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THE CRYSTAL STRUCTURE OF 1, 2 ISOTACTIC POLY-4-METHYL-PENTADIENE-1, 3

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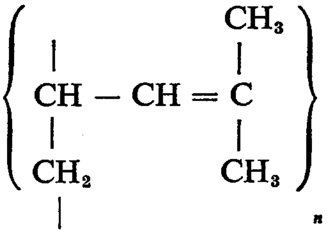
Abstract—The crystal structure of 1, 2 isotactic poly-4-methyl pentadiene



$$\left(\begin{array}{ccccc} & & & & \mathrm{CH_3}\\ | & & & & | \\ \mathrm{CH} & - & \mathrm{CH} & = & \mathrm{C} \\ | & & & & | \\ \mathrm{CH_2} & & & & \mathrm{CH_3} \\ | & & & & \end{array}\right)_n$$

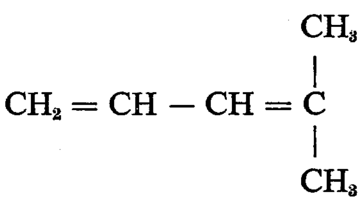
crystallized in modification II has been studied by X-ray diffraction spectra of stretched fibres.

The conformation of the macromolecule was determined using the Fourier transform method of a helix proposed by Cochran, Crick and Vand.

The molecule in the crystal state has a helix structure with 3·60 monomeric units per pitch and a periodicity per monomeric unit along the chain axis of 2·02 ± 0·02 Å ($M/N = 18/5$, $c = 36 \cdot 50$ Å fibre axis). The internal rotation angles along the main chain correspond to a succession of nearly *gauche* (± 282°45′) and nearly *trans* (± 171°30′) conformations. The study of the packing in the crystals has shown that the molecules are arranged in tetragonal, body centred, unit cells, ($a = 17 \cdot 80 \pm 0 \cdot 20$ Å) in such a way that each molecule is surrounded by four enantiomorphous helices.

The comparison between the observed intensities and the intensities calculated according to the $I\bar{4}$ and $I\bar{4}c2$ space groups shows that in the same site of the unit cell up and down isomorphous molecules may be disposed randomly.

CRYSTALLINE isotactic polymers of 4-methyl-1, 3-pentadiene



$$\begin{array}{ccccccc} & & & & & & \mathrm{CH_3} \\ & & & & & & | \\ \mathrm{CH_2} & = & \mathrm{CH} & - & \mathrm{CH} & = & \mathrm{C} \\ & & & & & & | \\ & & & & & & \mathrm{CH_3} \end{array}$$

with 1, 2 enchainment

have been obtained with the aid of stereospecific catalysts.⁽¹⁾ Isotactic poly-4-methyl-pentadiene cancrystallize in two different modifications. One form (modification I) is obtained from the polymer solutions either by evaporating the solvent at room temperature or by adding a precipitant. The other crystalline form (modification II) is obtained either by slowly cooling the molten polymer or by heating to about 100° the polymer crystallized in modification I.⁽¹⁾

The purpose of this paper is to describe the results of the X-ray study of the crystal structure of modification II of this polymer and to point out the structural analogies that can be foreseen between it and the crystalline isotactic poly-α-olefins and poly-alkylvinyl ethers already studied by us.(2-6)

The macromolecules of isotactic poly-4-methylpentene-1 and of poly-*iso*-propyl-vinylether, in the crystal state, have helix conformations containing 3·5 (7/2) and 3·4 (17/5) monomeric units per pitch respectively. It seems reasonable to expect that the macromolecules of 1, 2 isotactic poly-4-methylpentadiene, in the crystal state, have a helix conformation not very different from that of the above mentioned polymers.

FIBRE SPECTRA OF ISOTACTIC 1, 2 POLY-4-METHYLPENTADIENE

Fibres of poly-4-methylpentadiene, crystallized in modification II, suitable for X-ray examination, were obtained by annealing under tension in boiling water (10–15 hr) stretched ribbons of the polymer which were obtained from pressed sheets.

The X-ray diffraction patterns furnished by these fibres show diffraction spots and streaks, distributed along many sharply defined layer lines, superposed on a background having diffuse diffracted intensity. Table 1 shows the R (or ξ) and ζ coordinates (in the scale $1/d$, Å^{-1}) and the relative intensities corresponding to the various spots and streaks present in the fibre spectra (Fig. 1).

TABLE 1. REFLECTIONS PRESENT IN THE FIBRE PATTERN OF CRYSTALLINE ISOTACTIC 1, 2-POLY-4-METHYLPENTADIENE

(The R and ζ coordinates are expressed in $1/d$ scale (Å^{-1}). Diffuse streaks are clearly visible on the layer lines the ζ coordinates of which are: 0·1362 Å^{-1}, 0·2194 Å^{-1}, 0·2740 Å^{-1} and 0·3572 Å^{-1}).

	ζ						
	0·0000	0·0552	0·0820	0·1362	0·2194	0·2740	0·3572
R	0·113 vs	0·113 vw	0·135 vvw	0·126 ms	0·081 mw	0·078 m	0·201 vw
	0·159 ms	0·159 vvw	0·203 mw	0·204 m	0·111 m	0·238 w	0·232 w
	0·254 m	0·182 mw	0·227 w	0·232 mw	0·190 vvw	0·256 w	
	0·313 w	0·227 vw	0·296 vw	0·281 w	0·221 vvw	0·291 vw	
	0·357 vw			0·340 vw	0·239 vvw	0·329 vvw	
	0·399 vvw			0·385 vvw	0·322 vvw		
	0·450 vvw			0·407 vvw	0·394 vvw		
	0·465 w			0·455 vvw	0·423 vvw		
	0·475 vvw						
	0·506 vw						
	0·568 w						
	0·571 w						

From the figures of the ζ coordinates, it is possible to define an identity period along the chain axis of 36·50 ± 0·30 Å. The l indices of the layer lines present in the fibre patterns assume, according to this value of the c axis, the figures reported in Table 2.

