Crystal Structure of Polyaldehydes

P. Corradini[a]

[a] LABORATORIO DI CHIMICA GENERALE E INORGANICA CENTRO, NAZIONALE DI CHIMICA DELLE MACROMOLECOLE DEL C.N.R., NAPOLI, ITALY

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P. CORRADINI

LABORATORIO DI CHIMICA GENERALE E INORGANICA
CENTRO NAZIONALE DI CHIMICA DELLE MACROMOLECOLE
DEL C.N.R., SEZ.VII, NAPOLI, ITALY

Crystalline polymers of formaldehyde were recognized by Staudinger (1) in 1927 as having a polyacetalic structure.

Higher aldehydes were for the first time polymerized to linear polymers having a polyacetalic constitution by Letort and Richard in 1936 (2).

In 1959 the obtaining of crystalline polymers from aldehydes higher than propionaldehyde was announced by Novak and Whalley (3), who were followed in 1960 by Natta and co-workers (4) and Vogl (5), who succeeded in getting crystalline polymers from a large number of aldehydes, including acetaldehyde, propionaldehyde, and isobutyraldehyde.

The development of methods of stabilization against depolymerization of the polymers of aldehydes by the du Pont company and other companies and the subsequent beginning of the production of polyformaldehyde on a commercial scale under the trade name Delrin aroused the interest of some research laboratories in resuming the study of the crystal structure of polyformaldehyde, and the need of configurational assignment gave a vigorous impulse to the study of the x-ray structure of polymers of higher aldehydes.

As a result the crystal structure of a number of polymers having polyacetalic enchainment have been described during the last five years.

We shall refer now to the main results of these studies.

CONSTITUTION AND CONFIGURATION

In order that a polymer may be crystallizable, it must have in general a regular constitution and a regular configuration. Polyacetalic polymers have a regular constitution described by the enchainment of conventional base units of the type

$$(-O-C-)_n \begin{smallmatrix} R' \\ | \\ R'' \end{smallmatrix}$$
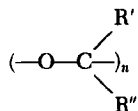
Let us consider the need for regularity in the configuration.

Following Dunitz and Prelog (6), we shall use the term "configuration" to mean the specification of the spatial arrangement of bonds in a molecule (of a given constitution) without regard to the multiplicity of spatial arrangements that may arise by rotation about single bonds.

When the two groups R' and R'' are different as, for instance, the hydrogen and methyl groups in polyacetaldehyde, the carbon atoms of the chain constitute stereoisomeric centers. An elegant way of seeing this fact, which we shall introduce because of its usefulness in the treatment of conformations, is as follows (Fig. 1).

If we call (a) and (b) the two bonds of the chain adjacent to the carbon atom to which the two different substituents are attached, it may be seen that, even in the case in which such a carbon atom is not optically active, the two bonds (a) and (b) are different from a configurational viewpoint.

We shall designate with the mark (+) a bond adjacent to the stereoisomeric center C_i along a chain $-O_i-C_iR'R''-O_{i+1}$ such that, as we look down the $O_{i-1}-C_i$ bond or the C_i-O_i bond, we see the substituents O_{i+1}, R', R'', or O_i, R', R'', succeed each other in a clockwise rotation. R' is conventionally defined as a bulkier substituent than R''.

We can define a (−) bond in an analogous manner.

It is clear that, if (a) is (+) in respect to the stereoisomeric center C_i, then (b) must be (−), and vice versa.

Two monomeric units are identical, from the configurational viewpoint, when corresponding bonds are characterized by the same set of (+) and (−) marks; they are configurationally enantio-
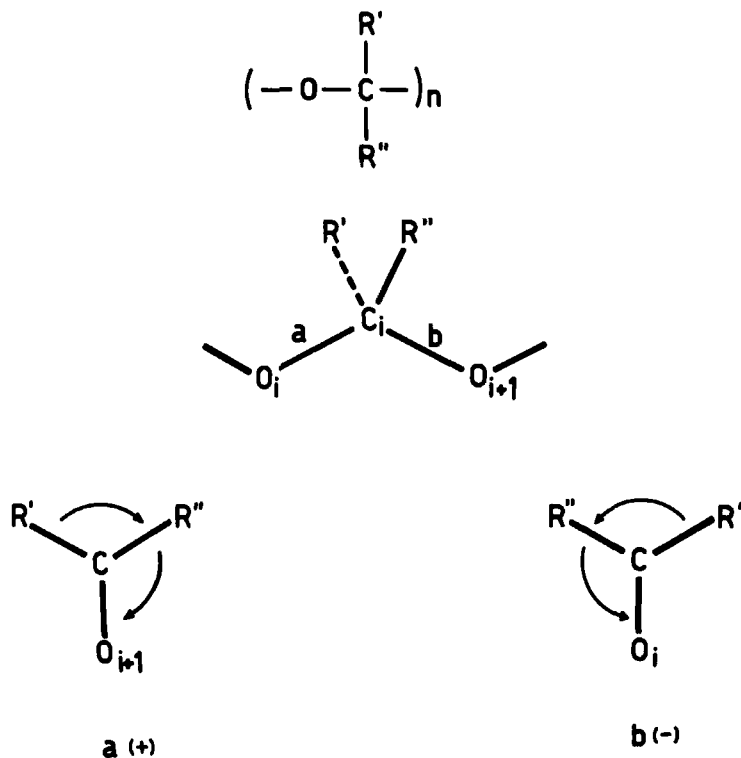
$$\left(-O-\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{C}}-\right)_n$$

FIG. 1. Definition of (+) or (−) bonds.

morphous if corresponding bonds are characterized by opposite signs.

It may be seen easily in the case of polyaldehydes (and also in the case of vinyl polymers) that there are only two possibilities of stereoregular enchainment of order 1. In the isotactic configuration the polymer is formed by monomeric units that have regular enchainment and are configurationally identical for long sequences of the chain; the syndiotactic polymer is formed by monomeric units with regular enchainment, alternately enantiomorphous from a configurational viewpoint.

