General Considerations on the Structure of Crystalline Polyhydrocarbons (*).

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Owing to the discovery of stereospecific polymerization processes effected in our Institute, we were able to determine, in the last few years, the crystal structure of a great number of new polymers. In this work we will discuss the general principles, leading to the determination of the shape and mode of packing of macromolecules in the crystals [1].

1. – Stereoisomerism in head-to-tail aliphatic linear polymers.

Before explaining the principles and discussing, in accordance with them, the crystal structure of some macromolecular compounds, we would like to emphasize the importance of stereoisomeric phenomena in order to determine the ability of the polymers to crystallize.

There are different types of stereoisomerism in organic chemistry, generally distinguished into two classes:

  1) geometrical stereoisomerism, whenever the same chemical formula may correspond to intrinsecally different geometrical configurations (*e.g.*, in compounds containing a double bond, or in cyclic saturated compounds);

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2) optical stereoisomerism, whenever a molecule cannot assume, by not prohibited rotations around single bonds, the enantiomorphous configuration (this is in most cases due to the presence of carbon atoms linked to four different substituents [2]).

These two cases are both important in macromolecular chemistry.

Since the definition of crystal implies a three-dimensional order, in order that a polymer be crystallizable, a regularity in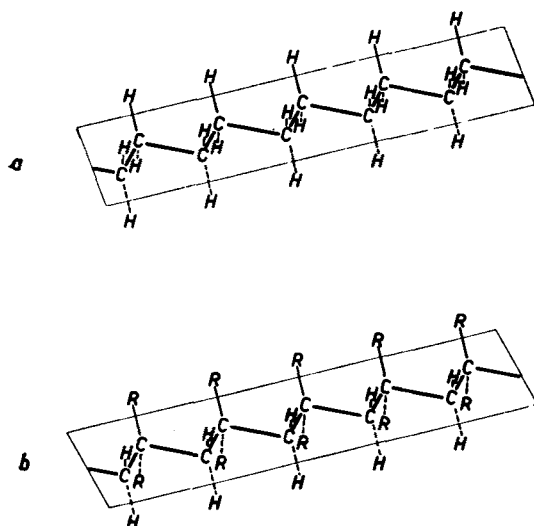 the succession of configurations of its monomeric units is necessarily required. A crystalline polymer can be obtained, in fact, only when all monomeric units belonging to a long chain segment show the same configuration, or when enantiomorphous configurations follow each other orderly. On the contrary, amorphous polymers are obtained when different stereoisomeric configurations of the same monomeric unit, e.g. cis and trans, or those « left » and «right» handed, follow each other disorderly. The stereospecific polymerization processes, first carried out in our Institute, permitted us to obtain head-to-tail linear polymers of alpha-olefins and di-olefins arranged according to regular successions of monomeric units, having equivalent steric configurations. These polymers are, generally, characterized by a high degree of crystallinity.

Fig. 1. – A head-to-tail succession of (a) ethylenic (—CH$_2$—CH$_2$—) or (b) vinylidenic (—CH$_2$—CR$_2$—) monomeric units may be realized in one way only (main chain arbitrarily stretched on a plane).

Before their discovery only a relatively limited number of crystalline synthetic hydrocarbon polymers were known.

Those obtained by poly-addition generally derived from monomers, such as ethylene or some vinylidenic monomers containing at least two symmetry planes in their molecules (isobutylene, vinylidenechloride).

When these symmetrical molecules undergo a polymerization process, only one type of head-to-tail enchainment may occur, as shown in Fig. 1. On the contrary, alpha-olefins and di-olefins may give rise to various types of stereo-isomeric modes of enchainment; actually all synthetic polymers of alpha-olefins and di-olefins, prepared before the discovery of stereospecific catalysis,

were amorphous. Fig. 2 shows molecules of stereoisomeric vinyl polymers with the chain arbitrarily settled on a plane; the isotactic [3] polymers in which successive head-to-tail monomeric units show the same steric configuration; syndiotactic polymers [4], in which successive head-to-tail monomeric units show alternatively opposite steric configurations; atactic polymers in which successive head-to-tail monomeric units, having different configurations, are randomly distributed along the chain.

