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Structure of Isotactic Polyaldehydes

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INTRODUCTION

As has been reported in previous papers,[1] in our Institute we have prepared crystalline polymers having a polyacetalic chemical structure of a great number of aldehydes, by polymerization of the monomer at low temperature, at room pressure and in the presence of small amounts of metalloorganic compounds. Previously, attempts to obtain crystalline polymers from aldehydes had given good results only for the first of the series: formaldehyde.[2] All the polymers described in literature and obtained from aldehydes higher than formaldehyde appeared amorphous by x-ray examination.[3]

Only after our first stereospecific polymerizations of aldehydes, we learned that, independent of our studies, Novak and Whalley[4] had succeeded in obtaining crystalline polymers of isobutyraldehyde and heptanoic aldehyde by operating at very high pressure. Soon after our first publications, Furukawa et al.[5] reported they had obtained crystalline polymers of some aldehydes using metalloorganic compounds as catalysts, and then Vogl[6] described crystalline polymers of acetic aldehyde and of some higher aldehydes obtained in the presence of other catalysts preferably constituted of lithium alkoxides. In these publications, however, the crystalline structures of the polymers obtained were not described nor was the type of steric order described, according to which the monomeric units follow each other along the polymeric chain.

The lack of crystallinity in the polymers of higher aldehydes and the presence of crystallinity in formaldehyde polymers correspond to what occurred in the α-olefin polymers known before 1954.

In fact, before the discovery of stereospecific polymerization processes[7] only crystalline polymers of the first of the series of unbranched olefins (ethylene) were known, while the polymers of higher linear olefins (propylene, butene, pentene, etc.) known at that time were amorphous.[8]

The reason for the lack of crystallinity is the same in both cases: when enchaining themselves to give a head-to-tail polymer, the monomeric units of monomers such as propylene (acetalic monomeric units) may assume two different steric configurations (see Fig. 1), one being the specular image of the other but not superposable; in the case of olefins, only by means of stereospecific catalysts was it possible to steer the polyaddi-

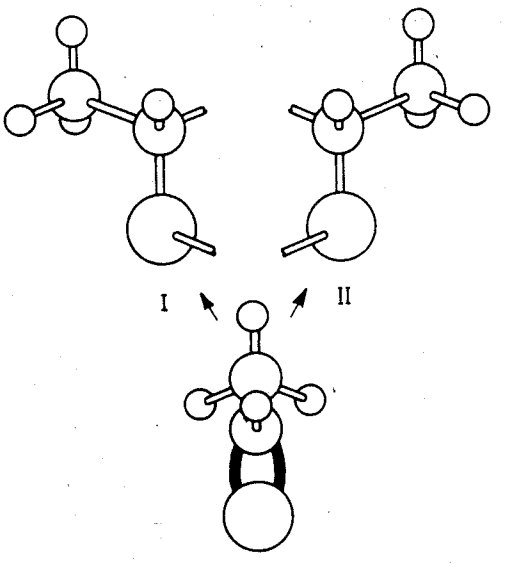
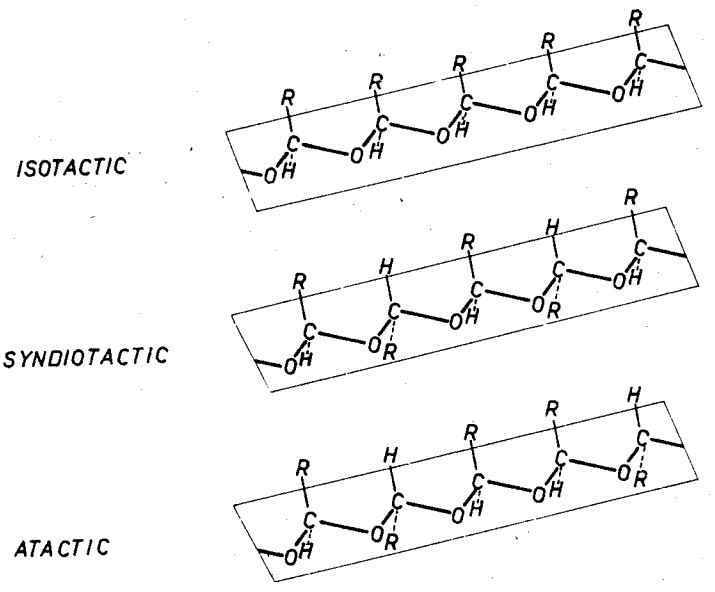


Fig. 1. Possible configurations the monomeric unit of acetaldehyde may assume.



R
|
—O—CH—

Fig. 2. Various types of possible head-to-tail successions of acetalic (—O—CH—) monomeric units: isotactic, syndiotactic, atactic (random); main chain arbitrarily stretched on a plane.

tion reaction so as to have a regular succession of those configurations in the polymer.[9]

In fact, in order to have a crystalline polymer, it is essential that its monomeric units possess such configurations as to be able to assume equivalent positions toward an axis.[10] Under this condition, we could demonstrate that only two modes of simple ordered succession of monomeric units of the $—CH_2—CHR—$ type (and therefore also —O—CHR—) can give crystallizable polymers. The structures corresponding to these

two modes of ordered succession (Fig. 2) have been called by us "isotactic" and "syndiotactic," respectively.[11]

In analogy with what has been observed for α-olefins, from which it was possible to obtain crystalline polymers having either an isotactic or a syndiotactic structure,[12] it could be expected that in the case of polyaldehydes, if it were possible to find stereospecific catalysts able to link the —O—CHR— monomeric units even in a sterically regular way, the resulting polymers would be crystalline.

The synthesis of the aldehyde crystalline polymers has been performed in this Institute by using catalysts acting with an anionic coordinated mechanism, as described in a previous paper of ours.[13]

We shall report in this paper the results achieved by x-ray examination of crystalline polymers synthesized from acetaldehyde, propionaldehyde, and *n*-butyraldehyde.

X-RAY SPECTRA OF CRYSTALLINE POLYALDEHYDES

The crystalline polymers of aldehydes have been obtained by us[1] by operating at room pressure at a temperature of −78°C., using trialkyl or triaryl aluminum compounds as catalysts, in the presence of *n*-heptane or toluene as polymerization media. The crude polymers thus obtained are generally remarkably crystalline by x-ray examination, and it is possible

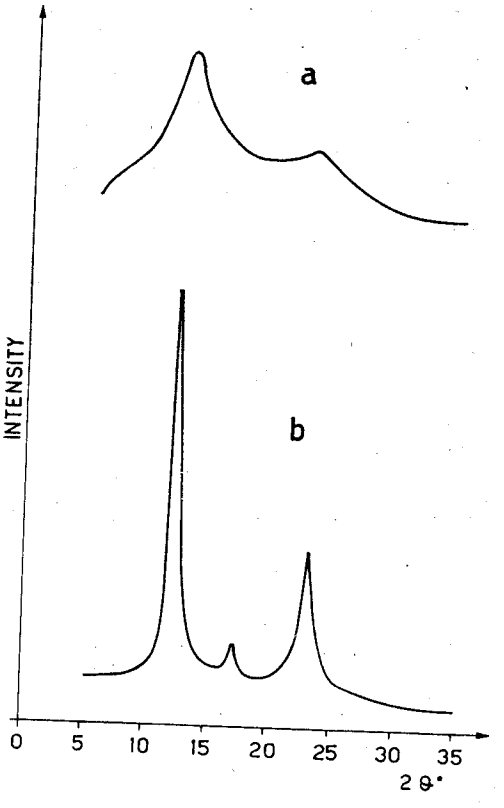


Fig. 3. X-ray powder spectra (CuKα) registered with a Geiger counter of acetone-extract (*a*) and of a residue to the acetone (*b*) of polyacetaldehyde.

