, which are very similar to those obtainable for natural rubber.

TABLE I. – *Physical properties of vulcanized polybutadienes with a high content in cis 1,4 stereoisomer (pure gum recipe).*

cis 1-4 content	92 – 93%	98 – 99%
Mooney viscosity ML 4	90 – 95	70 – 80
Tensile stress (psi)	800 –1 100	2 500 –2 800
Elongation at break %	900 –1 000	850 – 950
Modulus at 300% elongation (psi) .	140 – 180	140 – 180
Resilience at 20 °C %	80 – 85	85 – 88
Hardness, Shore A	45 – 50	45 – 50

Compounding recipe:

Polybutadiene	100
Stearic acid	2
Zinc oxide	3
Sulphur	1
Vulcafor MBTS (di-2-benzothiazyl disulphide) . . .	1,3
Nonox D (phenyl-β-naphtylamine)	1
Cure: 145 °C × 45 min.	

1. – Roentgenographic data.

The cis 1,4 polybutadiene has a melting point of about +1 °C; but as it was above quoted, it may exist in the crystalline state under stretching also at room temperature and even at higher temperatures.

The X-ray spectra of the polymer have been effected by us in a cylindrical

camera for samples stretched at $(300 \div 400)\%$ and cooled at about $-30\,°C$ with a jet of carbon dioxide from dry ice, in order to have reflections as sharp as possible.

The examined samples supply fiber photographs very rich in reflections
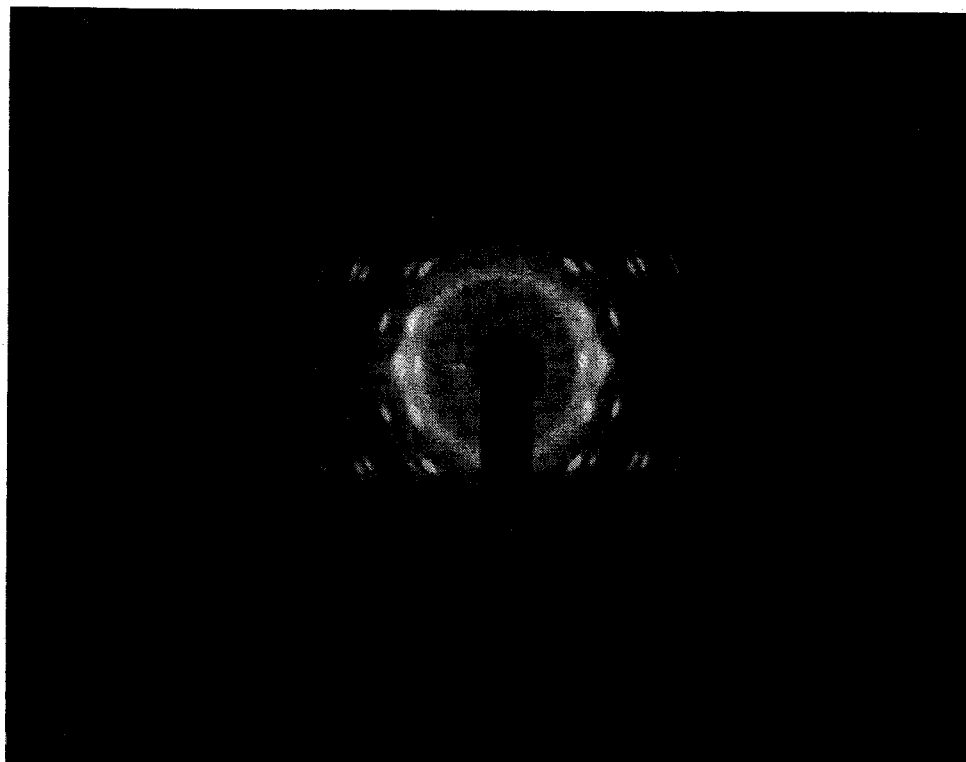

Fig. 1. – Fiber spectrum of cis 1,4 polybutadiene.

which denote a high order degree both for equatorial and longitudinal directions (Fig. 1).

The establishment of the unit cell was effected by the standard methods of the reciprocal lattice [6].