In the field of di-olefin polymers other stereoisomeric phenomena of geometrical type appear: polyisoprene regular stereoisomers with 1,4 enchainment occur in nature; natural rubber has nearly a complete cis structure($\sim 97\%$), guttapercha has a trans structure. Other new stereoisomers of diolefins with 1,2 enchainment, which do not exist in nature, have been synthesized in our Laboratory in the last five years.

The configurations of the four possible regular stereoisomers of polybutadiene, whose structure was studied by us, are shown in Fig. 3 [5]. Stereoisomeric phenomena are practically interesting in the field of polymers, since the most interesting physical and technological properties of isotactic polymers of alpha-

Fig. 2. – Various types of possible head-to-tail successions of vinylic (—CH$_2$CHR—) monomeric units: isotactic, syndiotactic, atactic (random); (main chain arbitrarily stretched on a plane).

olefins and of some new stereoisomers of polydiolefins, in the field of plastic materials and textile fibers, are due to the ability of crystallizing of these polymers [6]. Atactic polymers of alpha-olefins cannot crystallize and possess completely different properties. Their practical interest is confined to products with very high molecular weight, which give a particular type of elastomers.

The most characteristic features connected with crystallinity, such as the conformation of the chain in the crystalline state, the relative positions of the chains in the crystal, the degree of freedom of rotation of lateral groups, the rate of crystallization, the size, the distribution and the orientation of the crystals and so on, determine the most interesting technical characteristics of these polymers, i.e. hardness, mechanical properties such as modulus, ultimate tensile strength and elasticity, melting temperature range, molding properties and the possibility of giving high tenacity fibers.
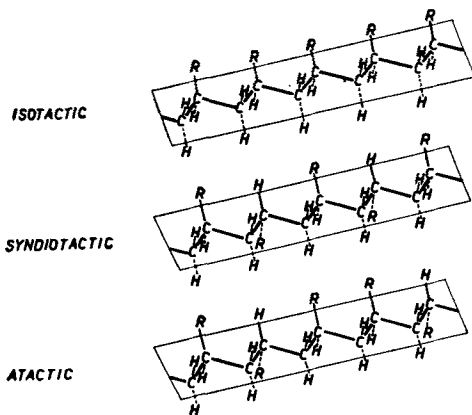
POLYBUTADIENE 1-4 cis

POLYBUTADIENE 1-4 trans

POLYBUTADIENE 1-2 isotactic

POLYBUTADIENE 1-2 syndiotactic
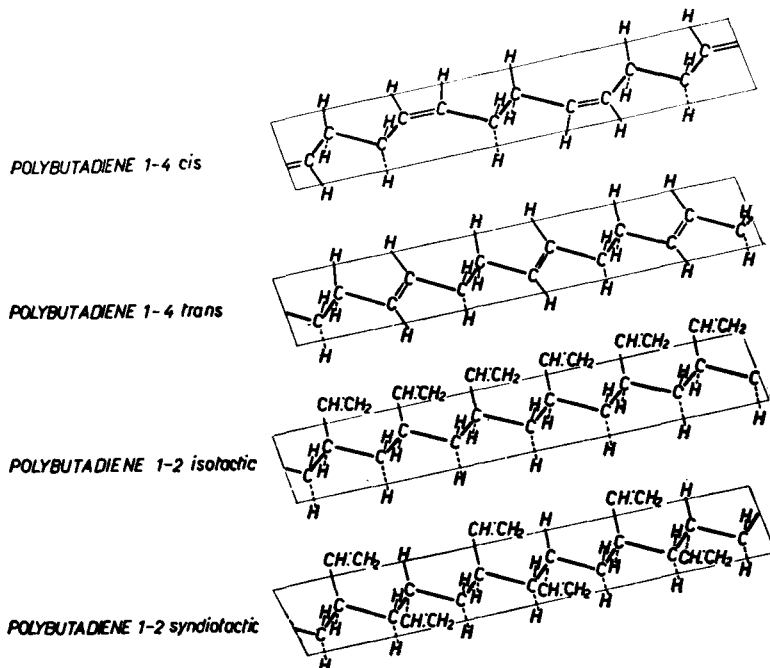
Fig. 3. – Regular successions of stereoisomeric butadiene monomeric units: cis 1-4, trans 1-4, isotactic 1-2, syndiotactic 1-2 (main chain arbitrarily stretched on a plane).