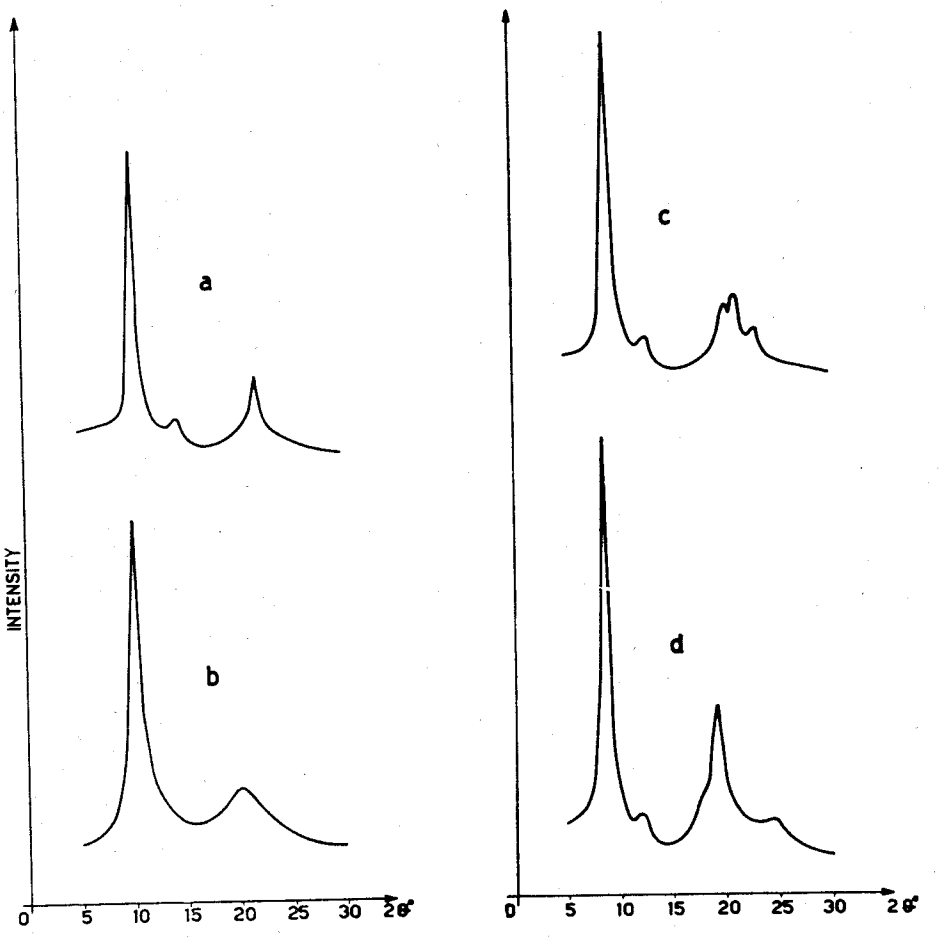


Fig. 4. X-ray powder spectrum (CuKα) of the residues to the benzene extraction of (*a*) polypropionaldehyde, (*b*) polyisobutyraldehyde, (*c*) poly-*n*-butyraldehyde, and (*d*) polyisovaleroaldehyde.

to increase the percentage of crystallinity of the polymer by extracting amorphous or slightly crystalline fractions from the crude polymerizate by means of suitable solvents. These fractions are formed during polymerization in amounts of few per cent units. Figure 3, as an example, shows the x-ray spectra registered by a Geiger counter (CuKα), for a boiling acetone extract and for the residue of acetone extraction of polyacetaldehyde.

The spectrum belonging to the acetone extract, typical of an amorphous substance, is similar to the one obtainable from samples of polyacetaldehyde prepared according to Letort's method.

The x-ray spectra registered by a Geiger counter for the benzene extraction residues of other crystalline polyaldehydes are shown in Figure 4.

In Table I the most relevant interplanar distances and the relative intensity fit for characterizing the spectra of some crystalline polyaldehydes are reported.

The interplanar distance, corresponding to the first diffraction maximum which is also the sharpest in the spectrum, increases with an increase in

TABLE I

Comparison of Most Important Bragg Distances of Some Crystalline Polyaldehydes

Polyacetaldehyde		Polypropionaldehyde		Polyisobutyraldehyde		Poly-*n*-butyraldehyde		Polyisovaleroaldehyde	
d, A.	Relative intensity	*d*, A.	Relative intensity	*d*, A.	Relative intensity	*d*, A.	Relative intensity	*d*, A.	Relative intensity
7.30	100	8.76	100	9.06	100	10.01	100	10.31	100
5.15	7	6.19	6	4.38	30	7.08	6	7.28	8
3.87	35	4.08	20			4.48	15	4.60	32
						4.22	15	3.60	8
						3.89	4		

the number of carbon atoms present in the aldehyde. It corresponds to a general property of crystalline polymeric substances, the first diffraction maxima of which are due to planes which are equatorial to the chain axis. Their lattice distances for polymers of homologous series of monomers increase as the bulk of the side groups increases.

The indexing of diffractions has been carried out for some polyaldehydes by examining spectra obtained from oriented fibers of the polymers. The data obtained have been used for the direct interpretation of the powder spectrum of other polyaldehydes.

The techniques suitable for obtaining oriented fibers from polyaldehydes on a laboratory scale have been described in a previous paper.[13] By way of example, a fiber spectrum obtained from polyacetaldehyde is shown in Figure 5. The sharpness and the high number of reflections (more than one hundred) has permitted reconstruction of the polymer unit cell. In polyacetaldehyde, the identity period along the chain axis c is 4.79 A. By oscillating the fiber, normal to its axis in a Weissenberg camera, such a value has been confirmed by the presence of a particularly strong reflection having the indexes (004), with a Bragg distance d equal to 1.197 A.

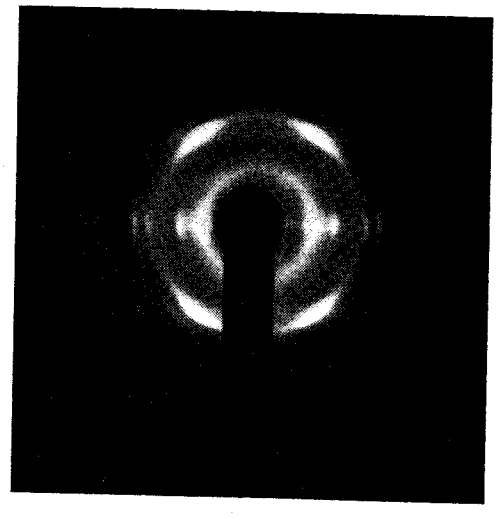


Fig. 5. Fiber photograph of isotactic polyacetaldehyde.