The two possible regular configurations of order 1 may be symbolically indicated as in Fig. 2.

Whereas in the case of vinyl polymers both isotactic and syndiotactic polymers are known, in the case of aldehyde polymers only isotactic polymers having a crystalline structure have been de-

ISOTACTIC

$$- \overset{(+)}{O} - \overset{(-)}{CH} - \overset{(+)}{O} - \overset{(-)}{CH} - \overset{(+)}{O} - \overset{(-)}{CH} -$$
$$\quad\quad\ \ | \quad\quad\quad\ | \quad\quad\quad\ |$$
$$\quad\quad\ \ R \quad\quad\quad R \quad\quad\quad R$$

SYNDIOTACTIC

$$- \overset{(+)}{O} - \overset{(-)}{CH} - \overset{(-)}{O} - \overset{(+)}{CH} - \overset{(+)}{O} - \overset{(-)}{CH} -$$
$$\quad\quad\ \ | \quad\quad\quad\ | \quad\quad\quad\ |$$
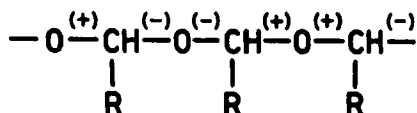$$\quad\quad\ \ R \quad\quad\quad R \quad\quad\quad R$$
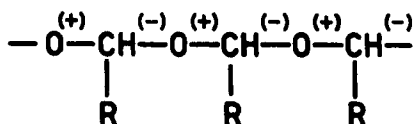
FIG. 2. Schematic representation of an isotactic and of a syndiotactic polyaldehyde (R + H).

scribed. In the amorphous polymers there is an irregular succession of (+)(−) and (−)(+) units along the chain.

GENERAL PRINCIPLES RELATING TO CONFORMATION

We accept the viewpoint that the conformations of a molecule are the different spatial arrangements of the atoms in a molecule of a given constitution and configuration and that they may arise through rotation about single bonds (6).

Thus, the assignment of the conformation of a macromolecule in the crystal state corresponds to the specification of the internal rotation angles that characterize its molecular structure (the molecular structure being established by the specification of the complete ensemble of internal coordinates, that is, bond lengths, bond angles, and torsion, or internal rotation, angles).

The conformation of a macromolecule satisfies two principles evidenced in successive steps by Huggins (7), Bunn (8), Pauling et al. (9), and Natta and Corradini (10), as follows.

1. *Equivalence principle.* The conformation of the chain in the crystal state is defined by a succession of equivalent structural units. The structural unit coincides in general with one monomeric

unit or half-monomeric unit; exceptionally it corresponds to two monomeric units (11). Successive structural units occupy geometrically (not necessarily crystallographically) equivalent positions with respect to a crystallographic axis of repetition.

2. *Principle of the minimal internal conformational energy.* The conformation of a chain in a crystal approaches that one of minimal internal conformational energy that should be taken by an isolated chain subjected to the restrictions imposed by the equivalence postulate.

Configuration and accessible conformations are closely related through the principles of equivalence and minimal internal conformational energy. Natta et al. (12) have shown that in accordance with the equivalence principle an isotactic polymer of the type

$$(O\text{---}CH\text{---})_n$$
$$|$$
$$R$$
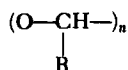
can only have helicoidal conformations in the crystal state that correspond to a succession of internal rotation angles along the chain of the type $\sigma_1, \sigma_2, \sigma_1, \sigma_2, \ldots$ (Fig. 3).
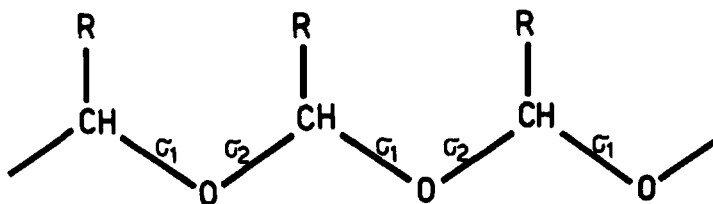
$$\left(-O-\underset{\underset{R}{|}}{C}H-\right)_n$$
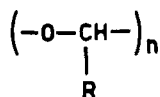

FIG. 3. Succession of internal rotation angles in an isotactic polyaldehyde.

The internal rotation angle σ_i represents the angle between the plane l_{i-1}, l_i, and the plane l_i, l_{i+1}, and defines the conformation of the chain around the bond l_i (Fig. 4).

The convention used for measuring internal rotation angles is as follows (Fig. 5) (13).
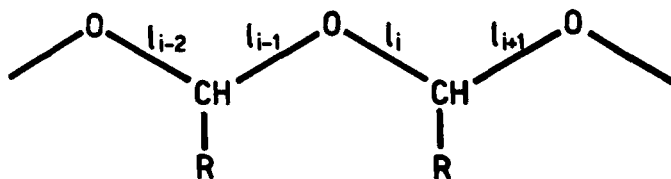
FIG. 4. Definition of internal rotation angle.

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 (that is, 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 on L_1, or (which is the same thing) if, looking parallel to L_2 from L_1, L_1 must be rotated clockwise by an angle smaller than 180° in order to superpose it on L_3.

As we shall see later, for polymers of aldehydes higher than formaldehyde the principle of the minimal internal conformational energy leads to the expectation that bonds defined as (+) from the configurational viewpoint have a conformation characterized by an internal rotation angle of between 0° and 180°, whereas bonds
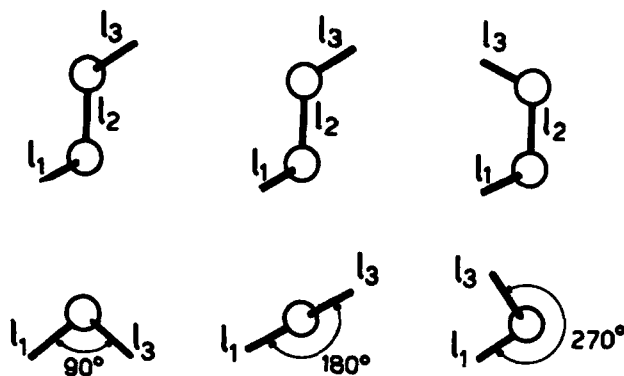

FIG. 5. Convention used for measuring the internal rotation angles (σ).
[From *J. Polymer Sci.*, 51, 512 (1963).]

defined as (−) from the configurational viewpoint have a conformation characterized by an internal rotation angle of between 0° and −180°.