In this paper we shall examine the conditions to which the polymer is subjected to be crystallizable and the shape and mode of packing it will realize in the crystalline state.

2. – Shape and mode of packing of macromolecular chains in the crystals.

Regularity in the succession of monomeric units is the first requisite, as we have already seen, for a linear polymer to be crystallizable. As the definition of crystal implies three-dimensional order, a possible lack of order along the chain prevents in general any possibility of crystallization. It is actually observed that:

1) In linear crystalline polymers the axis of the macromolecule runs parallel to a crystallographic axis of the crystal. Moreover, in all known structures all the monomeric units have been found to occupy geometrically equivalent positions with regard to this axis (*) (*equivalence postulate*).

(*) This is a sufficient, but not a necessary condition, to ensure order along the chain. Because this condition appears to be most frequently verified, it may be taken as a work postulate.

2) The conformation of the chain in a crystal approaches the one of minimum potential energy, that should be assumed by an *isolated* chain oriented along an axis, with the restrictions contained in the equivalence postulate. This means that lateral packing contacts (between neighbouring chains) generally play a secondary role in determining the conformation of the chain in comparison with the contacts internal in the chain. Thus, lateral packing contacts cause only slight deviations of the form of the chain from the one foreseeable only on the basis of the above considerations.

3) The chains approach themselves parallel each other at intermolecular distances similar to those realized in low molecular weight compounds, to fill possibly any hole between themselves. With this restriction, as many as possible elements of symmetry of the isolated chain are maintained in the lattice. That is, equivalent atoms of different monomeric units along an axis tend to assume equivalent positions in regard to the atoms of neighbouring chains.

Let us discuss orderly the bearing of these statements in the crystal structure of polymers.

2·1. *Equivalence postulate.* – According to the equivalence postulate, all the monomeric units which form a macromolecular chain occupy equivalent positions along an axis in the crystalline state.

In turn, a condition to be fulfilled by a crystallizable polymer, is that its monomeric units have configurations, as required in order that they may occupy equivalent positions along an axis. Let us call *isoclined* two monomeric units, whose equivalent atoms have the same z co-ordinates after a suitable translation of the origin along the chain axis z; *anticlined*, two monomeric units whose equivalent atoms have the same z co-ordinates after a suitable translation of the origin accompanied by a reversal of direction of the z-axis.

Repetition of equivalent monomeric units may be obtained along an axis in the following ways:

1) Repetition of isoclined isomorphous equivalent units: through the operation of a translation c/p along z, accompanied by a rotation $2\pi(P/p)$ in a plane perpendicular to z. A helix is thus generated which contains p monomeric units and P pitches within the period c (helix type succession).

2) Repetition of isoclined alternately enantiomorphous equivalent units: through the operation of a translation $c/2$, accompanied by a reflection in a plane containing the axis of the chain (glide-plane type succession).

3) Repetition of isomorphous alternately anticlined equivalent units: along a helix associated with twofold axes perpendicular to z.

4) Repetition of enantiomorphous anticlined equivalent units: through a translation along z associated with a symmetry plane perpendicular to z or a symmetry centre.

All head-to-tail crystallizable polymers, in which the two possible chain directions are intrinsically non-equivalent (for instance, a polyamide $(-(CH_2)_m-NH-CO-)_n$ or 1-4 polyisoprene $(-CH_2-CH=CH-\overset{\overset{\displaystyle CH_3}{|}}{CH}-)_n)$ must be built up in the crystal of *isoclined* equivalent units. Hence, only the helix and the glide-plane type structures are possible. In particular, a polyamide containing asymmetric carbon atoms, such as a crystalline protein, must necessarily have a helix type chain structure.

All the four types of regular repetitions, described by us, are possible for vinyl head-to-tail polymers. In fact, for these polymers, the two possible chain directions can be considered intrinsically equivalent; however, we must distinguish two intrinsically different (that is stereoisomeric) types of regular successions. Isotactic polymers are the vinyl polymers able « per se » to assume a helix type structure (or, eventually, the structure type 4). Syndiotactic polymers are the vinyl polymers able « per se » to assume a glide-plane type structure (or, eventually, the structure type 3).