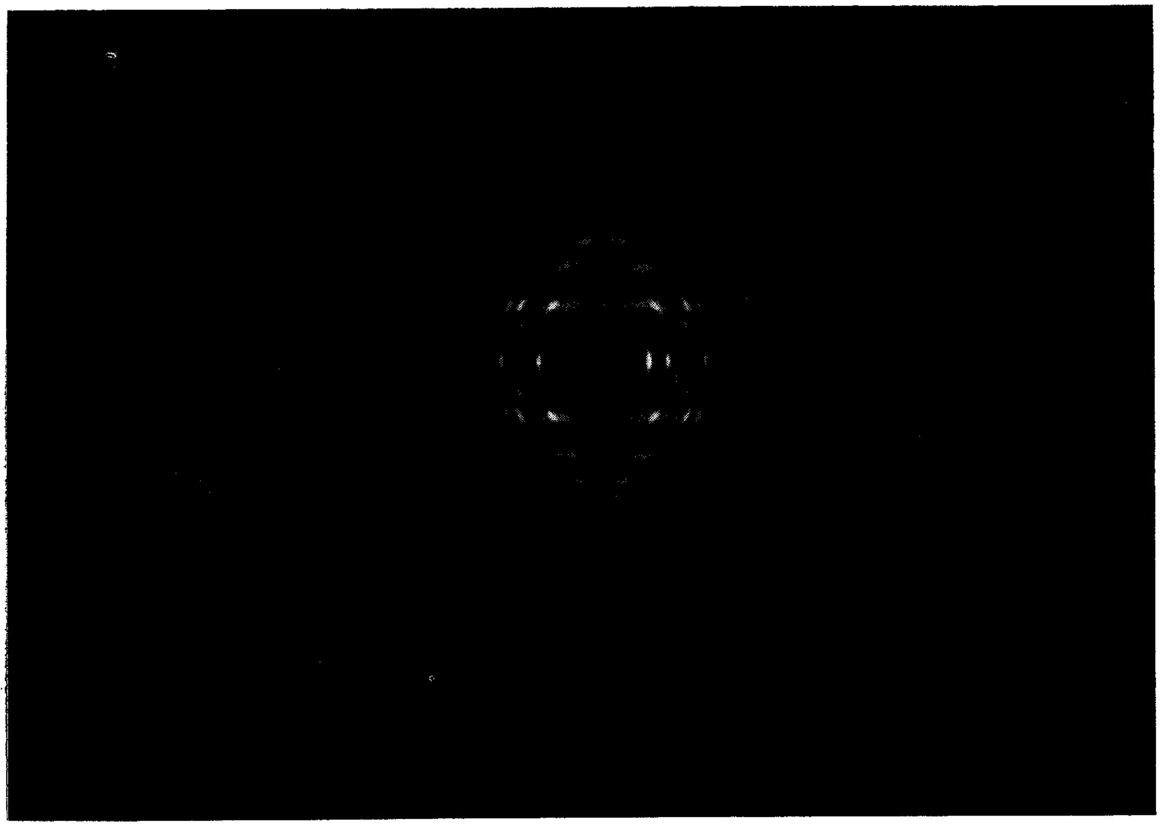


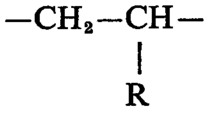
FIG. 1. Fibre photograph of isotactic-1, 2-poly-4-methylpentadiene.

TABLE 2. DETERMINATION OF THE HELIX REPEAT OF ISOTACTIC 1, 2-POLY-4-METHYLPENTADIENE FROM THE ζ EXPERIMENTAL VALUES

ζ (Å^{-1})	c/l (Å)	l	c (Å)
0·0552	18·11	2	36·22
0·0820	12·18	3	36·54
0·1362	7·34	5	36·70
0·2194	4·55	8	36·40
0·2740	3·65	10	36·50
0·3572	2·799	13	36·39
0·4100	2·433	15	36·50

CONFORMATION OF THE MAIN CHAIN OF ISOTACTIC -1, 2 POLY-4-METHYLPENTADIENE

In the pattern taken with the fibre axis perpendicular to the rotation axis of a cylindrical camera, a sharp and intense nearly equatorial reflection is observed; its Bragg distance d corresponds to $2{\cdot}02 \pm 0{\cdot}02$ Å. The chain repeat being 36·50 Å, 18 monomeric units are contained in the identity period. The number of pitches of the helix along which the



$$-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{R}}}{\mathrm{CH}}-$$

monomeric units are arranged has been established from a qualitative examination of the distribution of the diffracted intensities on the layers.

The radial intensity distribution of an isolated helical molecule can be calculated by the following relationship derived by Corradini and Pasquon⁽⁶⁾ (cf. Ref. 7):

$$F^2(R,l) = \Sigma_n\left[\Sigma_j f_j Jn(2\pi Rr_j)\, cos\left(\frac{2\pi l z_j}{c} - n\phi_j\right)\right]^2 + $$

$$+ \Sigma_n\left[\Sigma_j f_j Jn(2\pi Rr_j)\, sin\left(\frac{2\pi l z_j}{c} - n\phi_j\right)\right]^2 \qquad (1)$$

where:

R is the radial cylindrical coordinate in reciprocal space (Å^{-1});
l is the index of the layer;
f_j is the atomic scattering factor of the j^{th} atom;
c is the fibre repeat (Å);
r_j, ϕ_j, z_j are the cylindrical coordinates of the j^{th} atom of the monomeric unit (r_j, z_j in Å, ϕ_j in rad);
Jn is the Bessel function of n-th order (n being an integer);
F^2 (R, l) is the integral intensity due to a single macromolecule corresponding to the R and l coordinates.

The n index of the Bessel functions and the l value of the layer line are integers and are subjected to the following condition:

$$\frac{l}{c} = \frac{n}{P} + \frac{m}{p} \qquad (2)$$

where m is an arbitrary integral number, P is the pitch of the helix and p is the periodicity per monomeric unit along the chain axis c.

Although relation (1) does not account for the intermolecular diffraction effects, it always gives a qualitative picture of the intensity distribution in the X-ray diffraction pattern. It is well known that the smaller is the lowest index n given by Eqn. (2) on the layer under examination, the greater are the average values given by Eqn. (1) and the more the intensity will be concentrated near the meridian of the fibre pattern.

From the figures reported in Table 1, it can be easily seen that the distribution of the diffracted intensities, corresponding to the various values of l, agrees at least qualitatively with a helix with 5 pitches per chain repeat, and 3·6 monomeric units per pitch. The lowest value of the Bessel functions index n allowed on each layer of the fibre spectrum for a 18/5 helix is reported in Table 3. In accordance with this, the intensity distribution tends to be the strongest and to be concentrated near the meridian of the fibre spectra in correspondence with the 5 and the 13 layer lines ($n = +1$ and $n = -1$ respectively).

TABLE 3. LOWEST n INDEX OF THE BESSEL FUNCTIONS, ON THE BASIS OF A 18/5 HELIX, FOR EACH VALUE OF l

l	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
n	0	−7	+4	−3	+8	+1	−6	+5	−2	+9	+2	−5	+6	−1	−8	3	−4	+7	0

PROPOSED MODEL OF THE MACROMOLECULE OF CRYSTALLINE ISOTACTIC 1, 2 POLY-4-METHYLPENTADIENE

The helical parameters of the main chain, based on a 18/5 helix, have been derived from the general relationships given by Hughes and Lauer⁽⁸⁾ and by measuring the internal rotation angles σ_1 and σ_2 according to the convention proposed by Natta, Corradini and Bassi⁽⁹⁾:

$$p = \frac{l_1 (\cos\phi_1 \cos\phi_2 - \cos\theta - \sin\phi_1 \sin\phi_2 \cos\sigma_1)^{\frac{1}{2}} + l_2 (\cos\phi_1 \cos\phi_2 - \cos\theta - \sin\phi_1 \sin\phi_2 \cos\sigma_2)^{\frac{1}{2}}}{\sqrt{2}\sin(\theta/2)}$$

and

$$2\cos\theta = \cos\phi_1 \cos\phi_2 (1 + \cos\sigma_1 \cos\sigma_2) - \sin\phi_1 \sin\phi_2 (\cos\sigma_1 + \cos\sigma_2) + \\ + (\cos\phi_1 + \cos\phi_2)\sin\sigma_1 \sin\sigma_2 + \cos\sigma_1 \cos\sigma_2 - 1$$

where p is the periodicity per monomeric unit along the chain axis; $l_1 = l_2 = 1{\cdot}54$ Å is the C—C bond length, σ_1 and σ_2 are the internal rotation angles, θ is the angle between the projections normal to the chain axis of two identical atoms following one another on the same helix, ϕ_1 and ϕ_2 are the valence angles.

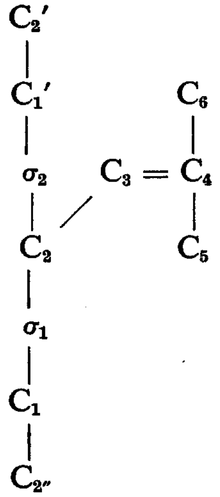
In our case $p = 2{\cdot}02$ Å, $\theta = 100° = \frac{360° \times 5}{18}$. We have assumed that $l_1 = l_2 = 1{\cdot}54$ Å. Furthermore, we have assumed that the valence angle of the chain at the tertiary carbon atom is 110° (ϕ_1) and the valence angle of the chain at the CH_2 group is 113° (ϕ_2), in accordance with literature data.⁽¹⁰⁾

On the basis of these assumptions, according to the above reported relationships for a helix growing anticlockwise, we have $\sigma_1 = 282°45'$ and $\sigma_2 = 171°30'$.

Having thus defined the conformation of the main chain, we have tried to find a model of the macromolecule that, besides permitting a good spatial arrangement of the side groups between themselves and with regard to the C atoms of the main chain, should qualitatively justify the distribution of the intensities in the diffraction pattern.