In the case of polyformaldehyde all bonds along the chain are indistinguishable with respect to constitution and configuration.

It is not unexpected then, that the independent structural unit that characterizes the conformation of the polymers of formaldehyde in the crystal state corresponds—as allowed by the equivalence principle—to one half of a monomeric unit.

The conformation of the chain corresponds to a helix having twofold axes perpendicular to the chain axis and passing through the oxygen and carbon atoms. The succession of internal rotation angles is . . . , $\sigma_1, \sigma_1, \sigma_1, \sigma_1, \ldots$ (Fig. 6).
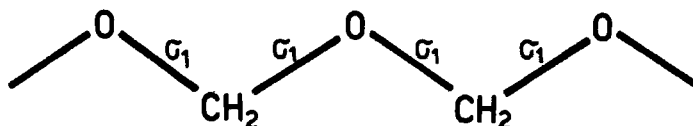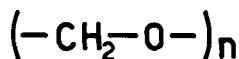
$$\left(-CH_2-O-\right)_n$$

FIG. 6. Succession of internal rotation angles in polioxymethylene.

Let us now see the implications of the principle of minimal internal conformational energy as far as the internal rotation angles that characterize the chain conformation of polyaldehydes are concerned. Suppose we assign the conformation of a macromolecule, after having given reasonable values to the bond lengths and valence angles (which are almost invariant from one molecule to another), by specifying the succession of internal rotation angles. In a first approximation the internal energy may be calculated as a function of the internal rotation angles σ_1, which characterize the conformation.

Assuming that the single contributions are additive, we have

$$V = \Sigma_i V(\sigma_i) + \Sigma_i V(\sigma_i, \sigma_{i+1}) + \cdots$$

where V is the quantity to be minimized.

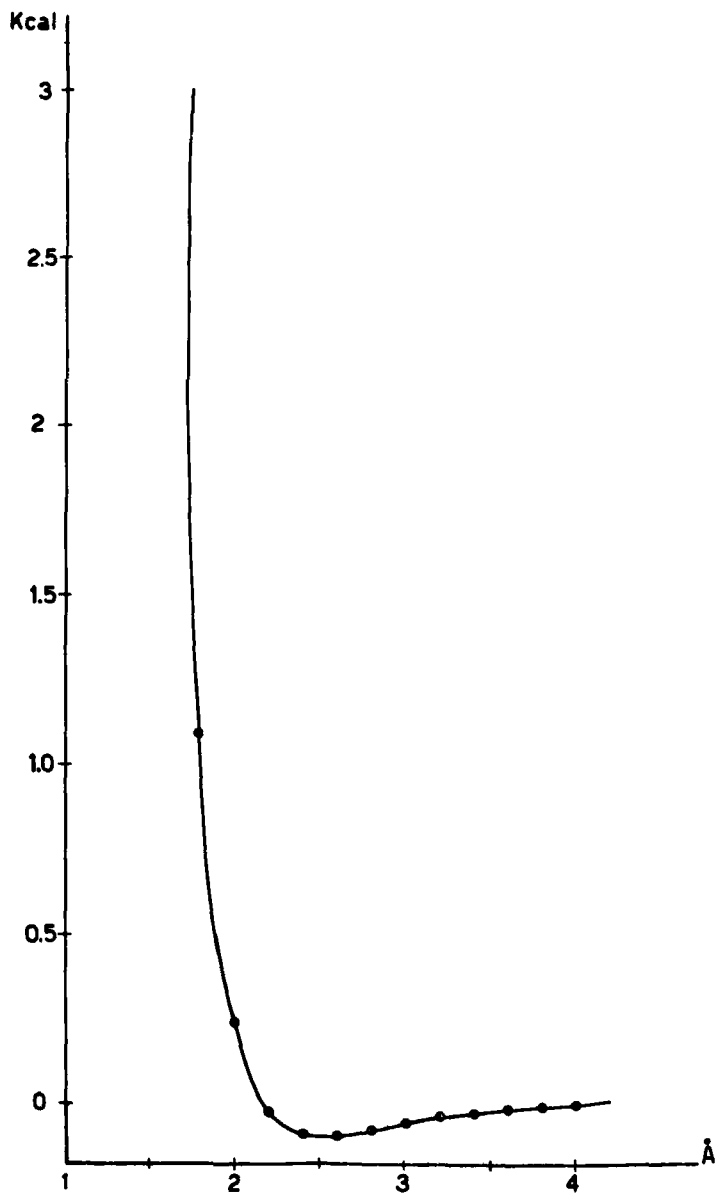FIG. 7. Graphical representation of the potential function for nonbonded hydrogen atoms. [From *J. Am. Chem. Soc.*, **83**, 4538 (1961).]
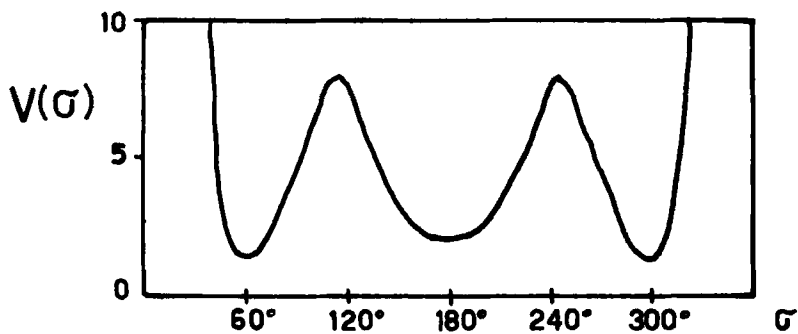
FIG. 8. Plot of the internal conformational energy of polyoxymethylene versus σ.
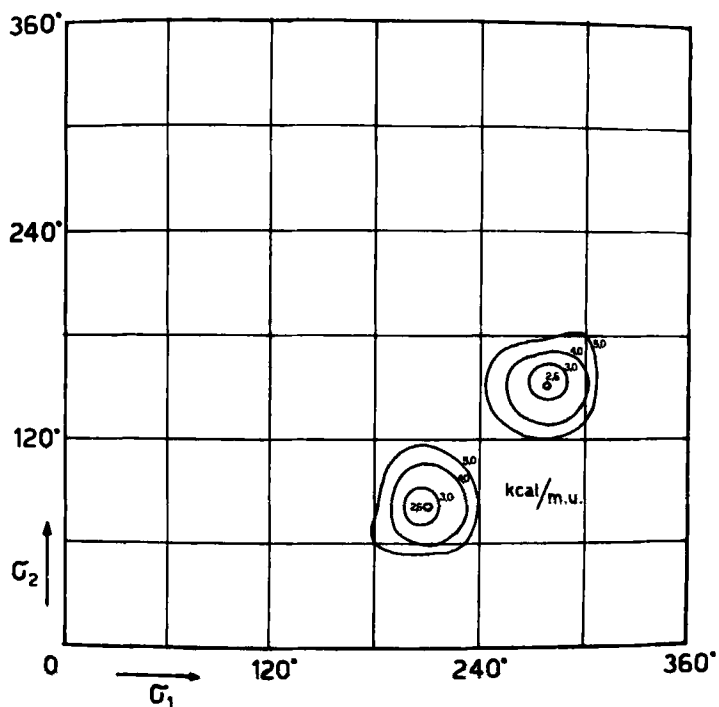
FIG. 9. Internal energy of an isotactic polyacetaldehyde chain for different helicoidal conformations. [(From *Polymer Sci., USSR English Transl.,* 4(1), 911 (1963).]