Other polymers, as we shall see later, may be expected, from the point of view of the equivalence postulate only, to crystallize in both the helix or the glide-plane type structure, without any intrinsic difference
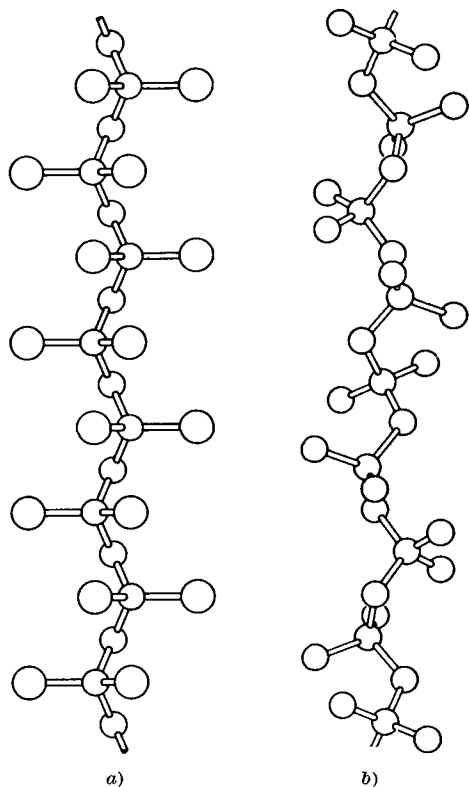

a)   b)

Fig. 4. – Model of the assumed structure of (left) polyvinylidene chloride (glide-plane type) as compared with the one found by A. LIQUORI [42] for (right) polyisobutylene (helix type).

of stereoisomeric type (Fig. 4) (polyisobutylene, helix type; polyvinylidene chloride, probably glide-plane type). This happens when the *monomeric unit* (for instance $-CH_2-CR_2-$) by not prohibited rotations around single bonds, may assume a conformation superposable with its mirror image.

The general rules, above outlined, require, for their practical application to the study of new structures, a knowledge of the conformation that the chain is likely to assume in the crystalline state. We should expect that the conformation of the portion of chain, which takes part in a crystalline zone, is the one which nearly corresponds to a minimum of potential energy for the molecule in free conditions (*e.g.* in the melting or in ideal solution) under the restrictions imposed by the equivalence postulate.
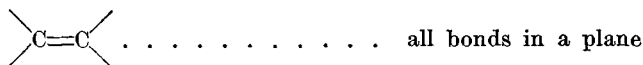
The actual conformation of the chain has in turn a great influence in determining the possible modes of packing of the chains in the crystal, and some physical properties of the polymer, such as the temperature and entropy of fusion.

2'2. *Shape of the macromolecule in the crystal state.* – Stable conformations of a chain should in principle satisfy, as it happens for low molecular weight compounds, the following conditions:

1) Bond length conditions [7].

2) Bond angle conditions [8].

3) Planarity of certain groups of atoms [9].

4) Staggered carbon-carbon bonds.

5) As comfortable as possible Van der Waals distances between non-bonded atoms within the chain.

TABLE I. – *Significant atomic distances and bond angles observed in polymers examined in this and in other papers of this series.*

C—C	1.54 Å
C=C	1.32 Å
C—C (benzene ring).	1.40 Å
C—C—C	110° ÷ 116°
C=C—C	120° ÷ 125°
C—C—C (benzene ring)	120°

$\diagup$C=C$\diagdown$ . . . .   all bonds in a plane

$\diagup$C—N$\diagdown$ (with O double bond) . . . .   all bonds in a plane

(benzene ring)— . . . .   all bonds in a plane

A compromise between these 5 conditions is generally achieved in actual structures, as we shall see later in more detail.

There is no need to illustrate the first three points: a discussion is only needed for the two last ones.

1) Principle of staggered bonds. The fourth point was emphasized first by PITZER and coll. [10] with regard to low molecular weight hydrocarbons, such as butane. He showed, on the basis of thermodynamical calculations, that the trans conformation of the butane chain was more stable than the gauche conformation, both conformations however lying in a minimum of potential energy. Cis conformations of the butane chain are, on the contrary, thermodynamically unstable. C. W. BUNN was the first who applied [11] these ideas to the conformation of polymeric chains, and we could confirm them in a great number of cases. Because of its importance, the fourth point needs a detailed discussion.
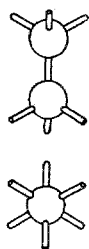

Fig. 5. – Positions of minimum energy of the valence bonds of two tetrahedral singly linked carbon atoms (side and end views).