In Figure 6 a complete reconstruction of the reciprocal lattice for crystalline polyacetaldehyde is shown.

The indexing of all the reflections is possible on the basis of a tetragonal unit cell having $a = 14.63 \pm 0.05$ A. The $O'K'H'$ pattern represents the reciprocal lattice on the equator, having axes $a^* = b^* = 0.1054$ (in λ/d units). The $H'K'$ circle encloses the values corresponding to $2 \sin \vartheta < 1$. For the sake of simplicity, we confined ourselves to reproducing only the reflections observed in this range; this is justified by the fact that, for all the known polymers, the observation of reflections in the range of the reflection sphere comprised between $1 < 2 \sin \vartheta < 2$, is very difficult.

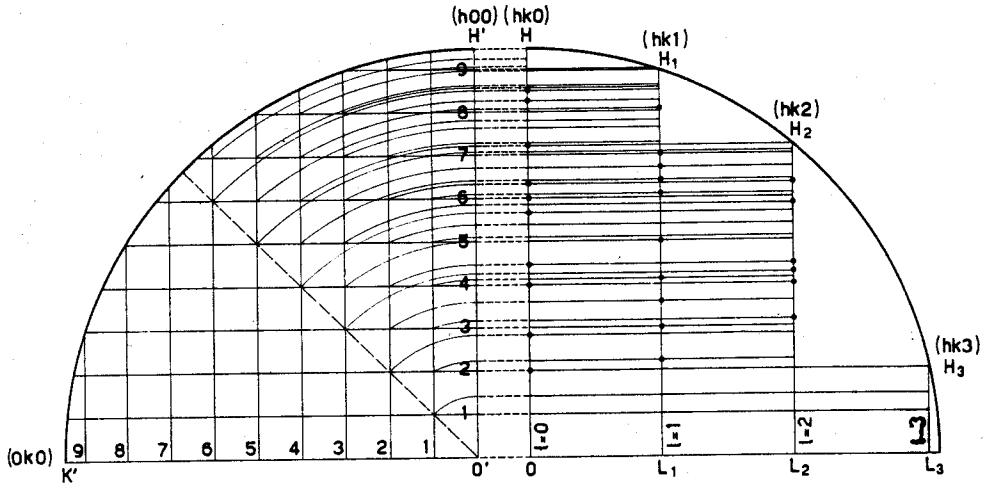


Fig. 6. Reciprocal lattice of isotactic polyacetaldehyde.

On the OH line we have reported, with dotted lines for the $(hk0)$ reflections, the values of $2 \sin \vartheta < 1$ which can be observed for all the possible values of h and k.

The values actually observed have been marked by a black circle and correspond, as can be easily observed, only to even values of h and k indices. Normally to the OH axis, we have reported $OL_1 = L_1L_2 = L_2L_3$ segments of length equal to $c^* = 0.3219$ (still in λ/d units).

Therefore, on the L_1H_1, L_2H_2, etc. lines the values of $2 \sin \vartheta$, can be observed, measured starting from 0, for the $(hk1)$, $(hk2)$ etc. reflections, respectively. Also, in this case, the observed values have been marked by a black circle.

On the first layer $(hk1)$ only reflections having $h + k = 2n + 1$ are observed; on the second layer, only reflections having $h + k = 2n$ are observed.

On the other hand, from the spectrum obtained by oscillation of the fiber normal to its axis, the only reflection observed of the $00l$ type corresponds to $l = 4$. The reflections (hkl) having $h + k + l \neq 2n$, the reflections $(hk0)$ having $h \neq 2n$ and $k \neq 2n$, and the reflections $00l$ having $l \neq 4n$ are absent. These extinctions are characteristic for the $I4_1/a$ space group with 16 equivalent points in general position.[14]

Supposing that in the unit cell 16 monomeric units are present, one calculates a density of 1.14 g./cm.^{3}, which is in very good agreement with the experimental value.

The examination of normal polyaldehydes higher than acetaldehyde was carried out directly on the powder spectra.

The spectrum given by polypropionaldehyde is very poor in reflections[15] by analogy with polyacetaldehyde; that is to say, assuming a tetragonal unit cell and the $I4_1/a$ space group, it is possible to index all the reflections on the basis of a lattice having c = 4.8 A. and a = 17.50 A. The resulting density (1.05 g./cm.^{3}), supposing that the unit cell contains 16 monomeric units, is in good accordance with the experimental value.

The spectrum obtained from n-butyraldehyde[15] also agrees with a tetragonal unit cell. The space group is $I4_1/a$ and its unit cell results are a = 20.01 A., c = 4.78 A., d (calc.) = 0.997 g./cm.^{3}.

In the case of polyisobutyraldehyde,[15] the fiber spectra give a c identity period longer than the one of the described polyaldehydes, which is equal to 5.2 A.

CHAIN CONFORMATION OF CRYSTALLINE POLYALDEHYDES

The number of monomeric units contained in the unit cell of polyacetaldehyde is 16; since the number of equivalent points in general positions contained in the $I4_1/a$ space group is 16, the monomeric units of each chain necessarily must repeat themselves along symmetry elements of the group.

The only symmetry elements of the group permitting a repetition with translation along the c axis are the two fourfold right-handed 4_1 screw axes and the two fourfold left-handed 4_3 screw axes.[14] Consequently, the chain must necessarily have a helix shape. This result enables us to ascribe an isotactic configuration to the polymer.[16]

The knowledge of the chain symmetry and of the repetition period along its axis permitted us to reconstruct the geometrical form of the chain.

We have reasonably supposed the C—O—C and O—C—O angles to be tetrahedral (Φ = 109°30′) and assumed for the C—O distance the value of 1.43 A. which is the average of the best values found for similar low molecular weight compounds.[17] Under these conditions, it is possible to determine the internal rotation angles σ_1 and σ_2 referring to the O—C bonds which characterize the conformation of the helix-shaped chain.

The convention, by which such angles have been measured by us, so that they should be consistent with the formulas we report below, differs from the one used in our preceding paper[18] and is as follows (Fig. 7).

Calling L_1, L_2, and L_3 three successive bonds along the chain, we establish that the σ angle between the L_1L_2 and L_2L_3 planes (i.e., the angle of internal rotation referring to L_2), is smaller than 180° if, looking parallel to L_2 from L_3, L_3 must be rotated clockwise by an angle smaller than 180° in order to superpose it to L_3; or (which is the same) if, looking parallel to

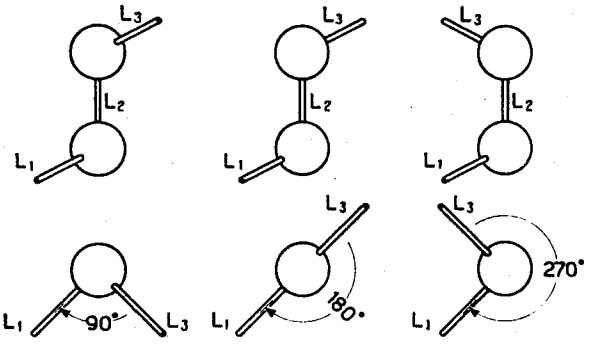


Fig. 7. Convention used to measure the internal rotation angles (σ).