The unit cell appeared monoclinic; its constants are $a = 4.60$ Å, $b = 9.50$ Å, $c = 8.60$ Å (fiber axis). The axis c is inclined on the axis a; the angle between the axes results $\beta = 109°$ (all data within about 1% accuracy).

The calculated density, assuming that in the unit cell 4 monomeric units are contained, is 1.01, in accordance with the experimental value.

The most characteristic extinction, which becomes evident from the reciprocal lattice description is that of hkl reflections with $h+k = 2n+1$. This extinction is common to 5 monoclinic space groups say C_s^3, C_s^4, C_2^3, C_{2h}^3, C_{2h}^1 [7].

Some of these space groups are characterized by further extinctions, as

reported below:

$$C_s^3 \text{ none}; \quad C_s^4 \quad h\,0\,l \quad \text{if} \quad l = 2n + 1; \quad C_2^3 \text{ none}$$

$$C_{ih}^3 \text{ none}; \quad C_{2h}^3 \quad h\,0\,l \quad \text{if} \quad l = 2n + 1$$

Actually, it was not possible to observe any reflection $h\,0\,l$ with $l = 2n+1$: then we found it advisable to retain C_s^1 and C_{2h}^6 as the most probable space groups.

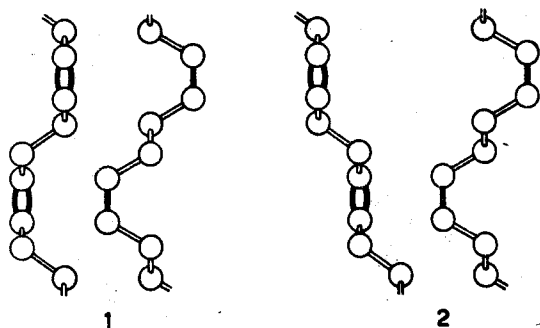As well known, the univocous establishment of the space group of the unit cell of a polymer must be generally delayed, until reasonable considerations relative to the symmetry of the macromolecules and to their mode of packing may be made. Two different conformations are possible for the monomeric unit on the basis of the principle of staggered simple bonds [8] we have already discussed in previous works. They are schematically illustrated in Fig. 2, where we have shown for each of them two projections, normal to the chain axis.

Fig. 2. – Possible conformations of a succession of 1,4 cis polybutadiene monomeric units satisfying the principle of staggered bonds.

In natural rubber, the conformation 2 is actually present in the crystalline state [9].

In our case the period calculated for the conformation 2 with normal distances and angles (8.4 Å) is in much better agreement with the period we found experimentally (8.6 Å) than with the period calculated for the conformation 1 (8.1 Å).

In the type 2 conformation the arrangement of the monomeric units gives rise to a glide plane type chain, which satisfies the principles of staggered bonds and the minimum energy postulate [8]. The chain contains symmetry centers and, as said above, a glide plane with translation. These symmetry elements are contained all together in the space group C_{2h}^6. These considerations brought us to effect the study of the structure models corresponding to this space group and to compare the experimental and calculated intensities, in order to reach a confirmation of the space group. On the basis of this assumption since two chains in $0\,0\,0$ and $\frac{1}{2}\frac{1}{2}0$ must be contained in the cell, the positions of only two carbon atoms are enough for describing the whole structure.
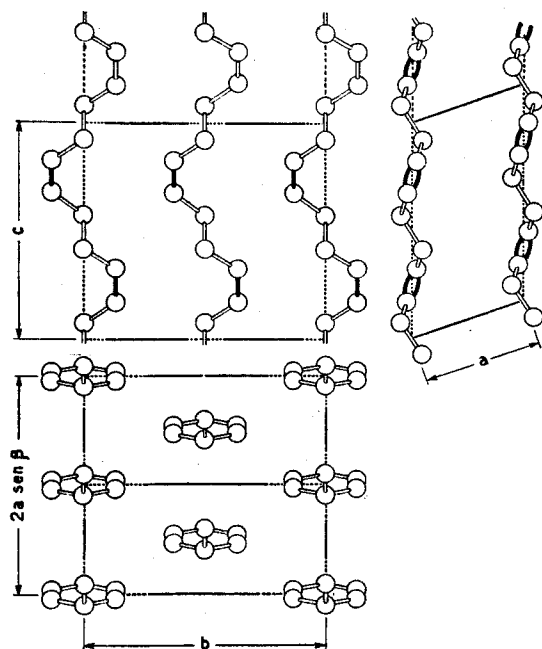
A very good agreement between experimental and calculated intensities (Table III) was obtained assuming the co-ordinates given in Table II.