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To the interaction terms, depending upon a single internal rotation angle, can be given the same shape of the known barriers that hinder the rotation around single bonds in small molecules.

Experiments show that in the case of the C—O bond rotation is hindered (to a lesser extent, however, than in the case of a C—C single bond) and the magnitude of the potential barrier is about 1 kcal/mole.

It can be shown that the effect of this barrier is negligible in determining the chain conformation of polyaldehydes.

The energy due to van der Waals interaction contacts between atoms separated by four or more bonds [corresponding to terms such as $V(\sigma_i, \sigma_{i+1})$] can be approximately calculated by several equations, given by different writers as a function of the atom–atom separation distances. Figure 7 shows the aspect of the curve for hydrogen atoms according to Hendrickson (14).

The first calculation of this kind was performed by De Santis et al. (15) in the case of polyformaldehyde, assuming a succession of identical internal rotation angles (Fig. 8).

Two equivalent, sharp energy minima are observed in the σ–E graph, corresponding fairly well to the experimentally observed chain conformations.
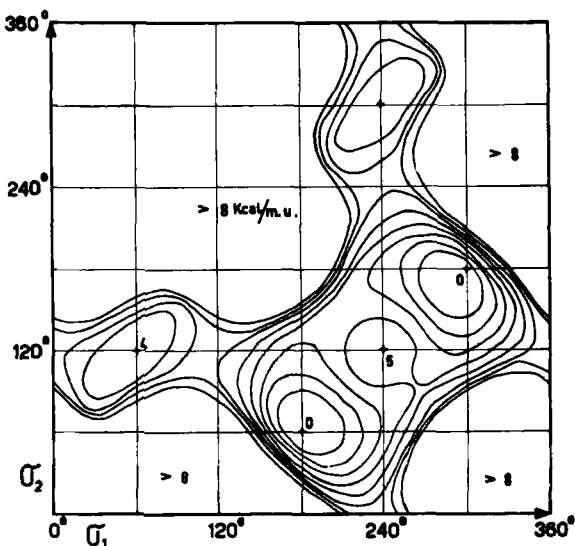

FIG. 10. Internal energy of an isotactic polypropylene chain for different helicoidal conformations. [From J. Polymer Sci., 58, 1196 (1962).]

Since then the calculation of the internal energy has been made for polyacetaldehyde by Borisova and Birshtein (16) (Fig. 9).

The σ_1—σ_2-E plot shows two minima corresponding to two equivalent enantiomorphous helices with internal rotation angles very close to the experimentally observed ones. The bottom of the trough is less flat than that calculated by Natta et al. (12) for polypropylene (Fig. 10), and the minima are displaced, in accordance with the experimental observations.

These calculations show clearly the heuristic power of the equivalence and minimal-energy principles.

Polyoxymethylene

Let us now discuss in a somewhat more detailed way the crystal structure of polyoxymethylene.

The most recent studies have been performed by Carazzolo (17), who has also studied the corresponding polymers, in which, in the place of the oxygen atom, there is sulfur, selenium, or tellurium (18).