The following bond lengths and valence angles have been taken:

$$C{-}C = 1{\cdot}54\ \text{Å} \qquad C{=}C = 1{\cdot}34\ \text{Å} \qquad C_1\hat{C}_2C'_1 = 113°$$



$$C''_2\hat{C}_1C_2 = C_1\hat{C}_2C_3 = C'_1\hat{C}_2C_3 = 110°$$

$$C_2\hat{C}_3C_4 = C_3\hat{C}_4C_5 = C_3\hat{C}_4C_6 = C_5\hat{C}_4C_6 = 120°$$

In order to locate the side groups we have to define only one further internal rotation angle, that is the angle $\sigma_3 \equiv \widehat{(\overline{C_1C_2C_3})\,(\overline{C_2C_3C_4})}$, the atoms C_2, C_3, C_4, C_5 and C_6 being in the same plane.

Assuming that the main chain is a right-handed helix (i.e. growing anticlockwise) we have:

$$\sigma_1 = \widehat{(\overline{C''_2C_1C_2})\,(\overline{C_1C_2C'_1})} = 282°45'$$

and

$$\sigma_2 = \widehat{(\overline{C_1C_2C'_1})\,(\overline{C_2C'_1C''_2})} = 171°30'$$

if we put $\sigma_3 = \widehat{(\overline{C_1C_2C_3})\,(\overline{C_2C_3C_4})} = 240°$, the shortest intermolecular distances for C atoms spaced by four or more bonds become all of the order of 4 Å (Fig. 2). The value of 240° assumed by the σ_3 internal rotation angle is in accordance with the values found by us in the case of many crystalline polymers for the internal rotation angles around the single bonds adjacent to a double bond.(11-17)

We have assumed this model of the macromolecule of isotactic 1, 2 poly-4-methyl-pentadiene as the most probable and we have checked it by calculating, according to Eqn. 1, the radial intensity distribution of a single macromolecule.

The cylindrical coordinates of the atoms of the monomeric unit are reported in Table 4. Figure 3 shows the comparison between the calculated radial intensity distribution and the observed distribution of the diffracted intensity on the various layer lines. The calculations have been performed by taking into account for every *l*-th layer only the Bessel functions having index *n* below 5 (see Table 3).

As expected for a nearly correct model, the calculated intensity well agrees both with the observed intensity distributed on the diffuse streaks and with the distribution of the sharp reflections observed on the layers of the fibre photograph.

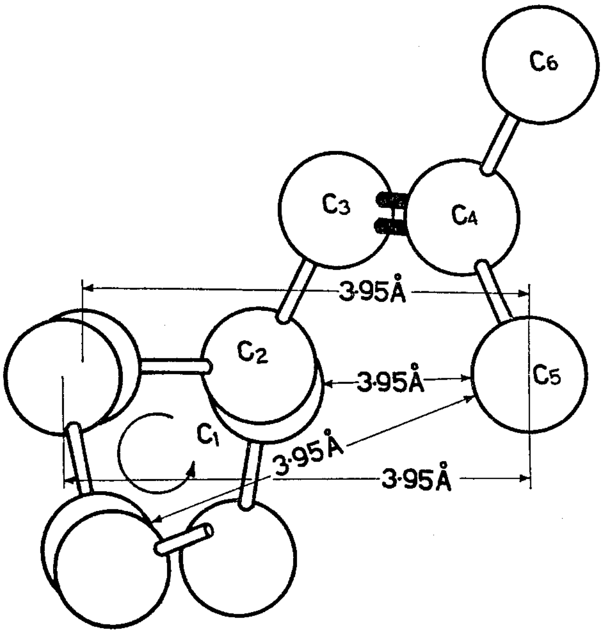


FIG. 2. End view of the proposed model of isotactic-1, 2-poly-4-methylpentadiene. Some of the most significant C—C intramolecular contact distances are indicated.

This evidence suggests that the model proposed for the macromolecule of crystalline poly-4-methylpentadiene is not too far from the actual one (Fig. 4). This model is also substantiated by packing considerations as we shall show in the following section.

TABLE 4. CYLINDRICAL COORDINATES OF THE C ATOMS OF THE MONOMERIC UNIT OF ISOTACTIC 1, 2-POLY4-METHYLPENTADIENE

	r(Å)	z(Å)	ϕ(rad)
C_1	0·987	0·000	0·0000
C_2	1·035	1·533	0·1571
C_3	2·475	1·950	0·3665
C_4	3·175	2·775	0·0785
C_5	3·125	3·263	$\overline{0\cdot3665}$
C_6	4·513	3·225	0·2182

PACKING OF THE MACROMOLECULES OF ISOTACTIC -1, 2 POLY-4-METHYLPENTADIENE

The reflections of the fibre pattern of isotactic-1, 2 poly-4-methylpentadiene may be interpreted on the basis of a tetragonal unit cell with $a = 17\cdot80 \pm 0\cdot20$ Å and

$c = 36{\cdot}50 \pm 0{\cdot}30$ Å. Four chains are contained in the unit cell and the crystalline density is $0{\cdot}85$ g/cm^3. The (hkl) reflections with $h + k + l \neq 2n$ are absent and this fact indicates that the tetragonal lattice is body centred (I).(18)

Frank, Keller and O'Connor(19) first pointed out that the molecules of the crystalline isotactic polymers characterized by complex helices (with the ratio M/N fractional,