TABLE II. – *Co-ordinates of the independent structural units of polybutadiene.*

	x/a	y/b	z/c
CH_2	0.112	0.000	0.088
CH	0.046	0.127	0.183

TABLE III. – *Comparison between the observed and calculated structure factors* $(B = 5.7\,\text{Å}^2)$.

$h\ k\ l$	F_c	F_o	$h\ k\ l$	F_c	F_o
0 2 0	32	37	2 4 1	< 1	—
1 1 0	42	45	3 1 $\bar{1}$	2	—
1 3 0	1	—	3 3 $\bar{1}$	1	—
0 4 0	—	—	3 1 1	4	—
2 0 0	15	16	2 6 $\bar{1}$ ⎫	5	7
2 2 0	2	—	1 7 $\bar{1}$ ⎭		
1 5 0	1	—	1 1 $\bar{2}$	16	21
2 4 0	6	—	0 2 2	11	13
0 6 0	10	12	1 1 2	16	18
3 1 0	< 1	—	1 3 $\bar{2}$	21	23
3 3 0	6	—	2 0 $\bar{2}$	12	12
1 7 0	9	9	2 2 $\bar{2}$ ⎫		
2 6 0	1	—	0 4 2 ⎬	25	19
0 8 0	10	12	1 3 2 ⎭		
3 5 0	4	—	2 0 2	19	18
1 1 $\bar{1}$ ⎫	32	35	1 5 $\bar{2}$	12	13
0 2 1 ⎭			2 4 $\bar{2}$ ⎫	13	10
1 1 1	17	21	2 2 2 ⎭		
1 3 $\bar{1}$	10	8	1 5 2	3	—
1 3 1	11	10	3 1 $\bar{2}$	5	—
0 4 1	1	—	0 6 2	3	—
2 2 $\bar{1}$	8	8	2 4 2	1	—
2 2 1	11	10	3 3 $\bar{2}$	3	—
1 5 $\bar{1}$	6	7	2 6 $\bar{2}$	6	—
1 5 1	7	7	1 7 $\bar{2}$	4	—
2 4 $\bar{1}$	< 1	—	3 1 2	10	9
0 6 1	8	9	0 0 2	6	6

In Fig. 3 the resulting mode of packing is shown.

As it may be seen, it is particularly simple and allows a homogeneous filling of the space. The contact distances between carbon atoms of neighbouring molecules are all greater than 3.8 Å, in good accordance with the results obtained examining other known structures. The Fourier projection of the electron density on (001) is shown in Fig. 4.

Fig. 3. – Model of the structure of cis 1,4 polybutadiene.
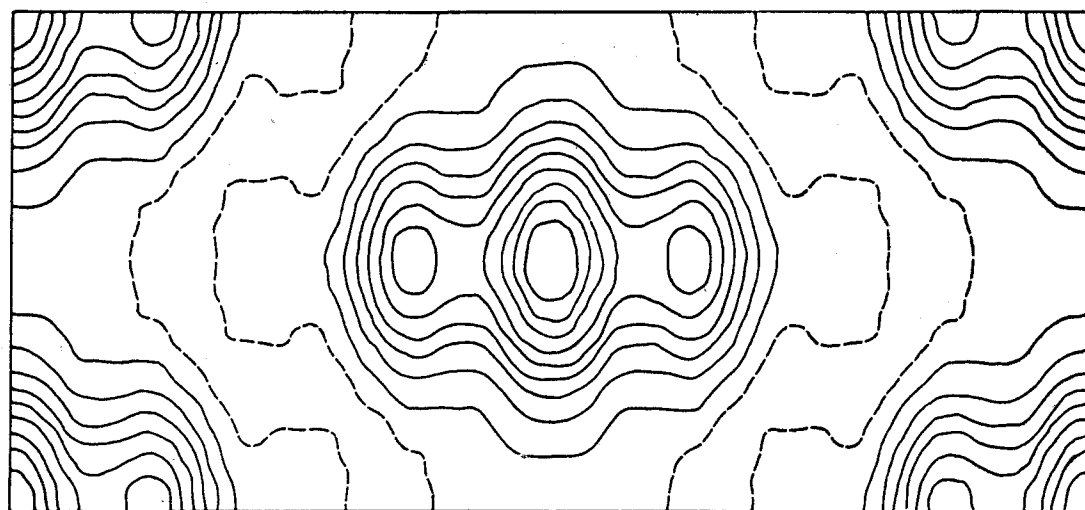
2 Å

Fig. 4. – Projection of the electron density on (001) (contours are drawn at $1e/Å^2$, the dashed line represents the $1e/Å^2$ level).