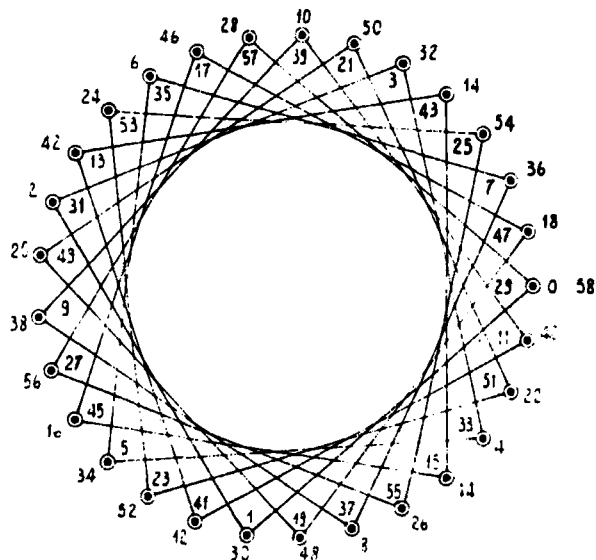Earlier a number of studies were performed for the purpose of

FIG. 11. Projection of the 29/16 helix of hexagonal polyoxymethylene on the plane normal to the chain axis. [From *J. Polymer Sci.*, **A1**, 1581 (1963).]

defining the structure of polyoxymethylene, the most reasonable model being that proposed by Huggins in 1945 (*19*). This corresponds to a helix having nine monomeric units in five turns instead of nine monomeric units in four turns, as early supposed by Sauter (*20*), in agreement with the stronger intensity of the fifth layer than of the fourth in the fiber diffraction pattern.

The repetition period per monomeric unit is 1.93 A. Carazzolo has shown that a more accurate interpretation of the x-ray diagram can be obtained by supposing that repetition along the chain axis occurs every twenty-nine monomeric units in sixteen turns (*17*) (Fig. 11).

The model of the chain that thus arises is very close to the 9/5 one (Fig. 12). It can be said on general grounds that what is possible
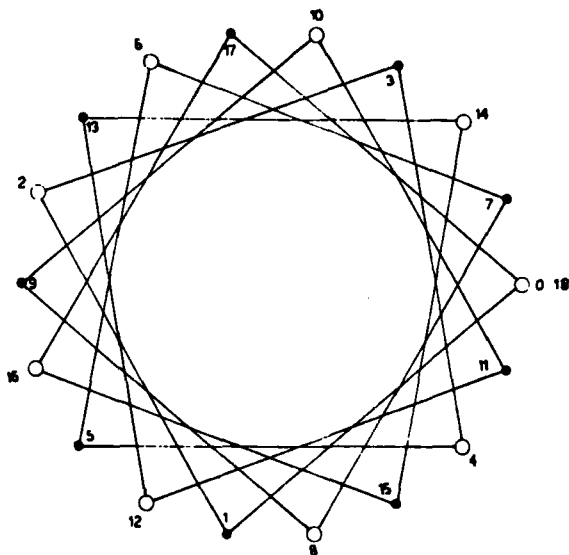
FIG. 12. Projection of the 9/5 helix of hexagonal polyoxymethylene normal to the chain axis. [From *J. Polymer Sci.*, A1, 1577 (1963).]

to assess with certainty for a helicoidal polymer is the period per monomeric unit (in this case 1.93 ± 0.01 A) and the number of monomeric units per turn (1.81 ± 0.01 A). Thus, we cannot say that the 9/5 helix is incorrect and the 29/16 correct. The ratio of the numbers 29 to 16, equal to 1.812, more closely approximates the number of monomeric units per turn, 1.81, which is obtained from the x-ray experiments, whereas the ratio 9/5 is equal to 1.80, but

the main features of the chain conformation do not change practi-
cally between the 9/5 and the 29/16 helix, in so far as repetition
period per monomer unit and internal rotation angles along the
chain are connected by a mathematical relationship involving only
the ratio of monomeric units per turn.

The internal rotation angle that characterizes the chain con-
formation of polyoxymethylene is of nearly 76°. Of course, the
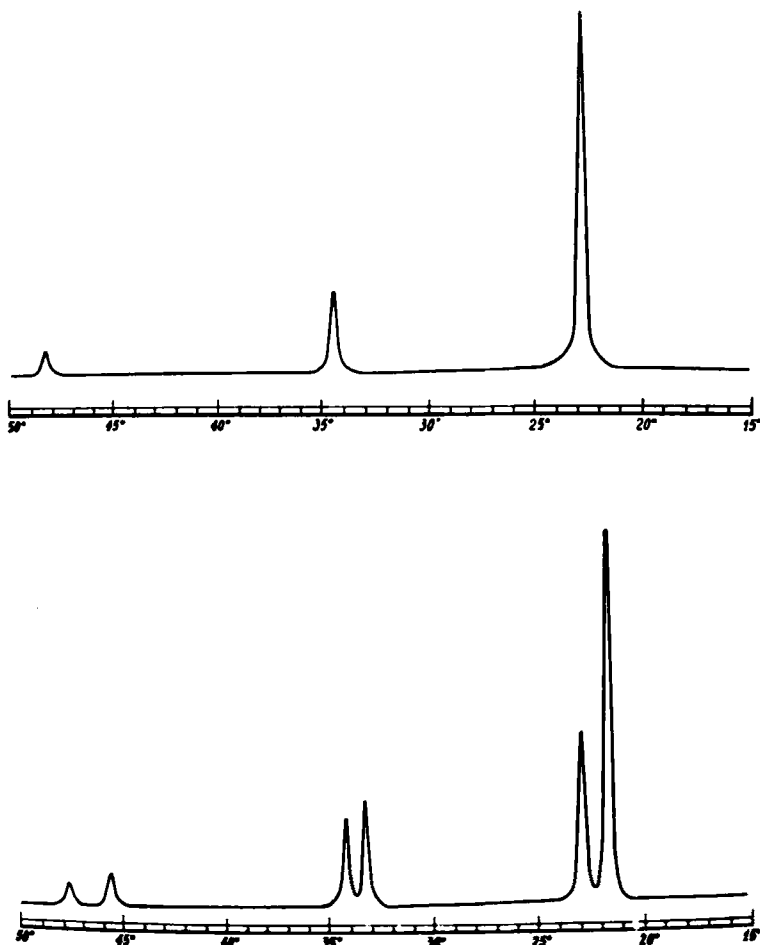enantiomorphous helix has an internal rotation angle of −76°. We