If one considers two carbon atoms C_1 and C_2, joined by a single bond, the positions of minimum energy of the other bonds coming out from C_1 and C_2 are those outlined in Fig. 5. This is probably due to repulsions between localized bonding electron pairs [12]. The application of this principle alone is not sufficient to find out which conformation will be assumed by a linear saturated chain. The number of possible stable conformations is however limited by the equivalence postulate and by condition 5 of this paragraph, which implies that carbon-carbon bonds tend to be more far off than C—H bonds, favouring the trans conformation. Thus we arrive, for an unbranched crystallizable paraffin, at a planar zig-zag structure of the whole chain. The presence of lateral methyl or more bulky groups, may lead to a gauche conformation of the chain, which is the reason of the threefold helical form assumed by the molecules of isotactic polymers. Evidently comfortable accomodation of bulky lateral groups is not compatible with the maintenance of a planar zig-zag chain for isotactic polymers. As examples, in Fig. 6 the structures of chain elements of polyethylene and polypropylene are shown. In Fig. 7 a model of the chain of poly-alpha-butylene is compared with a model of the staggered structure of diamond.
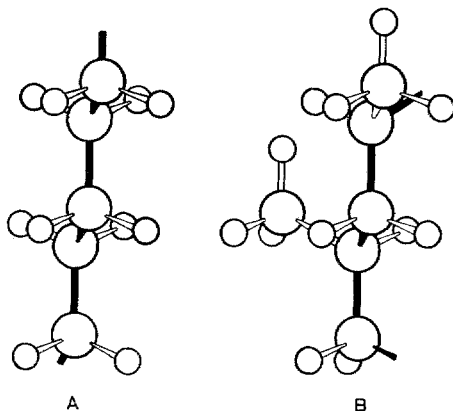

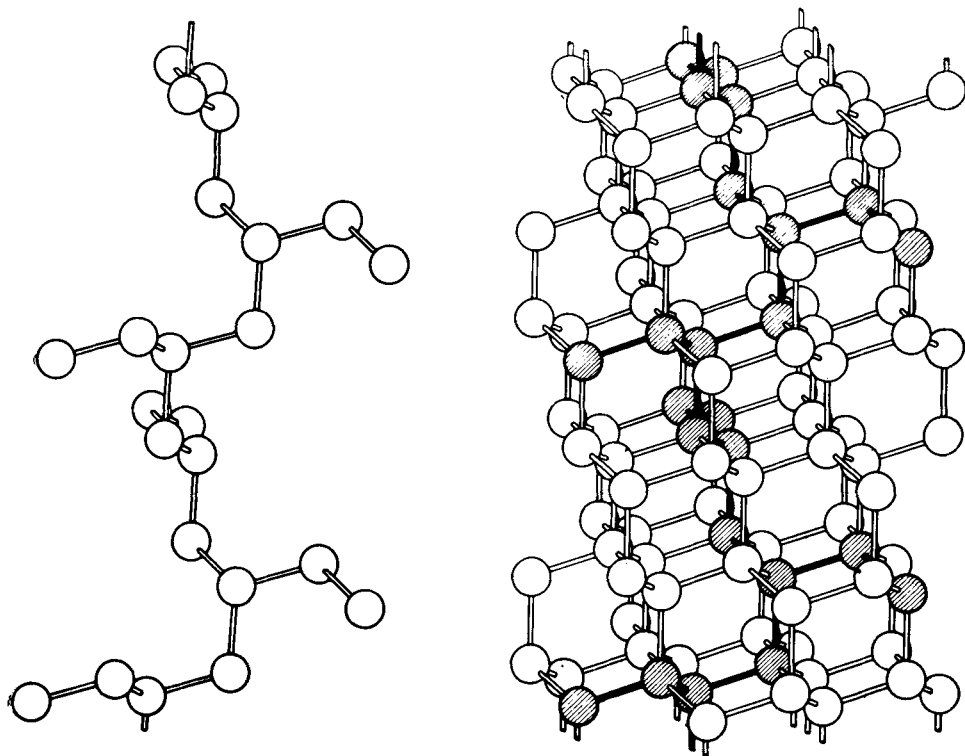Fig. 6. – Elements of polymer chains: Polyethylene (A), Polypropylene (B).