2. – Comparison of the chain structures of the different stereoisomeric polybutadienes.

By the synthesis of cis 1,4 polybutadiene and the determination of its structure the study of the series of the pure stereoisomers of polybutadiene

was completed; we think it is interesting, therefore, to compare the different structures we found. The case of 1,2 polymerization is analogous to the one of vinyl polymers; the two only possibilities of forming a crystallizable polymer having a regular and simple structure, are those of having an isotactic polymer (for which a threefold screw chain conformation was expected and has been actually found) or a syndiotactic polymer (for which the structural equivalence of the monomeric units is realized by the presence of a glide plane with translation along the fiber axis [1]).

Whereas the polymerization occurs with the formation of chains having 1,4 enchainment, one of the two possible pure stereoisomers (which have also been studied by us) is with regular cis 1,4 enchainment, and the other with
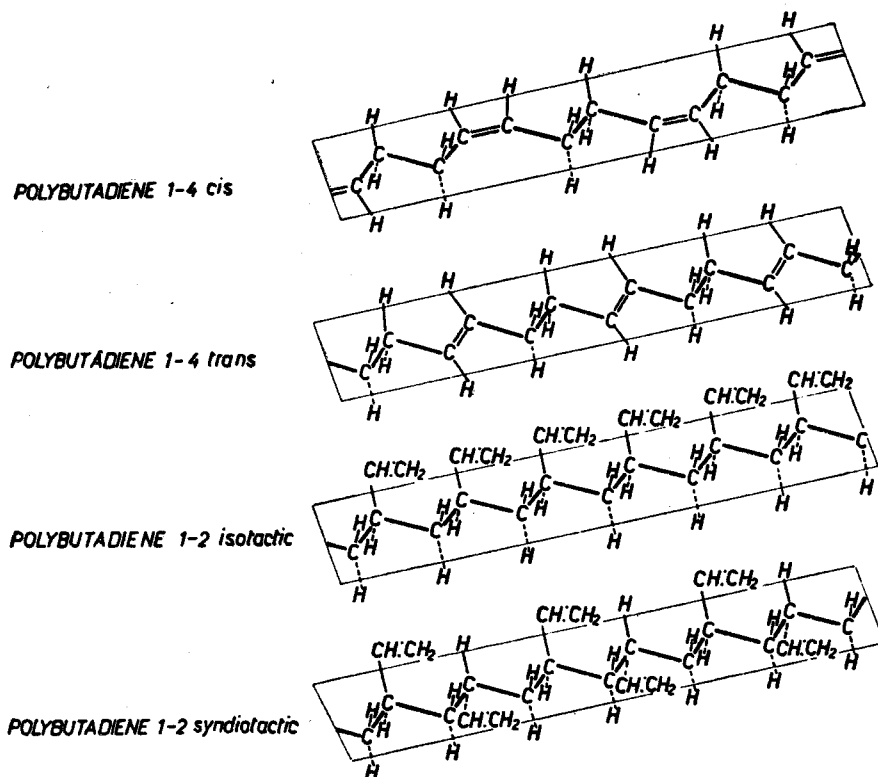

Fig. 5. – Configurations of the four possible regular chains of polybutadiene.

regular trans 1,4 enchainment. It is interesting to note how, in their pure state, both polymers having 1,2 enchainment and the one having trans 1,4 enchainment do not show elastomeric characteristics at room temperature, but, on the contrary, they show features of crystalline products, able to be oriented by mechanical treatments and, therefore, to form fibers. These features which were not foreseen for a polymer of butadiene, may be easily understood because of the high cristallinity at room temperature, the high molecular weight and the high melting temperature.