L_2 from L_1, L_1 must be rotated clockwise by an angle smaller than 180° in order to superpose it to L_3.

The repetition period along the chain axis for a monomeric unit d, the internal rotation angles σ_1 and σ_2, and the ϑ angle between the projections normal to the chain axis of two atoms following one another on the same helix are connected by the general relationship:

$$d = 2l \sin^2 \frac{\Phi}{2} \sin \frac{\sigma_1 + \sigma_2}{2} \frac{1}{\sin \vartheta/2} \tag{1}$$

$$2 \cos \vartheta = 2 \cos \sigma_1 \cos \sigma_2 + 2 \cos \Phi \sin \sigma_1 \sin \sigma_2 - \sin^2 \Phi (1 + \cos \sigma_1)(1 + \cos \sigma_2) \tag{2}$$

in which l is the length of the L bonds along the chain and Φ is the angle between two successive bonds.

In our case, experimentally we have $d = 4.78/4 = 1.95$ A.; $\vartheta = 90°$. By assuming, for the above mentioned reasons, $r = 1.43$ A. and $\Phi = 109°30'$ we obtain, by graphic resolution of eq. (2) under the condition established by eq. (1):

$\sigma_1 = 277.5°$	$\sigma_2 = 135°$	(right-handed helix)
$\sigma_1 = 82.5°$	$\sigma_2 = 225°$	(left-handed helix)

The r radius of the two coaxial helices, on which the oxygen and carbon atoms of the polyacetalic chain lie, respectively, can be obtained from the general expression:

$$r = \frac{(4l^2 \sin^2 \Phi/2 - d^2)^{1/2}}{2 \sin \vartheta/2}$$

and $r = 1.42$ A.

The resulting model, assuming also the two O—C—O and C—O—C angles to be equal to 109°30′, is shown in Figure 8.

Similarly, the models of the polypropionaldehyde and poly-*n*-butyraldehyde can be built up. While internal rotation angles of polyaldehydes with an identity period of 4.8 A. are, as we have already seen, $\sigma_1 = 85°$ and $\sigma_2 = -135°$, the values of the internal rotation angles of the chain

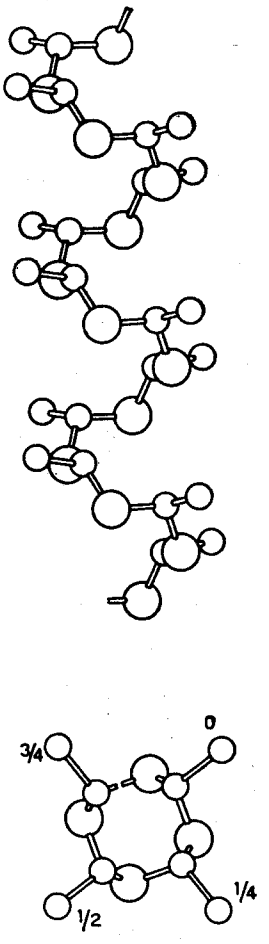


Fig. 8. Side and end views of the isotactic polyacetaldehyde macromolecule in the crystalline state.

bonds of the polyaldehydes with identity period of 5.2 A. are $\sigma_1 = 83°$, $\sigma_2 = -145°$.

The values of the internal rotation angles found for polyaldehydes are very different from those of other isotactic polymers; for example, the values of polypropylene are $\sigma_1 = 60°$ and $\sigma_2 = -180°$. However, for isotactic polymers, the helix of which has a fourfold symmetry, it is possible to find analogous values of the internal rotation angles, such as in the case of polyvinylcyclohexane as is shown in Table II.

It must be noticed that for all the aldehydes the exceptional deviation of the σ_2 angle from the value of $-180°$ leads to a remarkable contraction of the chain and to a very low value of the repetition period for monomeric unit along the chain axis. As compared with isotactic olefin polymers, the reason for this shortening is due to the smaller van der Waals' radius of oxygen with respect to the one of CH_2 groups.[10]

Bulky side groups cause an elongation of the chain itself. In fact, an accommodation between the couples of the two methyl groups of each monomeric unit at van der Waals' distances higher than 4 A. is possible for polyisobutyraldehyde only in this way.

On the other hand, in the case of isotactic vinyl polymers, bulky side groups generally cause a shortening of the periodicity for monomeric unit, as is also shown in Table II.

TABLE II

Repetition Periods along Chain Axis and Internal Rotation Angles σ_1 and σ_2 of Some Isotactic Polymers, the Chain of Which Is a Fourfold Helix

Polymer	Identity period, A.	σ_1	σ_2	Period of corresponding chain stretched on a plane, A.
Polyacetaldehyde Polypropionaldehyde Poly-*n*-butyraldehyde	4.8	85°	−135°	9.4
Polyisobutyraldehyde	5.2	83°	−145°	9.4
Polyvinylcyclohexane[22]	6.5	83°	−151°	10.1
Poly-3-methylbutene[22]	6.85	84°	−156°	10.1
Poly-*o*-methylstyrene[23] Poly-α-vinylnaphtalene[23] Poly-2,5-dimethylstyrene[24]	8.1	90°	−180°	10.1

MODE OF PACKING OF MACROMOLECULES

Four chain portions, two of them having right-handed conformations and the other two left-handed ones, corresponding to the two 4_1 and to the two 4_3 screw axes, are contained in the unit cell of polyacetaldehyde. In order to establish the orientation of the helix-shaped macromolecules in the unit cell and their positions along Z, we first studied whether, with the limits imposed by the size and symmetry of the lattice, there was a single solution of the problem which could furnish van der Waals contacts among atoms of different molecules, not lower than those usually found in low molecular weight compounds.

Contacts among different macromolecules have to be mainly expected among methyl groups, which are 2.9 A. distant from the chain axis, while the radius of the helix is 1.42 A.

Following a method used previously,[20] we have studied the contact distances among methyl groups of contiguous macromolecules for all the possible orientations of a macromolecule in respect to its axis. The results of such studies are shown in Figure 9.

The angle formed by one of the equatorial axes and by the *OD* line (joining the center of the macromolecule with a methyl group, Fig. 10) is plotted on the abscissas and for any possible orientation.