FIG. 13. Geiger spectrum (Cu K_α) of hexagonal (up) and orthorhombic
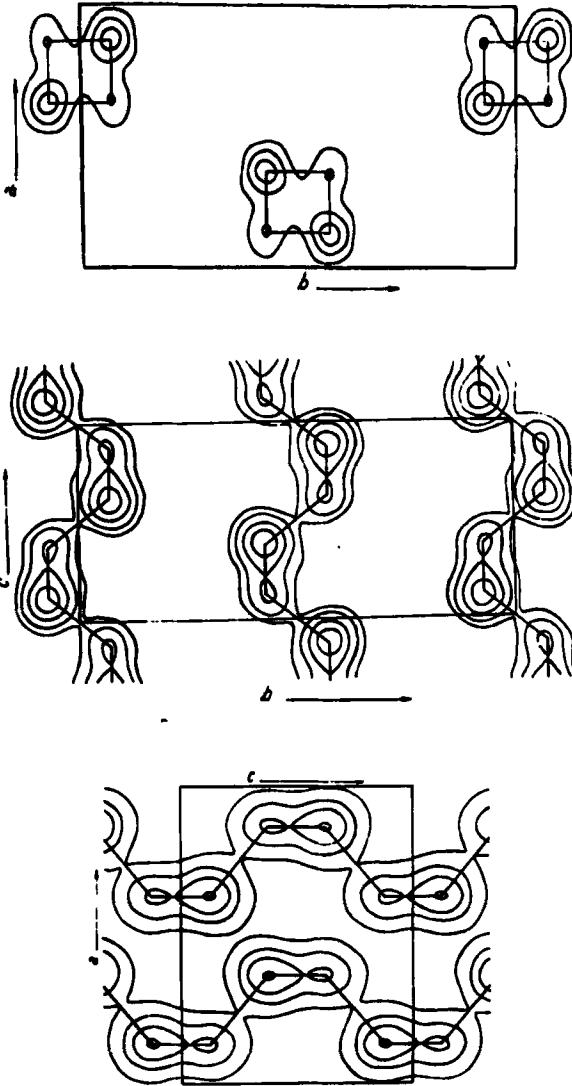(down) polyoxymethylene. [From *J. Polymer Sci.*, **A1**, 967 (1963).]

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FIG. 14. Two-dimensional Fourier projections (on *ab*, *bc*, and *ac* planes, respectively) of orthorhombic polyoxymethylene. [From *J. Polymer Sci.*, **A1**, 975 (1963).]

see here an indication of the preference of C—O chain bonds for assuming *gauche* conformations, a preference observed also in the structure of polyethylene oxide.

Polyoxymethylene can be obtained in a second crystalline modification, whose x-ray spectrum shows many similarities to the spectrum of the more common form (*21*) (Fig. 13). The more common form has a hexagonal unit cell, whereas the second modification is orthorhombic. The chains have similar conformations and modes of packing in the two forms. The difference is evidenced by the splitting of lines, which occurs in passing from the hexagonal to the orthorhombic unit cell (Fig. 14).
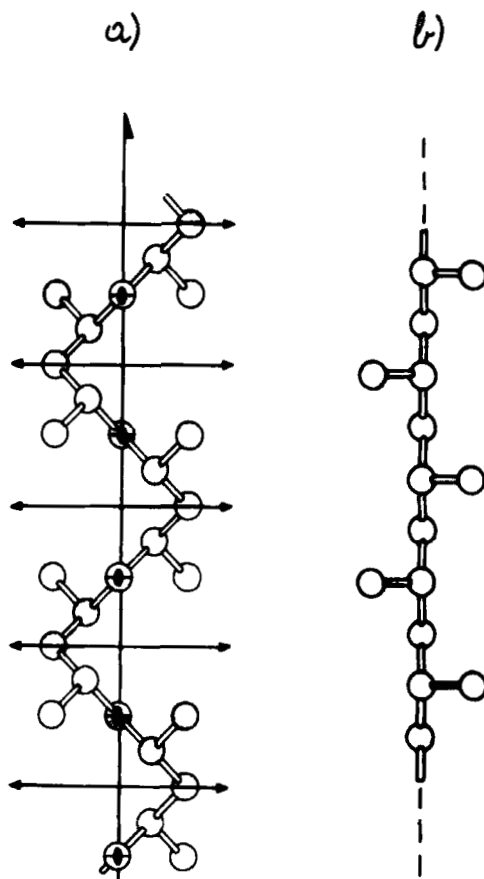

FIG. 15. Chain models of syndiotactic polypropylene: (a) with s(M/N)2 symmetry, (b) with *tc* symmetry.

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The chain is helicoidal and has two monomer units per turn instead of 1.80. The internal rotation angles that characterize the chain conformation are all equal, giving the chain a full symmetry 2_122 (not maintained in the lattice) like that of syndiotactic polypropylene.

Thus, polyoxymethylene shows us a common feature of many crystalline polymers: polymorphism.

In the field of macromolecules we can distinguish two broad categories of possible polymorphism: polymorphism due to a different chain conformation (conformational polymorphism) and polymorphism associated with identical chain conformations but with a different mode of packing (packing polymorphism).

Different chain conformations can be found in the same conformational potential-energy well (as in the case of polyoxymethylene) or in nonequivalent conformational potential-energy wells (that is, tc and $s(2/1)2$ syndiotactic polypropylene (Fig. 15) (22,23).

If we come back to the σ–E diagrams already shown (Fig. 8), we may easily see that polyoxymethylene shows polymorphism of chains having conformations within the same potential-energy well. The energy difference between the two conformations is well below 1 kcal per monomeric unit—that is, in a range in which lateral packing effects may still play a role in stabilizing one form over the other.