In Fig. 5 and 6, we have shown the models of the chains of the 4 stereo-

isomeric polymers of butadiene whose main chains are arbitrarily stretched on a plane (Fig. 5) and the conformations they actually assume in the crystalline state (Fig. 6). All the observed conformations satisfy the principle of the staggered simple bonds, also for the carbon atoms adjacent to the double bond.
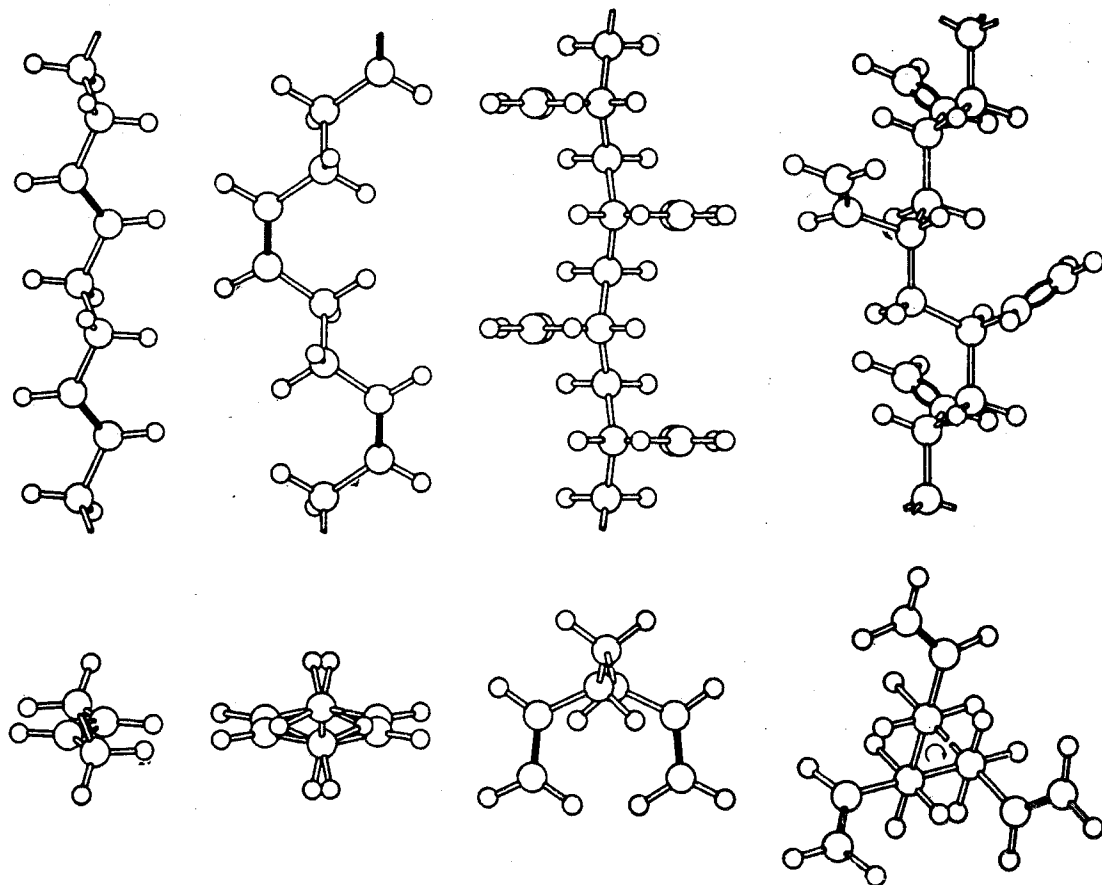

Fig. 6. – Conformations in the crystalline state of the four possible regular chains of four known polybutadiene (trans, cis 1-4 syndio-, isotactic 1-2).

The packing of the chains occurs for 1,2 syndiotactic polybutadiene and for cis 1,4 polybutadiene, whose chains contain glide planes with translation along the fiber axis, by a regular juxtaposition of the chains on these planes. These planes pack themselves one near another so that each chain has the highest number of neighbouring chains structurally equivalent among themselves.

For the trans 1,4 polybutadiene, the almost filiform chains are packed together in a pseudo-hexagonal lattice, whilst for the isotactic 1,2 polybutadiene, the packing is rhombohedral because of the presence of crystallographic screw axes, 3_1 and 3_2, in the lattice.