Fig. 7. – Model of the poly-alpha-butylene macromolecule: carbon atoms are staggered as in the diamond lattice.

If a double bond comes out from a carbon atom, it must be considered, with regard to the orientating effect on the other single bonds, as lying in a plane normal to that containing the two remaining single bonds. The π-electron concentration in this perpendicular plane probably influences the direction to be assumed by the remaining bonds of successive carbon atoms. It has been indeed emphasized that the most probable distribution of electrons in a double bond is the one in which two electron pairs lie in opposite sides of the plane defined by the other four bonds [13].

The resulting effect is that the single bonds adjacent to the double bond are in staggered positions, while the double bond is not (Fig. 8). As a consequence of that, a portion of chain containing four carbon atoms and a central double bond is planar, but the successive carbon atoms tend to be no more in the same plane (Fig. 9).

Fig. 8. – Positions of minimum energy of the single bonds of a carbon atom singly linked to a double-bonded one (side and end views).

I-4 TRANS   I-4 CIS
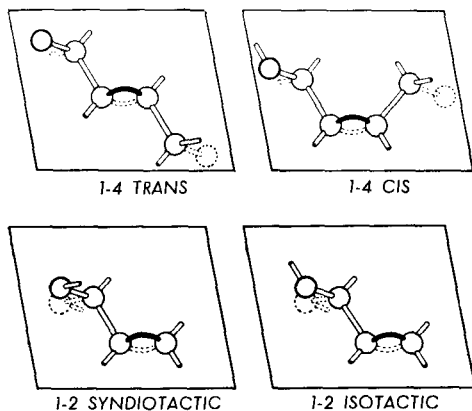
I-2 SYNDIOTACTIC   I-2 ISOTACTIC

Fig. 9. – Conformation of carbon-carbon bonds adjacent to double bonds, as found in crystalline polybutadiene isomers.

This tendency explains, as we shall see later, in particular cases, the conformation assumed by the monomeric units in all four crystalline polybutadiene stereoisomers (Fig. 10).

2) Van der Waals contacts. As we have already seen, Van der Waals repulsions, we dealt with in the fifth point set up in this section, are extremely important in determining the form of the chains, when atoms, large in comparison with hydrogen, or lateral chains are bonded to an aliphatic chain.
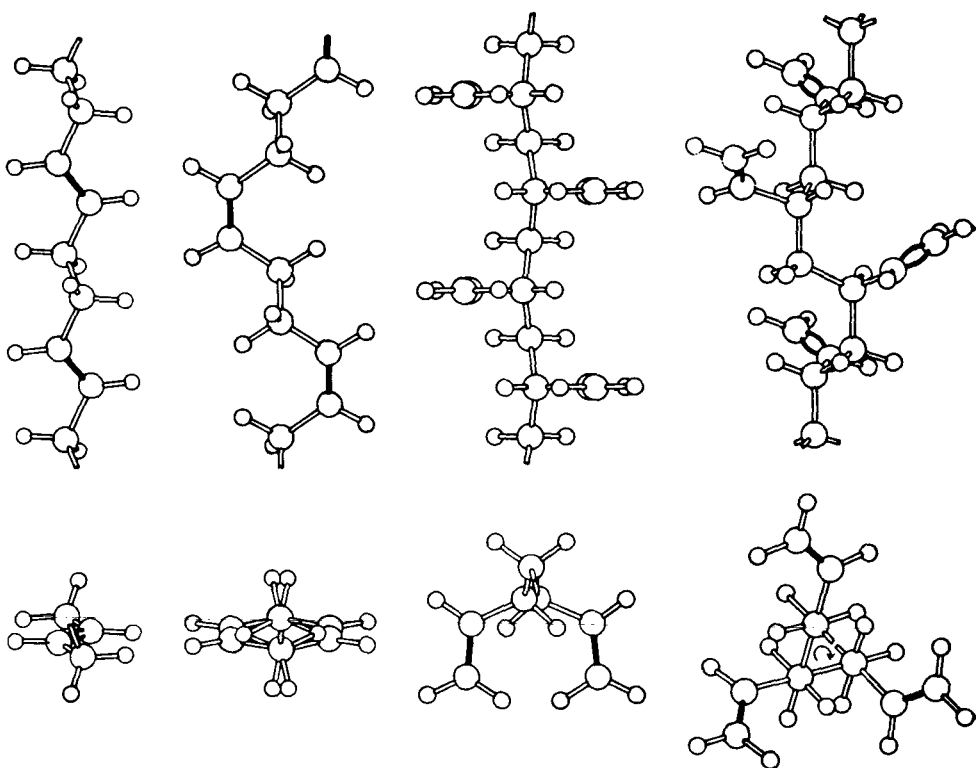
Indeed, an approach of two atoms