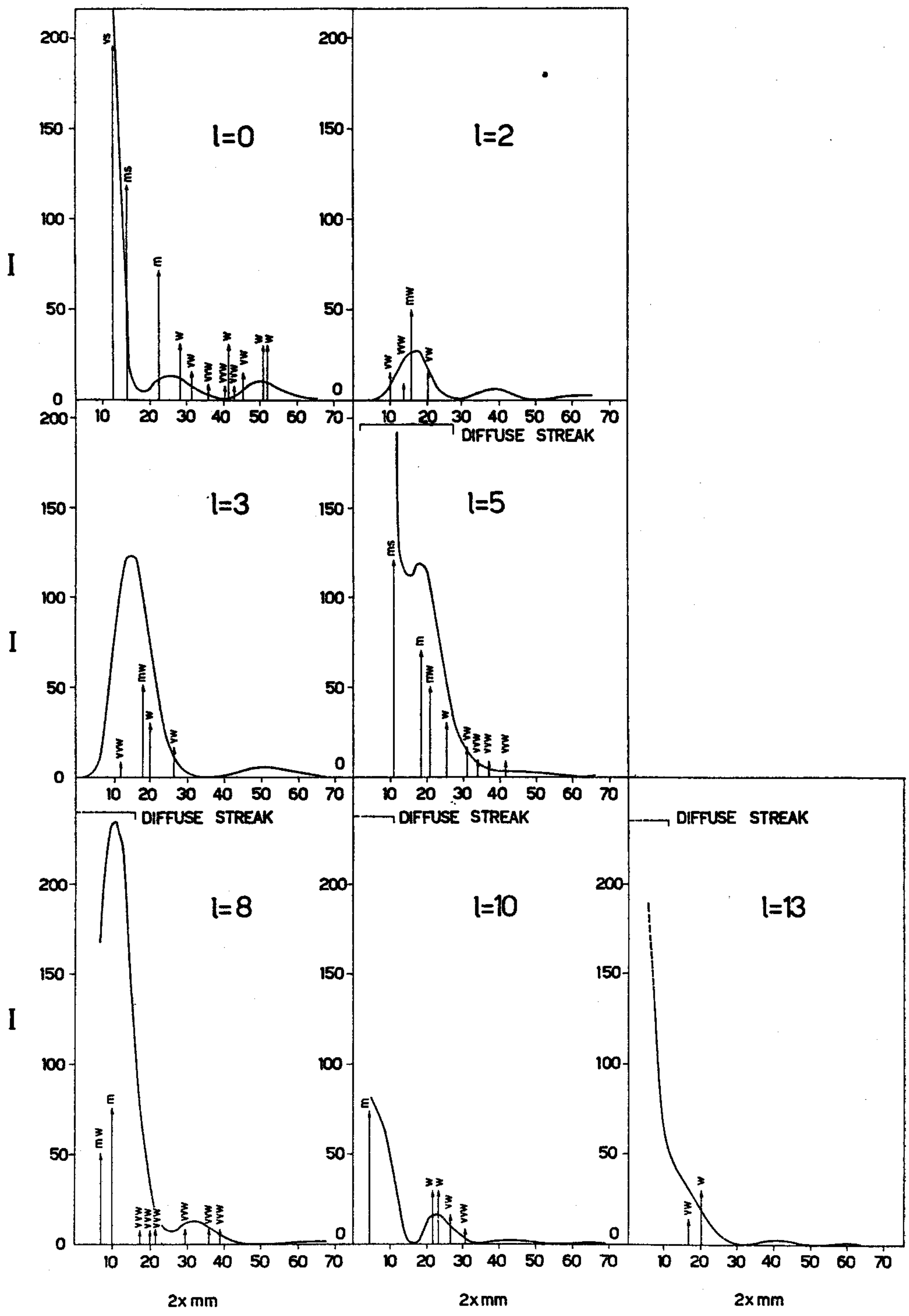


FIG. 3. Comparison between the calculated $I(R, l)$ function and the diffracted intensities (arrows) for crystalline isotactic 1, 2-poly-4-methlypentadiene.

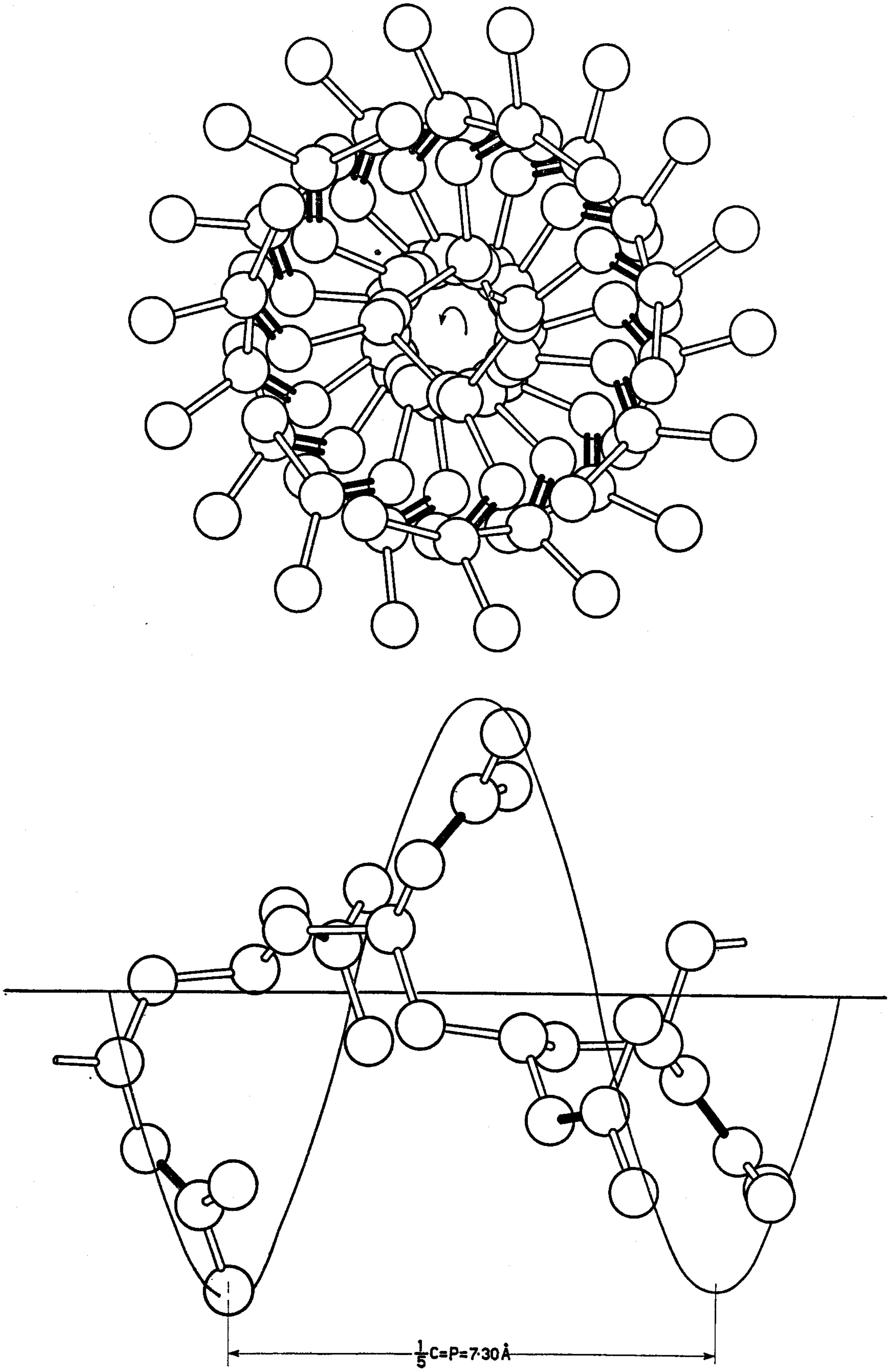


FIG. 4. Side and end views of the macromolecule of isotactic-1, 2-poly-4-methylpentadiene in the crystal state.

M = monomeric units per repeat length, N = number of pitches per repeat) tend to pack in tetragonal unit cells characterized by a $\bar{4}$ axis. Each molecule is surrounded by four enantiomorphous helices.

Subsequently, Noether(20) pointed out that the simplest space groups permitting such a type of packing are P$\bar{4}$ and I$\bar{4}$, whether M (number of monomeric units per repeat length) is odd or even. Furthermore, when M is even the helix contains a two-fold screw axis. In our case $M = 18$ and the most probable space group is I$\bar{4}$.

On the basis of close packing considerations, we came to the same conclusions. The macromolecules with M/N fractional have a shape similar to that of a screw. D_1 being the van der Waals radius of the main chain and D_2 the van der Waals radius of side group, when the ratio D_1/D_2 is between 0·3 and 0·8 the best packing is that shown in Fig. 5 with coordination number four.(21)

Each right-handed helix is surrounded by four left-handed helices and vice versa

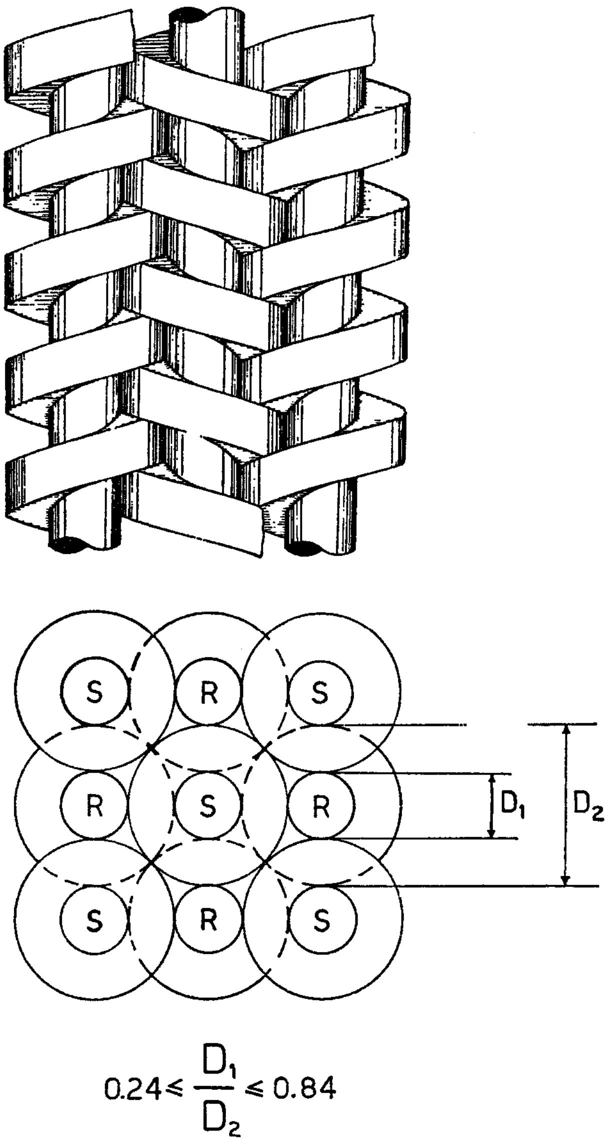


FIG. 5. Close packing of screws according to a tetragonal lattice. The screw-thread of a right-handed screw is interlocked in the screw-threads of four left-handed screws and vice versa.

and the most probable space groups are P$\bar{4}$ or I$\bar{4}$. For the I$\bar{4}$ space groups each molecule is surrounded by four enantiomorphous molecules, the side groups of which are oriented in the reversed direction with respect to the chain axis (i.e. each up right-handed macromolecule is surrounded by four down left-handed macromolecules and vice versa). If around each two-fold screw axis of the I$\bar{4}$ space group, isomorphous anticlined molecules (up and down side groups) may be disposed randomly, the space group is I$\bar{4}c2$.