Higher Polyaldehydes

The crystal structure of polyaldehydes having groups lateral to the main chain was studied by Natta et al. (13). We shall refer briefly to the structure of poylacetaldehyde, showing that it conforms to the two above-mentioned principles of equivalence and minimal internal conformational energy and to, moreover (as far as the complete mode of packing is concerned), the principle of closest packing as applied, for instance, by Kitaigorodsky (24) in the study of low-molecular-weight compounds. Incidentally, the resolution of the structure of polyacetaldehyde represents a nice example of the application of these principles to the solution of the conformational and configurational problem in a polymer.

In polyacetaldehyde the identity period along the chain axis c, measured from a fiber spectrum, is 4.79 A. A strong reflection having indexes 004 with a Bragg distance d equal to 1.197 A

indicates the presence of four monomeric units within the identity period.

From the same spectrum it was possible to index all the reflections on the basis of a tetragonal unit cell having $a = 14.65 \pm 0.05$ A. The extinctions observed were characteristic of the $I\ 4_1/a$ space group.

By a knowledge of the identity period and by supposing the C—Ô—C and O—Ĉ—O chain bond angles to be tetrahedral and assuming for the C—O distances the value of 1.43 A, which is the average of the best values found for similar low-molecular-weight compounds, it is possible to determine the internal rotation angles σ_1 and σ_2 referring to the C—O bonds which characterize the conformation of the helix-shaped chain.

The internal rotation angles σ_1 and σ_2 are $\sigma_1 = 277.5°$ and $\sigma_2 = 135°$ for the right-handed helix or $\sigma_1 = 82.5°$ and $\sigma_2 = 225°$ for the left-handed helix.

In Fig. 16 is shown the resulting chain conformation, which is approximately in the minimum of the graph of Fig. 9.
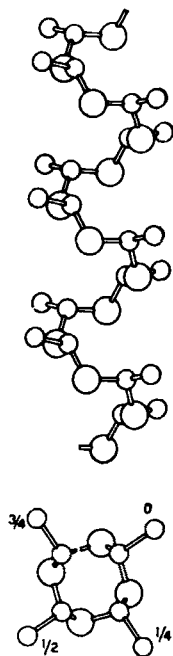

FIG. 16. Side and end views of the isotactic polyacetaldehyde macromolecule in the crystalline state. [From *J. Polymer Sci.*, 51, 513 (1961).]
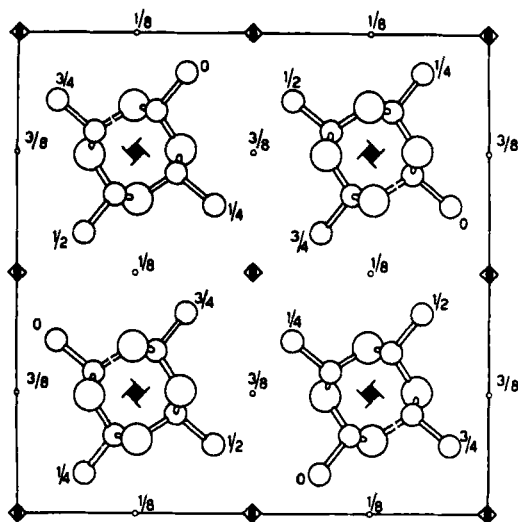
FIG. 17. Projection of the structure of isotactic polyacetaldehyde on (001). [From *J. Polymer Sci.*, **51**, 519 (1961).]
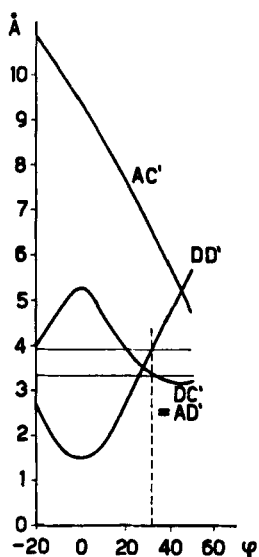

FIG. 18. Projection on the *ab* plane of the contact distances of methyl groups of adjacent polyacetaldehyde molecules versus the angle of rotation of the chains around the chain axis. [From *J. Polymer Sci.*, **51**, 515 (1961).]

In the unit cell of polyacetaldehyde are contained four chain portions, two of them having right-handed conformations and the other two left-handed ones, according to the $I \, 4_1/a$ space group (as shown in Fig. 17), and centered on the two 4_1 and on the two 4_3 screw axes.

To establish the orientation of the helix-shaped macromolecules in the unit cell and their positions along the c axis it was first studied whether with the limits imposed by the size and symmetry of the lattice there was a single solution of the problem that could furnish van der Waals' contacts, among atoms of different molecules not lower than those usually found in low-molecular-weight compounds.

Let us examine the contact distances among methyl groups of contiguous macromolecules for all the possible orientations of a macromolecule with respect to an axis. In Fig. 18 are shown the results of such analysis. Only the projections on the ab plane of the contact distances of methyl groups of adjacent polyacetaldehyde molecules are reported; φ is the angle formed by one of the equatorial axes and by the line joining the center of the macromolecule with a methyl group.

If we assume that the distance between two methyl groups cannot be lower than 4.1 A, the distance in projection on an ab plane cannot be lower than

$$[4.1^2 - (c/2)^2]^{1/2} = 3.33 \text{ A}$$

This can happen only in the favorable case in which the two methyl groups are as far apart as possible along c axis.

This strictly limits the possible solutions of the problem.

Furthermore, recalling that, if one of the two neighboring methyl groups is displaced along the c axis by $c/2$, the other is necessarily displaced by $c/4$, it is possible to deduce that the macromolecule is forced to assume the orientation with $\varphi = 33°$.

In the same way the structures of polypropionaldehyde and poly-n-butyraldehyde have been resolved (Figs. 19 and 20).