The projections on *ab* of the distances from the above-said methyl group to the two methyl groups of a contiguous molecule facing the former are plotted on the ordinates. If we assume that the distance between two methyl groups cannot be lower than 4.1 A., the distance, in projection on

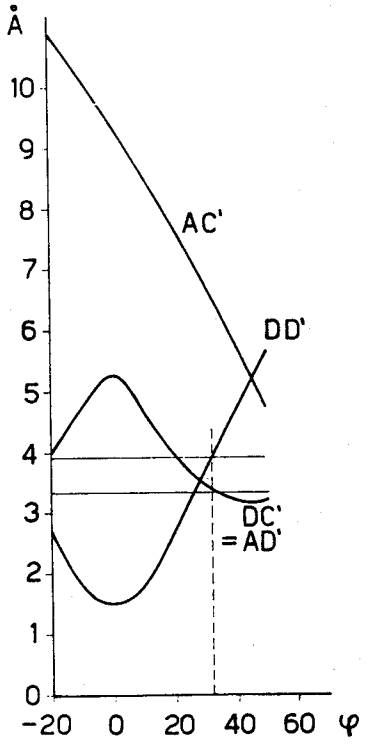


Fig. 9. Projection on the *ab* plane of the contact distances of methyl groups of adjacent polyacetaldehyde molecules.

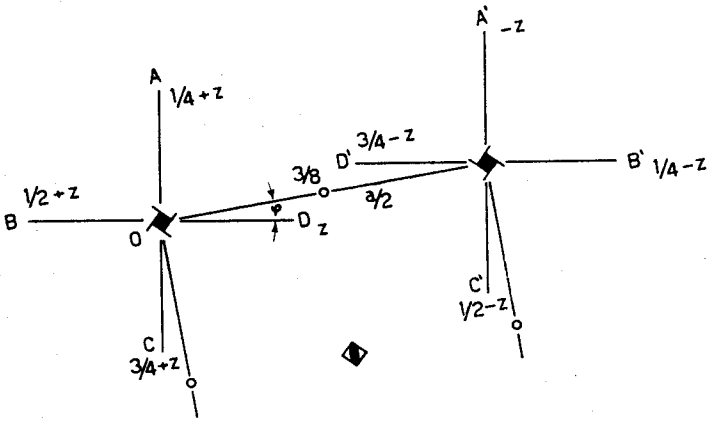


Fig. 10. Schematic drawing of two enantiomorphous macromolecules of polyacetaldehyde. (Only the positions of methyl groups are indicated.)

ab, cannot be lower than $((4.1)^2 - (c/2)^2)^{1/2} = 3.33$ A.; that happens only in the favorable case in which the two methyl groups are as far apart as possible along Z.

This strictly bounds the possible solutions of the problem. Furthermore, recalling that, if one of the two neighboring methyl groups is displaced along Z by $^1/_2\, c$, the other is necessarily displaced only by $^1/_4\, c$, it is possible to deduce that under the above-mentioned conditions, the macromolecule is forced to assume the orientation $\varphi = 33°$ (see Fig. 9).

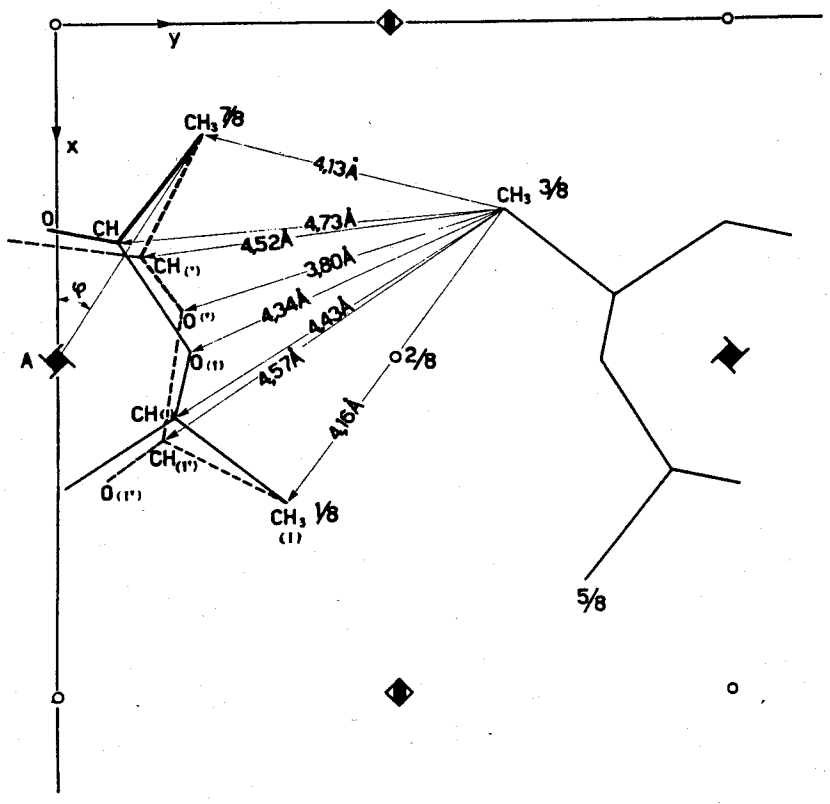


Fig. 11. Actual position in the unit cell of the independent structural unit of polyacetaldehyde (dashed lines indicate the position of its possible statistical vicariant).

Furthermore, for this orientation the contact distances among methyl groups which are symmetrically related by the inversion tetrades present in the unit cell are higher than 4.1 A.

To consider the contacts between the methyl groups and the chain atoms of the contiguous macromolecule, it must be borne in mind that, given a certain φ and therefore fixing the position of the methyl group and the spiralization direction of the chain, the chain itself may have two different orientations, anticlined between themselves, and not equivalent from the viewpoint of the intermolecular contacts, corresponding to the two possibilities that the AO line (joining the oxygen atom to the center of the chain) may form a $\varphi_0 > \varphi$ angle with the reference axis (full drawn molecule) or the $O^{(')}A$ line may form a $\varphi_0 < \varphi$ angle (dotted molecule) (Fig. 11).

The contact distances between methyl groups and chain atoms of the contiguous macromolecules do not allow us to choose one of the two possibilities: while the CH_3 . . . CH shortest distances are always higher than 4.5 A., the CH_3 . . . O shortest distances result, in one case, equal to 3.82 and in the other, 4.34 A. Such distances are, for both cases, higher than the value of analogous distances of van der Waals contacts found in low molecular weight compounds.

We therefore thought to settle the question of the two possible orientations of the macromolecules by the calculation of structure factors.

CALCULATION OF THE STRUCTURE

The calculation of the structure factors was performed for both the stocastically possible orientations and also for a model in which it had been assumed that anticlined macromolecules, having the same coordinates of the methyl groups and therefore the same spiralization direction, could statistically vicariate around the same fourfold screw axis.

This is just the same as to postulate a structure in which the two orientations, associated with the angle $\varphi = 33°$, are equally possible. The van der Waals contacts, in fact, do not seem to prevent that in the same site, isomorphous anticlined macromolecules may casually take the place of one another as it often happens in a great number of crystalline polymers.[21] Actually the calculation results have been quite satisfactory ($R = 14\%$ for the equatorial reflections) only for the last model. In Table III, the coordinates of an independent structural unit are given (full line of Fig. 11) and of its anticlined one (dashed line of Fig. 11), whereas in Table IV the agreement between observed and calculated structure factors is reported.