The occurrence of the I$\bar{4}c2$ space group imposes the systematic extinction of $(h0l)$ reflections with $h(l) \neq 2n$. In those regions of the fibre photographs of isotactic 1, 2 poly-4-methylpentadiene where the indexing of the reflections is possible without uncertainty, we have not observed any $(h0l)$ reflection with $h \neq 2n$, although, as shown later, the structure factors of those reflections calculated on the basis of the I$\bar{4}$ space group are very high for many of them. A point of uncertainty with regard to the

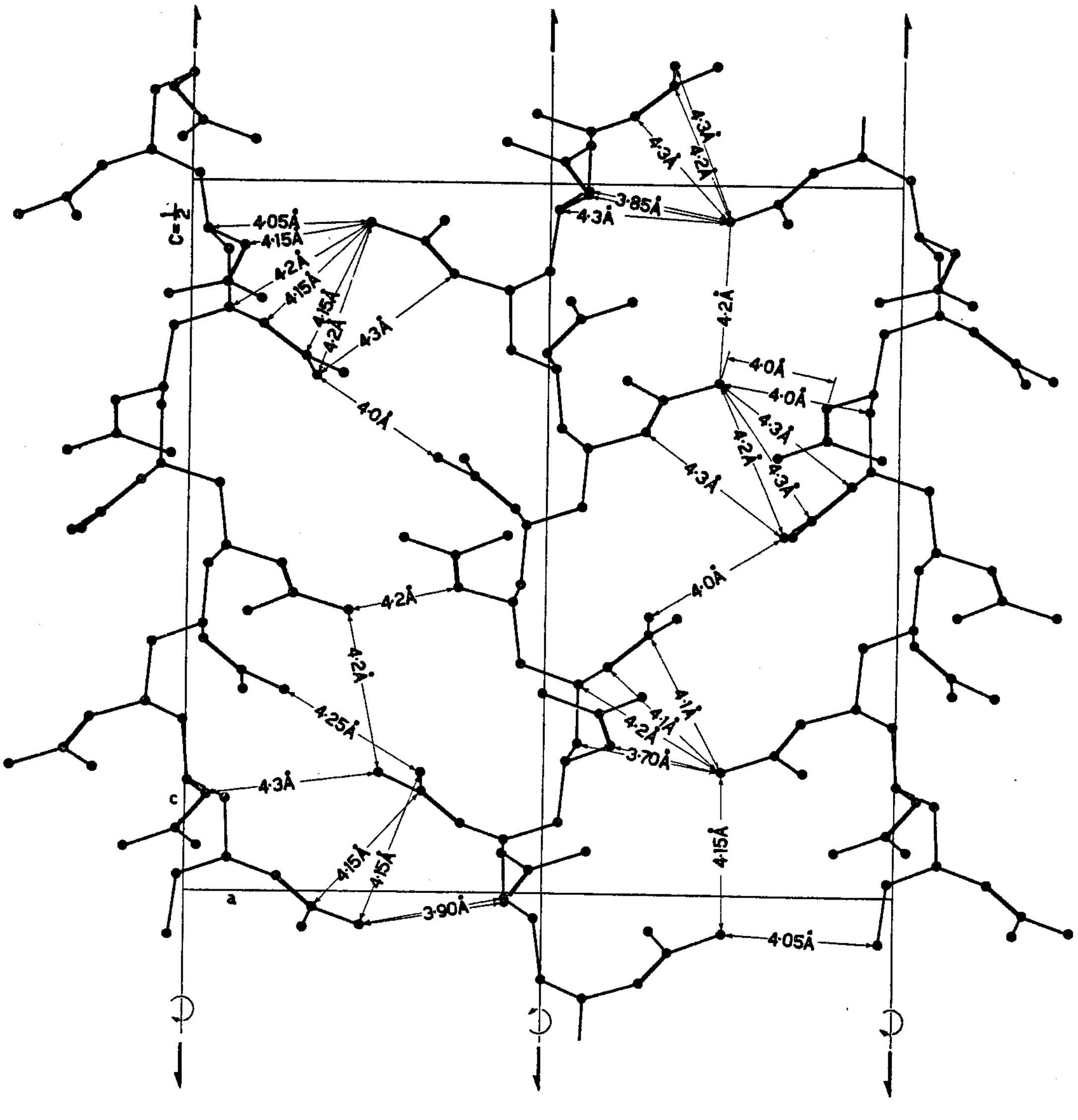


FIG. 6. Side view of a portion of the unit cell of crystalline isotactic-1, 2-poly-4-methyl-pentadiene. The macromolecules are arranged according to the I$\bar{4}$ space group, and the most significant C—C intermolecular contact distances are indicated.

(*h*0*l*) absences is due to the presence of some diffuse diffracted intensity in correspondence of the meridional region of the 13 layer lines where a 1013 reflection could be present. We think that this diffracted intensity may be explained, together with the other diffuse "streaks" present in the X-ray spectra, in terms of the continuous diffraction of an isolated helix due to the thermal disorder and to the lattice imperfections.

On the basis of the discussion above, the molecules of isotactic-1, 2 poly-4-methyl-pentadiene have been located in the unit cell according to the I$\bar{4}$ space group in such a way that the CH$_3$ groups of a molecule are displaced along the chain axis of about $1/2\ P$ ($\sim$4 Å) with respect to the CH$_3$ groups of a facing molecule, and that the van der Waals contact distances are all greater than 3·7 Å at least (Fig. 6).

It is worth noticing that the intermolecular van der Waals distances are good for this location of the molecules also if the packing is regulated by the I$\bar{4}c2$ space group;