All these structures are characterized by a close packing of fourfold helices; each right-handed helix is surrounded by four left-handed helices, and vice versa. These polymers provide a nice example of a structural resolution performed a priori with the aid of theoretical considerations on the mode of packing of macromolecules in a given unit cell.
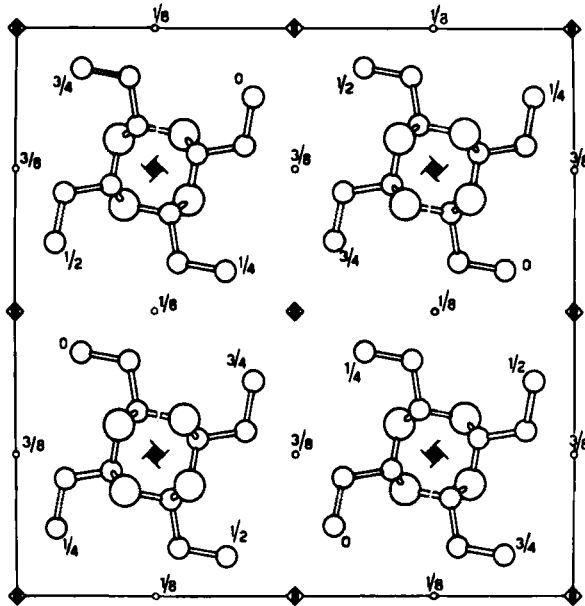
FIG. 19. Projection on the *ab* plane of the probable structure of isotactic polypropionaldehyde. [From *J. Polymer Sci.*, **51**, 521 (1961).]
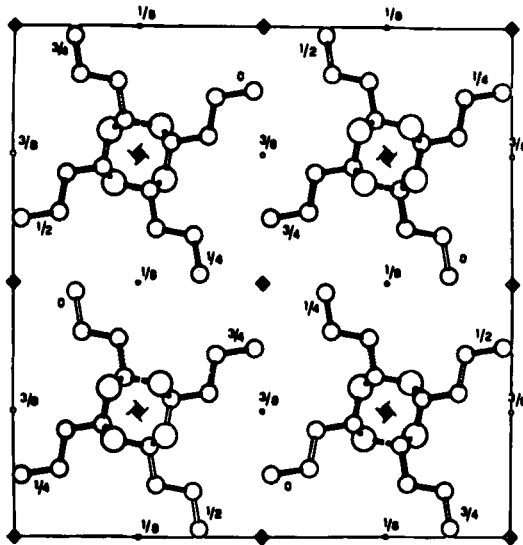
FIG. 20. Projection on the *ab* plane of the structure of isotactic poly-*n*-butyraldehyde. [From *J. Polymer Sci.*, **51**, 521 (1961).]

ISOMORPHISM OF POLYALDEHYDES

It is possible both in the case of polyaldehydes and in the case of many vinylic and dienic polymers to modify the crystal lattice of the polymer by the presence in the chain of monomeric units of different types without destroying the crystallinity, but causing continuous and regular variations of some of the crystal-lattice parameters and, consequently, of some physical properties (such as solubility and melting point).

From this point of view a very important condition is that the substitution be isosteric in order that the shape of the chain may be left approximately unchanged. The maintainance of the macromolecular conformation requires, of course, that the configuration also be preserved.

In other words, for a polymer to be crystallizable, it is more important to have a tactic order, such as an isotactic one, along the chain, than to have possible differences in the bulkiness of side groups.

It is possible to foresee two general types of isomorphous substi-
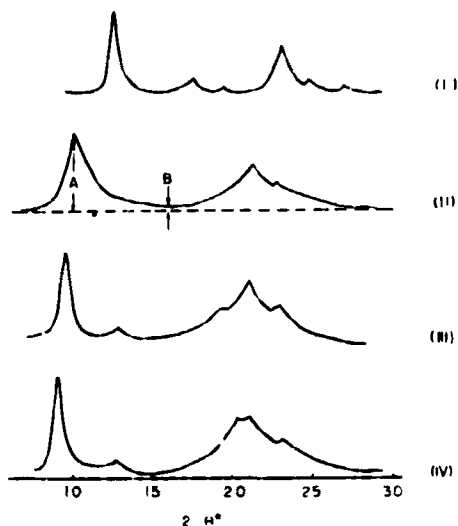

FIG. 21. X-ray powder spectra (Cu K_α) of polyacetaldehyde (I) of acetaldehyde–n-butyraldehyde copolymers containing 69.0 mole-% (II) and 36.0 mole-% (III) and of poly-n-butyraldehyde. [From *J. Polymer Sci.*, **B2**(2), 181 (1964).]

tution in the crystal lattice of a linear macromolecule: isomorphism of different chains, isomorphism of different monomeric units.

The latter type of isomorphism introduces a new concept in physical chemistry, one that is entirely peculiar to macromolecules. It defines the possibility of introducing in a statistical way monomeric units of different chemical structure along the chain of crystallizable polymer without preventing the crystallinity of the resulting copolymer but simply varying some of its lattice constants.

By polymerizing acetaldehyde and n-butyraldehyde with Et_2AlNPh_2 at $-78°C$ Tanaka and co-workers (25) obtained copolymers that are crystalline over the entire composition range (Fig. 21). These copolymers (at least for some limited compositions, acetaldehyde to butyraldehyde, 8/2 to 6/4) are completely soluble in many solvents but cannot be separated into fractions having different natures with the usual organic solvents.

The unit cells of these copolymers have the same tetragonal $I \, 4_1/a$ space group with the same identity period ($c = 4.8$ A) as each homopolymer, while only the lattice constant $a = b$ changes continuously with the copolymer composition.

From these results it can be seen that isomorphism of monomeric units occurs in the case of the copolymers.

The same isomorphism phenomenon has been observed in the binary copolymerization of propionaldehyde–n-butyraldehyde and isobutyraldehyde (25).

In the case of copolymers of isobutyraldehyde and other aldehydes the continuous variations of both lattice constants a and c were observed.

This result is caused by the fact that crystalline polyisobutyraldehyde also has the same tetragonal unit cell as the other three polyaldehydes, but the lattice constants a and c are different.

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