TABLE III

Isotactic Polyacetaldehyde: Coordinates of Independent Structural Unit (I) and Its Possible Statistical Vicariant (II)
(Origin in $\bar{1}$, Figure 11)

		x/a	y/b	z/c
I	CH_3	0.082	0.109	0.875
	CH	0.164	0.044	0.833
	O	0.153	0.995	0.577
II	CH_3(′)	0.082	0.109	0.875
	CH (′)	0.176	0.061	0.917
	O (′)	0.216	0.091	0.173

For the equatorial layer, as a comparison, we have reported, besides the structure factors calculated for the statistical structure, also the structure factors separately calculated for the structures corresponding to models I and II. For the reflections of the II layer line only the values of the calculated intensities are given because the quantitative evaluation of the observed intensities become uncertain owing to the longitudinal enlargement of the diffraction spots.

The observed structure factors have been obtained from the intensities by correcting them not only by the usual angular factors, but also by means of a factor, increasing with the diffraction angle, which takes into account the progressive longitudinal enlargement of the diffraction spots.

The observed structure factors in practice correspond to the square root of the corrected intensity. The applied temperature factor is $B = 13$ A.^{2}.

TABLE IV

Comparison between Observed and Calculated Structure Factors of Isotactic Polyacetaldehyde[a]

$h\ k\ 0$	2 sin	F_c I	F_c II	F_c, stat. struct.	F_0
2 0 0	0.211	116	115	116	127
2 2 0	0.299	56	60	58	50
4 0 0	0.423	27	40	34	40
4 2 0	0.472	46	24	69	47
4 4 0	0.597	35	10	23	20
6 0 0	0.634	6	32	19	19
6 2 0	0.668	24	50	35	36
6 4 0	0.762	53	27	38	40
8 0 0	0.845	8	15	4	—
8 2 0	0.871	7	36	22	21
6 6 0	0.896	24	5	15	13
8 4 0	0.945	11	13	2	—
10 0 0 8 6 0	1.056	14	11	9	11
10 2 0	1.077	12	1	6	—
10 4 0	1.137	5	8	6	—
8 8 0	1.195	<1	2	1	—
10 6 0	1.232	6	8	7	—
12 0 0	1.267	5	2	3	—

$h\ k\ 1$	2 sin	F_c stat. struct.	F_0
1 0 1	0.339	11	—
2 1 1	0.399	84	99
3 0 1	0.452	5	11
3 2 1	0.499	18	11
4 1 1	0.542	26	24
5 0 1 4 3 1	0.618	21	19
5 2 1	0.653	6	—
6 1 1	0.718	22	15
5 4 1	0.748	17	10
6 3 1	0.778	15	8
7 0 1	0.806	10	8
7 2 1	0.833	4	—
6 5 1	0.885	7	—
8 1 1 7 4 1	0.910	13	14
8 3 1	0.958	7	<9
9 0 1	1.003	2	—
9 2 1 7 6 1	1.025	8	<10
8 5 1	1.047	7	<10
9 4 1	1.088	6	—
10 1 1	1.109	9	<10

$h\ k\ 2$	2 sin	Int. stat. struct. (calc.)	Int. (obs.)
1 1 2	0.661	Not calc.	w
2 0 2	0.678	Not calc.	—
2 2 2	0.709	170	—
3 1 2	0.725	2343	mw
4 0 2	0.771	743	w
3 3 2	0.784	115	—
4 2 2	0.798	600	w
5 1 2	0.840	248	—
4 4 2	0.878	35	—
5 3 2	0.891	509	w
6 0 2	0.903	189	—
6 2 2	0.927	178	—
7 1 2 5 5 2	0.985	82	—
6 4 2	0.997	6	—
7 3 2	1.030	80	—
8 0 2	1.061	4	—

[a] In the calculated structure factors of (nkl) reflections, the different contributions to the reflection of the (hkl) and (khl) lattice planes have been taken into account. The calculated structure factors here reported correspond to $[F^2(hkl) + F^2(khl)]^{1/2}$, whereas intensities are proportional to $[F^2(hkl) + F^2(khl)]$. $B = 13$ A.^{2} (CuKα).

DISCUSSION OF STRUCTURE

With regard to the shape of the chain and the contacts among different macromolecules, we refer to what we have previously stated in this paper. It is interesting to notice that a phenomenon of statistical vicariance of isomorphous anticlined macromolecules takes place also in the polyacetaldehyde structure. Such a phenomenon had been previously observed by us in polypropylene, poly-α-butene, and polystyrene.[20]

The chain compactness and the scarce accessibility of the oxygen atoms, screened by the methyl groups, may explain the complete insolubility of the product in the usual solvents.

The fourfold symmetry of the chain favors a tetragonal symmetry of the unit cell with a right-handed helix surrounded by four left-handed helices and vice versa (Fig. 12). In general, such arrangement may take place either in the $I4_1/a$ space group or in the $I4_1/cd$ space group.

The crystalline polymers of acetaldehyde, propionaldehyde, *n*-butyraldehyde, and vinylcyclohexane[22] belong to the former space group, while the crystalline polymers of *o*-methyl styrene, α-vinylnaphthalene,[23] and 2,5-dimethylstyrene[24] previously studied by us (Table II), belong to the latter space group.

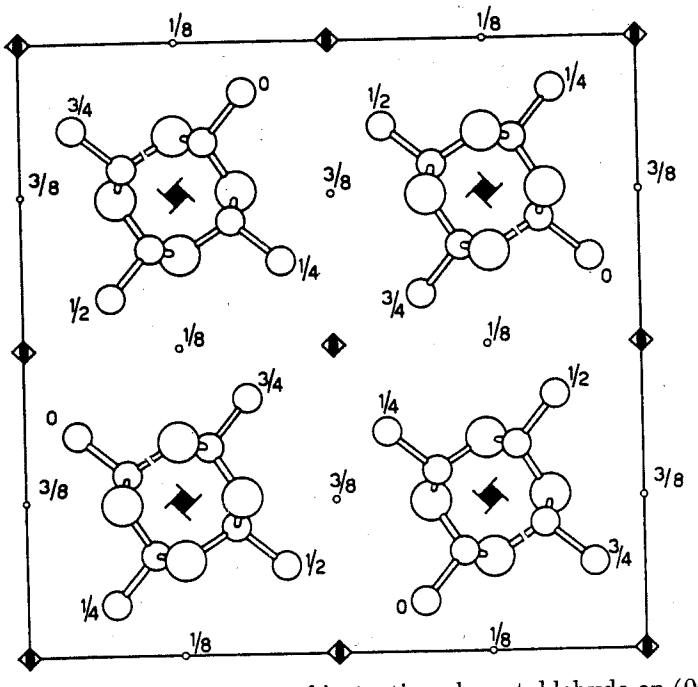


Fig. 12. Projection of the structure of isotactic polyacetaldehyde on (001). (For the sake of simplicity the statistical vicariance around each fourfold screw axis of anticlined isomorphous macromolecules has not been taken into account.)