3. - Comparison of the structure of cis 1,4 polybutadiene with that of cis 1,4 polyisoprene.

It is also interesting to compare the structure we have found for cis 1,4 polybutadiene with that of cis 1,4 polyisoprene in the crystalline state (natural rubber).

The crystalline structure of natural rubber has been studied several times by many Authors; but now it appears definitely resolved owing, above all, to the works performed by BUNN [10] and NYBURG [9]. Natural rubber, according to the latter, has a monoclinic unit cell, with axes at 90°, space group $P2_1/a$.

However, after examining the co-ordinates of the ten atoms of two monomeric units describing the independent structural unit (x, y, z) according to NYBURG, it may be easily noted that they are not independent one of another; the independent unit is actually formed by only one monomeric unit in x, y, z which along the chain is followed by another one in $\frac{1}{2} - x$, y, $\frac{1}{2}+z$. Under this condition (implicit in the Nyburg co-ordinates) the space group must be chosen as $Pbac$, which adds to the four general positions of $P2_1/a$ the other 4 obtainable by effecting the transformation $(\frac{1}{2} - x,\ y,\ \frac{1}{2}+z)$ on themselves. Also, according to NYBURG, molecules described by x, y, z co-ordinates, may be statistically replaced by the corresponding molecules having co-ordinates $(x,\ \frac{1}{8} - y,\ z)$. Only by this assumption it has been possible to obtain a good agreement between experimental and calculated intensities.

Nevertheless, the hypothesis of a completely random vicariance in the same crystal site of mirrored macromolecules in respect of the plane $y = \frac{1}{8}$ does give rise to some unsuitable Van der Waals contacts (< 3.2 Å) between carbon atoms of different chains.

The difficulties are less if, instead of an isomorphous statistical substitution of the single chain, we consider an isomorphous statistical substitution of two different types of layers of monomolecular thickness.

Let us consider (Fig. 7) the succession of molecules ABA, that can be described by the space group $Pbac$ on the projection on ab and ac. All the carbon atoms of the molecules are interested in intermolecular contacts and these contacts do not overcome those we have found for cis 1,4 polybutadiene.

A layer of molecules CDC ... packs, according to the space group $Pbac$, with the layer ABA. The contacts between C and D are analogous to those between A and B.

The contact of the molecule C with the molecules A and B is effected, on the contrary, only by the methyl group.

But then analogous contacts may be effected by a C'D' layer, mirrored in respect to the CD layer in the plane $y = \frac{1}{8}$. We think, therefore, that

there is evidence to believe that an ABAB layer may pack at pleasure with a CD or a C'D' layer. The total effect on the intensities is as if a mirror in $y = \frac{1}{8}$ actually existed; but the contacts between C and D' (of about 3.1 Å),
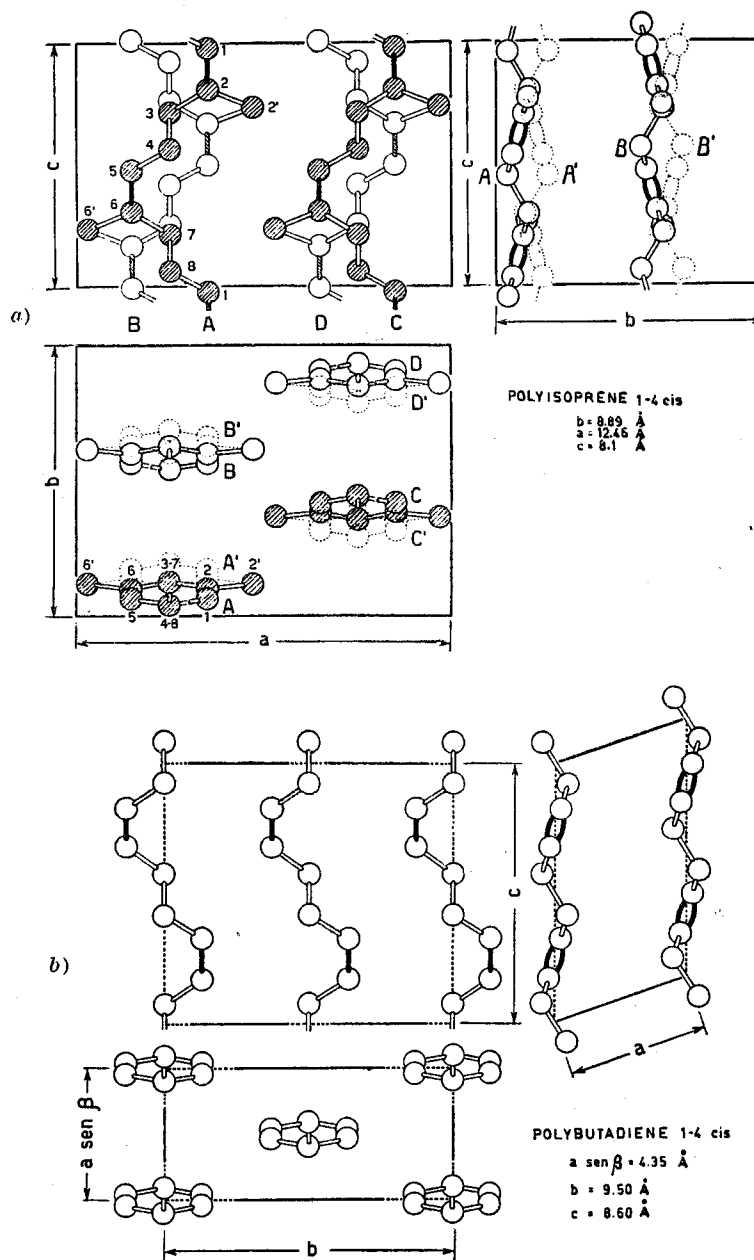
Fig. 7. – Comparison between the crystal structures of cis 1,4 polyisoprene and that of cis 1,4 polybutadiene.