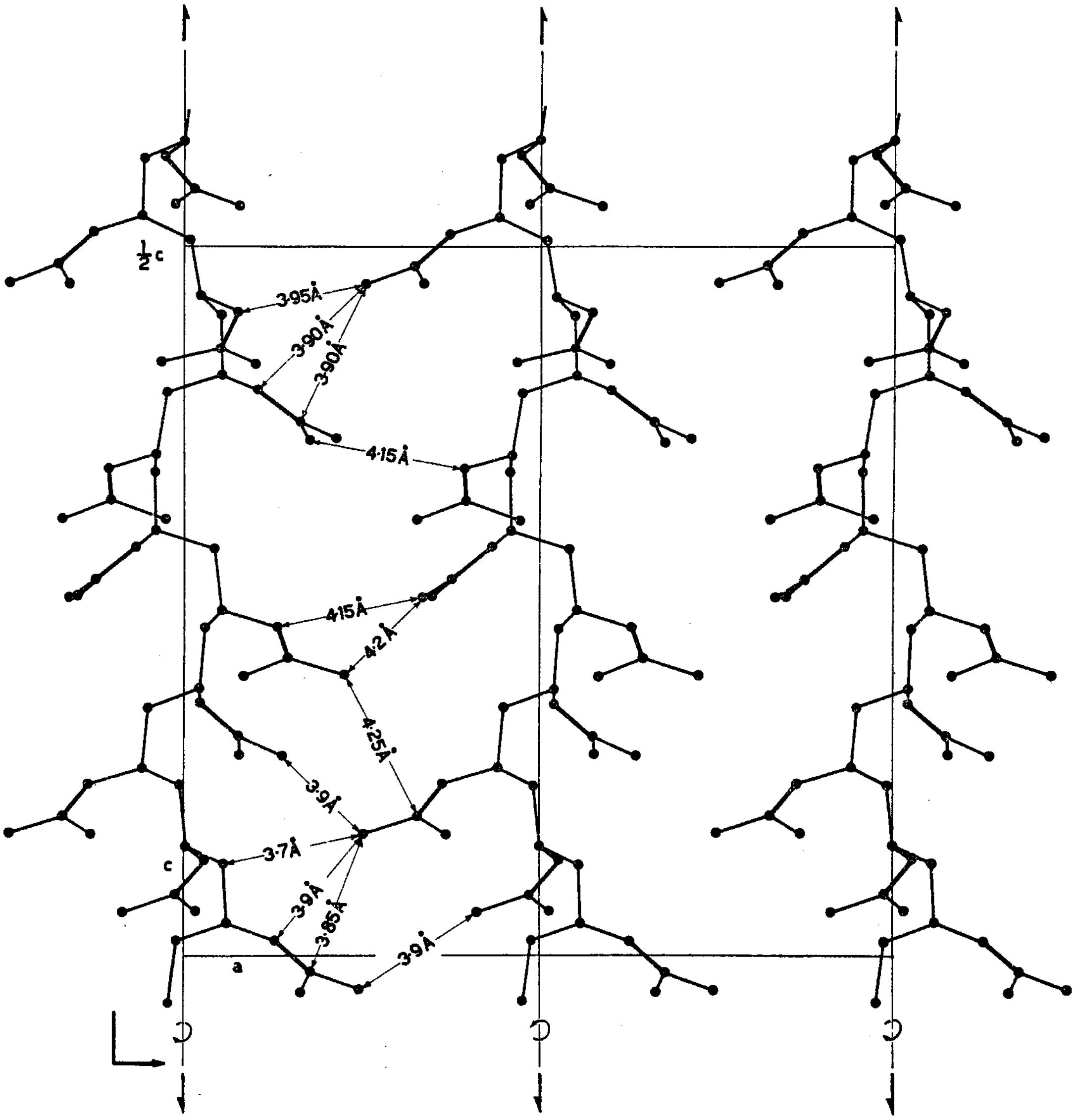


FIG. 7. Side view of a portion of the unit cell of crystalline isotactic-1, 2-poly-4-methyl-pentadiene. The macromolecules are arranged according to the I$\bar{4}c2$ space group.

i.e. if isomorphous anticlined molecules can be disposed randomly around each two-fold screw axis of the I$\bar{4}$ space group (Fig. 7).

As a check on the postulated structure, we carried out structure factor calculations for the packing conditions imposed by the I$\bar{4}$ and I$\bar{4}c2$ space groups. The atomic co-ordinates employed in the calculations are reported in Table 5. The accordance between the intensities of the observed reflections and the intensities calculated on the basis of both the I$\bar{4}$ and I$\bar{4}c2$ structures, derived from the packing considerations, is satisfactory for all reflections, except the $(h0l)$ with $h \neq 2n$ (Table 6).

TABLE 5. ATOMIC COORDINATES OF THE MONOMERIC UNIT OF ISOTACTIC-1, 2-POLY-4-METHYLPENTADIENE ($a = 17\cdot8$ Å, $c = 36\cdot50$ Å)

[The coordinates of the remaining 48 carbon atoms of the asymmetric unit can be easily derived bearing in mind that the chain is growing clockwise (left-handed); the displacement along the chain axis between linked monomeric units is $\frac{\Delta z}{c} = \frac{1}{18}c$ and the angular displacement from one monomeric unit to the successive is 100°.]

	x/a	y/b	z/c
C_1	0·3059	0·2497	0·0612
C_2	0·3090	0·2591	0·0190
C_3	0·3792	0·2999	0·0076
C_4	0·4277	0·2652	$\overline{0\cdot0151}$
C_5	0·4979	0·3041	$\overline{0\cdot0275}$
C_6	0·4136	0·1861	$\overline{0\cdot0285}$

The intensities of these reflections, calculated according to the I$\bar{4}$ space group, are in general very high while the experimental values, as shown above, seem to indicate that this class of reflections is absent from the X-ray spectra. The I$\bar{4}c2$ space group, which imposes the extinction of this class of reflections, seems to agree with the actual structure of the crystallites of isotactic poly-4-methylpentadiene better than the I$\bar{4}$ space group. This result can be explained by the assumption that a statistical disorder of up and down isomorphous molecules, around the two-fold screw axes, takes place in the crystals.

The occurrence in the polymer crystallites of a statistical disposition of this type has been suggested by us also in the case of many isotactic polymers such as polypropylene,(22) poly-α-butene,(23) polystyrene(24) and isotactic polyaldehydes.(25) This suggestion was based on the fact that the van der Waals contact distances are the same substituting, around the same screw axis of the unit cell, to a macromolecule an anticlined isomorphous molecule. Furthermore the agreement between the observed structure factors and the structure factors calculated assuming the occurrence of this statistical disposition ($C2/c$ space group for polypropylene and R$\bar{3}c$ space group for poly-α-butene and for polystyrene) seems to be better than when the random disposition of this type does not occur (Cc space group for polypropylene and R$3c$ space group for poly-α-butene and polystyrene). However, there are no systematic extinctions supporting the existence of a random disposition in polypropylene or in poly-α-butene.

TABLE 6. COMPARISON BETWEEN THE OBSERVED INTENSITIES OF ISOTACTIC-1, 2-POLY-4-METHYLPENTADIENE AND THE INTENSITIES CALCULATED ACCORDING TO THE $I\bar{4}$, $I\bar{4}c2$ AND $I4$ SPACE GROUPS

(The calculated intensities have been corrected for the usual angular factors of the fibre pattern; the contribution to the reflection of the (*hkl*) and (*khl*) lattice planes has been taken into account. The figures reported for the calculated intensities are referred to the intensity of a single spot of the fibre diagram. A disorder factor has been applied to the calculated intensities corresponding to a temperature factor with 2B = 16 Å^2.)

h k l	$\left(\frac{\sin\theta}{\lambda}\right)^2$	$I_{calc.}$ $I\bar{4}$	$I_{calc.}$ $I\bar{4}c2$	$I_{calc.}$ $I4$	$I_{obs.}$
1 1 0	0·0015	<1	<1	<1	—
2 0 0	0·0031	71,111	71,111	71,111	vs
2 2 0	0·0063	3394	3394	3394	ms
3 1 0	0·0079	3	1	3	—
4 0 0	0·0127	419	419	419	—
3 3 0	0·0143	2	2	2	—
4 2 0	0·0159	1392	1392	1392	m
5 1 0	0·0207	<1	<1	<1	—
4 4 0	0·0255	683	683	683	w
5 3 0	0·0271	<1	<1	<1	—
6 0 0	0·0287	433	433	433	—
6 2 0	0·0319	613	613	613	vw
7 1 0	0·0399	3	<1	4	vvw
5 5 0	0·0399				
6 4 0	0·0414	164	164	164	
7 3 0	0·0462	<1	<1	1	—
8 0 0	0·0510	5	5	5	vvw
8 2 0	0·0542	61	61	61	w
6 6 0	0·0574	60	60	60	vvw
7 5 0	0·0590	<1	<1	<1	—
8 4 0	0·0638	426	426	426	vw
9 1 0	0·0654	<1	<1	<1	—
9 3 0	0·0718	<1	<1	<1	—
7 7 0	0·0782	<1	<1	<1	—
10 0 0	0·0798	796	796	796	w
8 6 0	0·0798				
10 2 0	0·0829	440	440	440	w
9 5 0	0·0845	5	<1	5	—
10 4 0	0·0925	246	246	246	—
11 1 0	0·0973	4	4	4	—
1 1 2	0·0023	8	<1	<1	—
2 0 2	0·0039	529	529	576	vw
2 2 2	0·0071	1920	1920	2050	vvw
3 1 2	0·0087	3970	3970	<1	mw
4 0 2	0·0135	1505	1505	1545	vw
3 3 2	0·0151	15	<1	<1	—
4 2 2	0·0167	98	94	1440	—
5 1 2	0·0215	105	110	1	—
4 4 2	0·0262	4	4	5	—
5 3 2	0·0278	8	<1	<1	—
6 0 2	0·0294	2	2	20	—