MODE OF PACKING OF THE MOLECULE AND CALCULATION OF THE POLY-*n*-BUTYRALDEHYDE STRUCTURE

Though in the case of isotactic poly-*n*-butyraldehyde only powder spectra or spectra of partially oriented samples were available,[25] neverthe-

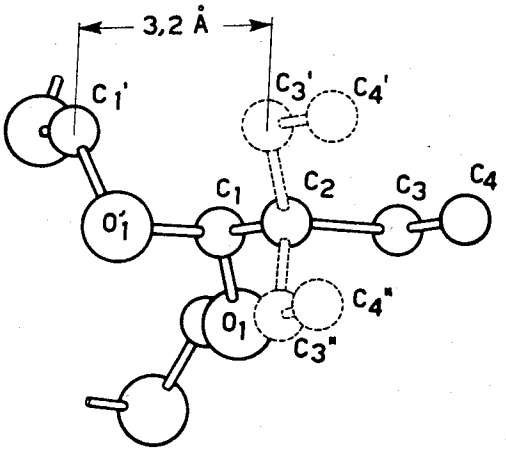
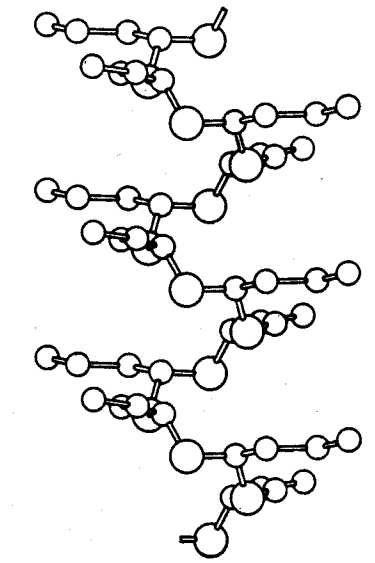


Fig. 13. Model of the independent structural unit of isotactic poly-*n*-butyraldehyde.



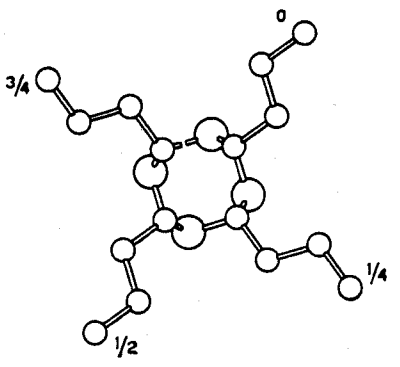


Fig. 14. Side and end views of a macromolecule of isotactic poly-*n*-butyraldehyde in the crystalline state.

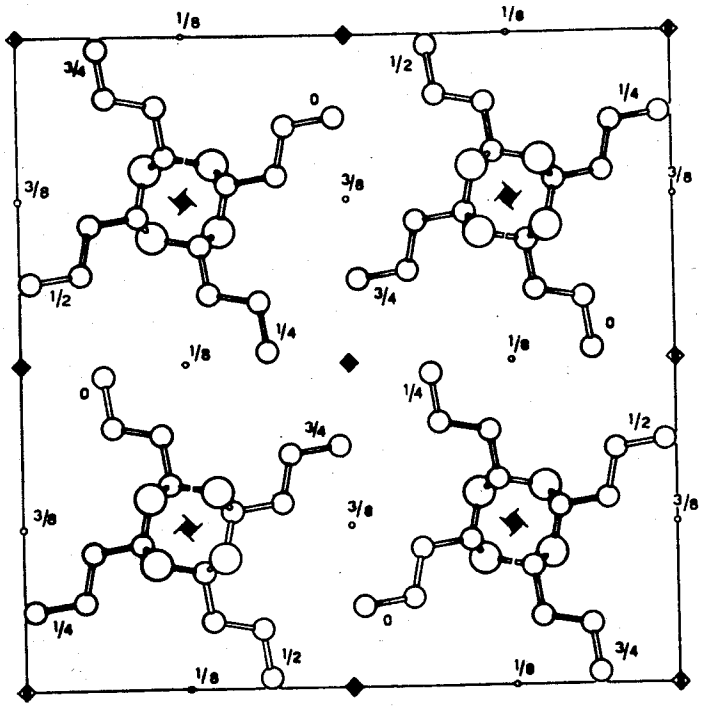


Fig. 15. Projection of the structure of isotactic poly-*n*-butyraldehyde on (001). (For the sake of simplicity the statistical vicariance around each fourfold screw axis of anticlined isomorphous macromolecules has not been taken into account.)

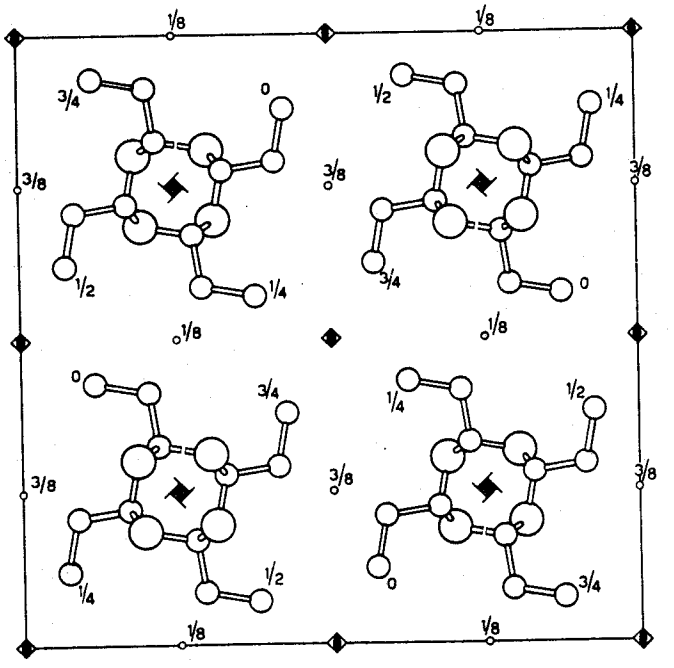


Fig. 16. Projection of (001) of the probable structure of isotactic polypropionaldehyde.

less we could index all the observed reflections. That is possible, as we have seen above, on the basis of a tetragonal unit cell, belonging to the $I4_1/a$ space group; its axes are: $a = 20.00$ A., $c = 4.80$ A.

The lack of superpositions, since the spectrum is simple, has encouraged us to calculate a trial model of the structure. The chain conformation is univocally determined by the identity period along its axis while the orientation of the side group has been assumed staggered with regard to the bonds along the chain. All the bonds successive to the first side bond have a *trans* conformation.

Among the three possible staggered conformations of the first bond of the side chain we have chosen only one of the two possible conformations which would be *trans* in respect of one of the two contiguous CO bonds. More precisely, we chose the *trans* conformation in respect to the CO bond, which is almost orthogonal to the chain axis (Fig. 13).