implied by the Nyburg model, who assumes the possibility of having an irregular succession CDC'D... does not occur any more.

Thus, the analogy with cis 1,4 polybutadiene is more complete. In both

cases the molecules follow one another almost at the same distance, along the symmetry plane with translation.

The presence of methyl groups leads, in the cis 1,4 polyisoprene, to an increase of the unit cell size in the direction normal to the symmetry plane with translation $c(a_{PI} > b_{PB})$ to the fact that b_{PI} is about the double of $a \sin \beta_{PB}$ because along the glide plane a succession of anticlined molecules must be represented.

We can finally observe that in all polymers whose chains contain a symmetry plane with translation (polyvinylchloride, syndiotactic 1,2 polybutadiene, cis 1,4 polybutadiene, cis 1,4 polyisoprene, this symmetry element is kept in the crystalline state and determines the space packing of the macromolecules among themselves.

REFERENCES

[1] G. Natta and P. Corradini: *Rend. Acc. Naz. Lincei*, 19 (18), 228 (1955); G. Natta and P. Corradini: *Journ. Polymer. Sci.*, 20, 251 (1956); G. Natta, P. Corradini, L. Porri and D. Morero: *Rend. Acc. Naz. Lincei*, 20 (8), 560 (1956); G. Natta, P. Corradini and I. W. Bassi: *Rend. Acc. Naz. Lincei*, 23 (8), 363 (1957); G. Natta, P. Corradini and L. Porri: *Rend. Acc. Naz. Lincei*, 20 (8), 728 (1956).

[2] G. Natta and P. Corradini: *Angew. Chemie.*, 68, 615 (1956).

[3] G. Natta, L. Porri, P. Corradini and D. Morero: *Chim. e Ind.*, 40, 362 (1958).

[4] G. Natta, L. Porri and P. Corradini: Brev. It. 566940 (1956); G. Natta, L. Porri, A. Mazzei and D. Morero: *La Chim. e l'Ind.*, 41, 398 (1959).

[5] G. Natta and G. Moraglio: unpublished data.

[6] P. Corradini and I. W. Bassi: *Ric. Sci.*, 28, 1435 (1958).

[7] *Int. Tabellen zur Bestimmung von Kristallstrukturen*, 2 (Berlin, 1935).

[8] G. Natta and P. Corradini: *Suppl. Nuovo Cimento*, 15, 9 (1960).

[9] S. C. Nyburg: *Acta Cryst.*, 7, 385 (1954).

[10] C. W. Bunn: *Proc. Roy. Soc.*, A 180, 40 (1942).