TABLE 6—(*continued*)

h k l	$\left(\frac{\sin\theta}{\lambda}\right)^2$	$I_{calc.}$ I $\bar{4}$	$I_{calc.}$ I $\bar{4}c2$	$I_{calc.}$ I 4	$I_{obs.}$
1 0 3	0·0024	< 1	—	228	—
2 1 3	0·0056	922	533	7952	vvw
3 0 3	0·0088	880	—	5400	—
3 2 3	0·0120	13,502	13,502	8600	mw
4 1 3	0·0152	5400	4040	5160	w
5 0 3	0·0216	2210	164	2120	—
4 3 3	0·0216				
5 2 3	0·0248	466	466	575	vw
6 1 3	0·0312	112	108	90	—
1 0 5	0·0055	14,450	—	35,912	—
2 1 5	0·0087	18,233	12,674	21,716	ms
3 0 5	0·0119	8868	—	4592	—
3 2 5	0·0151	10,201	2450	9458	m
4 1 5	0·0182	17,766	8934	8212	mw
5 0 5	0·0246	4977	2789	5242	w
4 3 5	0·0246				
5 2 5	0·0278	1847	392	2184	—
6 1 5	0·0342	919	908	780	vw
5 4 5	0·0374	537	245	528	—
6 3 5	0·0406	360	269	360	vvw
7 0 5	0·0438	140	—	117	—
7 2 5	0·0470	221	9	162	vvw
6 5 5	0·0534	84	1	108	—
8 1 5	0·0566	141	1	202	vvw
7 4 5	0·0566				
8 3 5	0·0629	23	2	110	—
9 0 5	0·0693	71	—	26	—
9 2 5	0·0725	178	1	114	—
7 6 5	0·0725				
1 1 8	0·0136	10,250	10,250	12,900	mw
2 0 8	0·0152	13,200	13,200	< 1	m
2 2 8	0·0184	6865	< 1	< 1	—
3 1 8	0·0200	9095	1990	16,750	vvw
4 0 8	0·0248	3	3	1	vvw
3 3 8	0·0264	32	32	1235	vvw
1 1 10	0·0205	5470	5470	5695	m
2 0 10	0·0220	4360	4360	< 1	
2 2 10	0·0252	32	< 1	< 1	—
3 1 10	0·0268	27	25	85	—
4 0 10	0·0316	716	716	1	w
3 3 10	0·0332	858	858	858	
4 2 10	0·0348	696	640	1	
5 1 10	0·0396	221	170	1250	vw
4 4 10	0·0444	26	< 1	< 1	
5 3 10	0·0460	220	220	313	vvw
6 0 10	0·0476	93	93	< 1	—
6 2 10	0·0508	46	27	< 1	—

TABLE 6—(*continued*)

h k l	$\left(\frac{\sin\theta}{\lambda}\right)^2$	$I_{calc.}$ $I\bar{4}$	$I_{calc.}$ $I\bar{4}c2$	$I_{calc.}$ $I4$	$I_{obs.}$
1 0 13	0·0327	vs. not calc.	—	vs. not calc.	mw
2 1 13	0·0359	3590	442	8160	
3 0 13	0·0391	1200	—	1082	—
3 2 13	0·0423	1041	912	1560	vw
4 1 13	0·0455	1790	1810	996	w
5 0 13	0·0519	345	107	329	—
4 3 13	0·0519				
5 2 13	0·0550	144	<1	85	—

In the case of isotactic 1, 2-poly-4-methylpentadiene, the random disposition of up and down isomorphous helices around the same chain axis is supported, besides the previous arguments, also by the absence of a class of reflections that may be assumed as systematic.

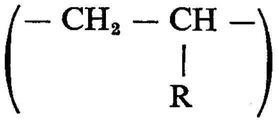
In order to evaluate the reliability of the chosen structure model, some structure factors calculations have been done for tetragonal I space groups other than $I\bar{4}$ and $I\bar{4}c2$. In the case of the space groups permitting only isomorphous chains in the unit cell, many of the deduced intermolecular van der Waals distances are scarcely acceptable (of the order of 2·5 to 3·0 Å) notwithstanding several trials of accommodation.

Although these packing considerations seem to exclude the possibility that the unit cell of poly-4-methylpentadiene contains only isomorphous helices, we have performed some structure factors calculations according to space groups permitting only isomorphous chains in the unit cell. The structure factors calculations led to results in disagreement with the intensities of the observed reflections. Table 6 reports the intensities of the reflections calculated according to the $I\bar{4}$, $I\bar{4}c2$ and the $I4$ space groups.

CONCLUSIONS

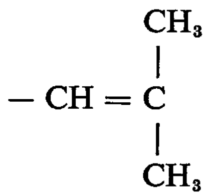
The conformation assumed in the crystal state by the macromolecule of isotactic 1, 2 poly-4-methylpentadiene has been established in this work. The macromolecule has a helix conformation characterized by 3·6 monomeric units per pitch. The internal rotation angles, around the bonds of the main chain for a helix growing anticlockwise, are $\sigma_1 = 282°45'$ and $\sigma_2 = 171°30'$. The plane defined by the C atoms of the side group bisects the angle formed by the C atoms of the main chain $C_1\hat{C}_2C_1'$ (internal rotation angles on the bond C—R = 240° and 120°). The unit cell is tetragonal and each right handed helix is surrounded by four left handed helices and vice versa. In the site where a right-handed helix is placed, there may be at random a right handed *up* helix or a right handed *down* helix. Obviously, the same happens also for the left handed helices. However, right and left handed helices may not replace each other, in the crystal, along the same chain axis.

The conformation of the macromolecule of isotactic-1, 2 poly-4-methylpentadiene found by us fits well with the conformations of the macromolecules of the isotactic polymers of 4-methylpentene-1, of 4-methylhexene-1 and of the corresponding vinylethers. It is well known that the symmetry and periodicity of the helices, along which the monomeric units



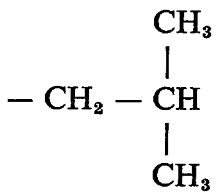
$$\left(-\mathrm{CH_2}-\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{CH}}}-\right)$$

of crystalline isotactic vinyl polymers are arranged, mainly depend on the steric requirements of the side group R. The steric requirements of the side group



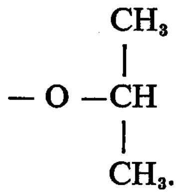
$$-\mathrm{CH}=\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{C}}}}}$$

of poly-4-methylpentadiene are not too far from the steric requirements of the side groups of poly-4-methylpentene-1



$$-\mathrm{CH_2}-\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}}}$$

and of poly-*iso*-propylvinylether



$$-\mathrm{O}-\overset{\displaystyle \mathrm{CH_3}}{\overset{|}{\underset{\displaystyle \mathrm{CH_3}.}{\underset{|}{\mathrm{CH}}}}}$$

Actually the helices of these crystalline isotactic polymers are very similar. The macromolecules of isotactic-1, 2 poly-4-methylpentadiene in the crystal state have a helix conformation containing 3·6 (18/5) monomeric units per pitch, the macromolecules of isotactic poly-4-methylpentene-1 and of isotactic poly-*iso*-polyvinylether, in the crystal state, have helix conformations containing 3·5 (7/2) and 3·4 (17/5) monomeric units per pitch respectively.(2-5)

The packing of the poly-4-methylpentadiene macromolecules in a tetragonal unit cell, in such a way that each molecule is surrounded by four enantiomorphous helices, is in accordance with the close packing principles. An analogous way of packing has been found also in the case of poly-4-methylpentene-1 and of poly-4-methylhexene-1. The similarity in the packing of the molecules of these isotactic polymers is the consequence of the great similarity of their macromolecular conformations. Table 7 reports the helical parameters and the most significant crystallographic data for some of these isotactic polymers.