In fact, the other two conformations which are also possible on the basis of the "staggered bonds" principle (broken line, Fig. 13) are to be rejected because they seem energetically unfavored in respect to the above-mentioned conformation (full line, Fig. 13). Therefore the conformation of the resulting macromolecule (Fig. 14) satisfies the "staggered bonds" principle; moreover, all the contact distances among atoms separated by more than three bonds are higher than the corresponding van der Waals distances. When rotating a macromolecule having the described encumbrance around the fourfold screw axis under the size and symmetry conditions imposed by the space group, it can be easily noticed that only two possible orientations exist, characterized by the same position of the end methyl group, as it happens in the case of polyacetaldehyde. The two orientations correspond to macromolecules anticlined among themselves. Then, in analogy with what we had done for polyacetaldehyde, we calculated the structure factors for both the stocastically possible orientations and also for a structure in every site of which anticlined macromolecules having the same coordinates of the methyl groups and therefore the same spiralization direction were supposed to vicariate statistically. Table V shows the coordinates of the two possible independent structural units,

TABLE V

Isotactic Poly-*n*-butyraldehyde: Coordinates of Independent Structural Unit (I) and Its Possible Statistical Vicariant (II)
(Origin in $\bar{1}$)

		x/a	*y/b*	*z/c*
I	C_1	0.228	0.068	0.806
	C_2	0.218	0.143	0.848
	C_3	0.143	0.159	0.854
	C_4	0.134	0.234	0.896
	O	0.197	0.048	0.550
II	C_1'	0.209	0.058	0.986
	C_2'	0.154	0.111	0.944
	C_3'	0.187	0.181	0.938
	C_4'	0.134	0.234	0.896
	O′	0.244	0.071	0.242

TABLE VI. Comparison between Calculated and Observed Structure Factors for Isotactic Poly-*n*-butyraldehyde[a]

h k l	2 sin ϑ	F_c I	F_c II	F_c stat. struct.	F_0
2 0 0	0.154	148	152	150	151
2 2 0	0.218	89	80	85	50
4 0 0	0.308	6	3	5	—
1 0 1	0.332	78	48	15	—
4 2 0	0.345	120	114	117	120
2 1 1	0.365	161	143	138	137
3 0 1	0.397	29	178	75	73
3 2 1	0.426	165	51	60	<34
4 4 0	0.436	40	22	32	—
4 1 1	0.453	22	64	37	43
6 0 0	0.462	23	58	40	
6 2 0	0.488	9	7	8	—
5 0 1 / 4 3 1	0.503	96	77	29	34
5 2 1	0.526	36	75	21	<34
6 4 0	0.556	38	30	34	—
6 1 1	0.569	14	31	17	—
5 4 1	0.590	54	45	26	—
6 3 1	0.609	18	32	10	—
8 0 0	0.616	10	11	10	—
7 0 1	0.629	42	3	19	—
8 2 0	0.636	60	63	61	54
7 2 1	0.648	28	39	6	—
1 1 2	0.653	39	37	38	39
6 6 0	0.654	11	34	23	
2 0 2	0.663	2	13	8	—
2 2 2	0.681	2	40	21	—
6 5 1	0.683	24	39	22	—
8 4 0	0.689	21	46	33	64
3 1 2	0.689	54	36	44	
8 1 1 / 7 4 1	0.701	38	31	27	—
4 0 2	0.714	25	27	26	—
3 3 2	0.723	23	8	15	—
4 2 2	0.731	22	28	25	49
8 3 1	0.734	35	34	33	
5 1 2	0.756	12	23	8	—
9 0 1	0.766	4	17	11	—
10 0 0 / 8 6 0	0.771	40	53	31	52
4 4 2	0.778	23	<1	12	—
9 2 1 / 7 6 1	0.781	25	18	21	—
10 2 0	0.786	54	3	28	—
5 3 2	0.786	31	14	19	—
6 0 2	0.793	8	41	24	—

[a] The F_0 values reported here correspond to the square root of the total intensity diffracted by the (*hkl*) lattice plane, after effecting the corrections for the usual angular factors. $F_c(hkl)$ and $F_c(h0l)$ have been multiplied by $(2)^{1/2}$. In the calculated values of the reflections (*hkl*) it has been taken into account the contribution to the reflection of the (*hkl*) and (*khl*) lattice planes. F_c (I), F_c (II) and F_c (statistical structure) have been corrected for a disorder factor corresponding to a temperature factor with B = 15 A.^{2} (CuKα).

while Table VI shows the agreement between the calculated and observed structure factors.

The agreement is satisfactory and, though it is not possible to deduce the degree of accuracy of the postulated coordinates, shows the substantial rightfulness of the proposed structure. Such a model is shown in Figure 15.

Though the number of reflections observed in the polypropionaldehyde spectra is remarkably lower than the number of reflections observed in the case of poly-*n*-butyraldehyde and polyacetaldehyde, analogous reasonings lead to the model schematically drawn in Figure 16.

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Synopsis

The crystalline polymers having a polyacetalic chemical structure, as obtained by us by polymerization at low temperature of aldehydes in the presence of stereospecific catalysts formed by metalloorganic compounds, show an isotactic structure. The chain conformations of different isotactic polyaldehydes are discussed, and in particular the crystalline structures of polyacetaldehyde, of poly-*n*-butyraldehyde and of polypropionaldehyde are described. The polymeric chains of these polyaldehydes have a fourfold helix conformation with a repetition period of 4.8 A., and the packing of the macromolecules corresponds to that of the tetragonal $I4_1/a$ space group. Around each fourfold screw axis present in the unit cell, isomorphous anticlined macromolecules can statistically vicariate.

Résumé

Les polymères cristallins ayant une structure chimique polyacétalique, que nous avons obtenus par des polymérisations à basse température, d'aldéhydes, en présence de catalyseurs stéréospécifiques constitués de composés organométalliques et à basse température, sont isotactiques. On discute la conformation de la chaîne de quelques polyaldehydes isotactiques et on décrit en particulier les structures cristallines de la polyacétaldéhyde, de la poly-*n*-butyraldéhyde et de la polypropionaldehyde. La chaîne polymérique de ces polyaldéhydes prend la conformation d'une hélice quaternaire avec une période de répétition de 4.8 Å; l'empaquettement des macromolécules se rapporte à celui du groupe spatial tétragonal $I4_1/a$. Autour de chaque axe quaternaire de l'hélice présente dans la cellule élémentaire, les macromolécules isomorphes anticlines peuvent se vicarier statistiquement.

Zusammenfassung

Die kristallinen Polymeren mit Polyacetalstruktur, die die autoren bei der Tieftemperatur-Polymerisation zahlreicher Aldehyde in Gegenwart von stereospezifischen Katalysatoren, bestehend aus metallorganischen Verbindungen, erhalten haben, zeigen isotaktische Struktur. Die Konformation der Polymerenkette verschiedener isotaktischer Polyaldehyde wird diskutiert und die Kristallstrukturen, insbesondere des Polyacet-, des Poly-*n*-butyr- und des Polypropionaldehyds werden beschrieben. Die Polymerenketten dieser Polyaldehyde nehmen im Kristallgitter die Form quaternärer Wendeln mit einer Identitätsperiode von 4,8 Å an, und die Raumpackangen der Makromolekeln entsprechen denen der tetragonalen Raumgruppe $I4_1/a$. Um jede der in der Elementarzelle vorhandenen quaternären Wendelachsen können sich in statistischer Weise antikline isomorphe Makromolekeln vikariieren.

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