A particular feature of the crystal structures of poly-4-methylpentadiene and of poly-4-methylpentene is that the calculated density of the crystalline polymer is lower than the density observed.(26-28)

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TABLE 7. COMPARISON BETWEEN THE HELICAL PARAMETERS AND THE TETRAGONAL UNIT CELLS OF SOME CRYSTALLINE ISOTACTIC POLYMERS

Polymer	$a = b$ (Å)	Periodicity per monomeric unit along the chain axis (Å)	Monomeric unit per pitch (M/N)	Density of crystals (g/cm^3)	Internal rotation angles along the main chain (*)	Valence angles along the main chain
Poly-4, 4-dimethyl butadiene 1-2	17·80	2·02	3·60 (18/5)	0·850	$\sigma_1 = 282°45'$ $\sigma_2 = 171°30'$	$\phi_1 = 110°$ $\phi_2 = 113°$
Poly-4-methylpentene 1	18·60	1·97	3·50 (7/2)	0·820	$\sigma_1 = 287°7'$ $\sigma_2 = 167°26'$	$\phi_1 = 110°$ $\phi_2 = 113°$
Poly-4-methylhexene 1	19·64	2·00	3·50 (7/2)	0·845	$\sigma_1 = 286°17'$ $\sigma_2 = 169°17'$	$\phi_1 = 110°$ $\phi_2 = 113°$
Poly-*i*-propylvinylether	17·20	2·09	3·40 (17/5)	0·925	$\sigma_1 = 290°$ $\sigma_2 = 170°$	$\phi_1 = \phi_2 = 114°30'$
Poly(R, S) [*sec* buthyl] vinylether	18·25	2·09	3·40 (17/5)	0·955	$\sigma_1 = 290°$ $\sigma_2 = 170°$	$\phi_1 = \phi_2 = 114°30'$

* For a right-handed helix.

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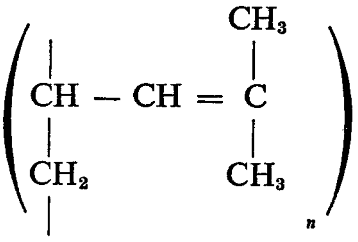
Résumé—On a déterminé à l'aide des spectres de diffraction de rayons X de fibres étirées, la structure cristalline de la modification II du polyméthyle-4-pentadiène 1-2 isotactique.



$$\left(\begin{array}{ccc} & & \mathrm{CH_3} \\ | & & | \\ \mathrm{CH} - & \mathrm{CH} = & \mathrm{C} \\ | & & | \\ \mathrm{CH_2} & & \mathrm{CH_3} \\ | & & \end{array}\right)_n$$

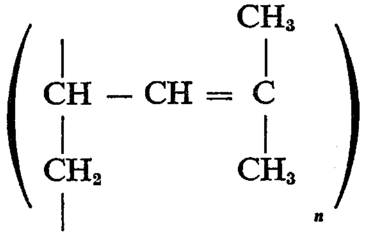
L'étude de la transformée de Fourier d'une macromolécule isolée a montré que les unités monomériques sont disposées sur une hélice à raison de 18 unités monomériques pour 5 spires. La péridicité de l'unité monomérique le long de l'axe de l'hélice est de 2·02 ± 0·02 Å ($c = 36, 50$ Å).

Les angles de rotation interne le long de la chaîne principale correspondent à une succession de conformations presque *gauches* (± 282°45′) et presque *trans* (± 171°30′).

L'étude de l'empilement dans les cristaux a montré que les molécules sont disposées en mailles élémentaires tétragonales I, ($a = 17{\cdot}80 \pm 0{\cdot}20$ Å) chaque molécule étant entourée de quatre hélices énantiomorphes.

La comparaison entre les intensités observées et celles calculées pour les groupes spaciaux $I\bar{4}$ et $I\bar{4}c2$ montre qu'en un point donné de la maille élémentaire on trouve de manière statistique des molécules isomorphes "up" et "down".

Sommario—Mediante lo studio di spettri di diffrazione ai raggi X di fibre stirate è stata definita la struttura cristallina della modificazione II del poli-4-metilpentadiene 1-2 isotattico



$$\left(\begin{array}{ccccc} | & & & & \mathrm{CH_3} \\ & & & & | \\ \mathrm{CH} & - & \mathrm{CH} & = & \mathrm{C} \\ | & & & & | \\ \mathrm{CH_2} & & & & \mathrm{CH_3} \\ | & & & & \end{array}\right)_n$$

Lo studio della trasformata di Fourier di una macromolecola isolata ha mostrato che le unità monomeriche si succedono lungo un'elica contenente 18 unità monomeriche su 5 passi della spirale.

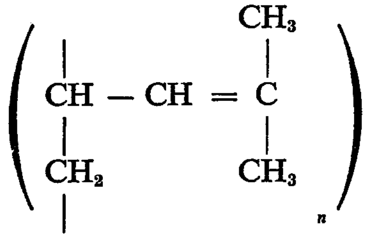
La periodicità per unità monomerica lungo l'asse dell'elica è di 2·02 ± 0·02 Å ($c = 36 \cdot 50$ Å).

Gli angoli di rotazione interna lungo la catena principale corrispondono ad una successione di conformazioni quasi *gauche* (± 282°45′) e quasi *trans* (± 171°30′).

Lo studio dell'impacchettamento nei cristalli ha mostrato che le molecole sono disposte in celle elementari tetragonali I ($a = 17 \cdot 80 \pm 0 \cdot 20$ Å) in modo tale che ciascuna molecola è circondata da quattro eliche enantiomorfe.

Il confronto tra le intensità osservate e quelle calcolate per i gruppi spaziali $I\bar{4}$ e $I\bar{4}c2$ mostra che nello stesso sito della cella unitaria possono vicariare in modo statistico molecole isomorfe "up" e "down".

Zusammenfassung—Die Kristallstruktur von isotaktischem 1, 2-Poly-4-methyl-pentadien



$$\left(\begin{array}{ccccc} | & & & & \mathrm{CH_3} \\ & & & & | \\ \mathrm{CH} & - & \mathrm{CH} & = & \mathrm{C} \\ | & & & & | \\ \mathrm{CH_2} & & & & \mathrm{CH_3} \\ | & & & & \end{array}\right)_n$$

in der Modifikation II wurde mittels Röntgenbeugungsspektren verstreckter Fasern untersucht. Die Konformation der Makromoleküle wurde unter Verwendung der von Cochran, Crick und Vand vorgeschlagenen Methode der Fourier-Transformaten einer Helix bestimmt. Die Molekülkette hat im kristallinen Zustand eine Helix-Struktur mit 3·6 Monomereinheiten pro Gang und eine Periodizität pro Monomereinheit längs der Kettenachse von 2·02 ± 0·02 Å (M/N = 18/5; $c = 36 \cdot 50$ Å Faserachse). Die inneren Rotationswinkel längs der Hauptkette entsprechen einer Aufeinanderfolge von annäherend *gauche*—(± 282°45′) und annäherend *trans*—(± 171°30′) Konformationen. Die Untersuchung der Kettenpackung im Kristall zeigt Anordnungen in tetragonalen I-Elementarzellen ($a = 17 \cdot 80 \pm 0 \cdot 20$ Å) solcher Art, dass jedes Molekül mit vier enantiomorphen Helices umgeben ist.

Der Vergleich zwischen beobachteten Intensitäten und denen, die entsprechend der $I\bar{4}$- und $I\bar{4}c2$-Raumgruppen berechnet wurden zeigt, dass an den gleichen Stellen der Elementarzelle up- und down-isomorphe Moleküle in statistischer Weise variieren können.