Fig. 10. – Chain conformations of the four crystalline polybutadiene stereoisomers as determined in our Institute.

not directly bonded at a distance below the one consented by Van der Waals forces leads to a large increase of potential energy, which opposes this approach.

Qualitatively correct Van der Waals distances between two atoms may be calculated on the basis of the additivity of Van der Waals covalent radii, when electrostatic interactions of the type involved in hydrogen bridges take no role [14]. Approximately, Van der Waals radii are 0.8 Å greater than the corresponding covalent radii. They cannot however be precisely defined, because only in a rough approximation atoms may be considered spherically shaped and therefore they much depend on the relative positions of the atoms and on the shape of the electron clouds.

The determination of the most probable shape of the macromolecule involves reconciliation of the five rules outlined above with the equivalence postulate to approach a minimum of potential energy. In many instances indeed, these five rules cannot rigorously hold together, expecially when substituents of large dimensions are present along the chain. For instance the lower heat of polymerization of isobutylene, as compared to the one of ethylene, should be attributed, partially at least, to the greater energy content of the chain C_nH_{2n} of polyisobutylene, in comparison with polyethylene, caused by the deformation of the bond sequence due to steric hindrance (as two CH_3 groups are joined to every two carbon atoms along the chain).

As a consequence of the minimum energy postulate, we may expect in some instances, while rules 1 and 3 are always holding:

1) A deformation of bond angles exceeding the normal values (*e.g.* more than 110° for C—C—C angle).

2) A modification of the form of the main chain contrasting the principle of staggered bonds.

3) A greater approach of certain atoms in the chain, at distances a little below normal Van der Waals ones.

In general the above-mentioned deformations of the various types of chains, take place simultaneously, but in different degrees, in order to approach a minimum of potential energy. For the prediction of the most stable conformations, the engineering principles used in the study of elastic structure deformations should be appliable [15].

Consequences of such deformations, to be discussed more deeply later, are, for instance, the non-planarity of the zig-zag chain of syndiotactic 1,2 polybutadiene, the deformation of bond angles in polypropylene, the four-fold instead of three-fold helix structure of poly-3-methylbutene.

The above outlined principles, which regard only interactions between atoms in the same chain, are of general character and should be sufficient to

establish the preferred conformations of small portions of chains also in the free state.

Also, in most cases and especially for hydrocarbon polymers, they allow us to predict, together with the equivalence postulate, the conformation to be assumed by a single chain in the crystalline state. As we have already noted, however, the need of uniformly filling space may cause slight modifications in the form of the chain from the one foreseeable as that of minimum energy in the free state.

2`3. *Mode of packing of the chains.* – The order in three dimensions of polymer chains to give a crystal may be only realized by a parallel orderly association of the chains, with contacts between atoms of different chains not exceeding the Van der Waals contacts established for low molecular weight compounds (see Table II).

TABLE II. – *Van der Waals contacts observed in polymers examined in this and in other papers of this series.*

$$CH_3\text{——}CH_3 \ldots \ldots \ldots \ldots \quad 4.0 \div 4.3 \text{ Å}$$
$$C_{ar}\text{——}C_{ar} \text{ (benzene ring)} \ldots \ldots \quad 3.5 \div 3.8 \text{ Å}$$
$$CH_2\text{——}CH_3 \ldots \ldots \ldots \ldots \quad 4.0 \div 4.3 \text{ Å}$$
$$H \text{ ——}H \ldots \ldots \ldots \ldots \quad 2.4 \div 2.7 \text{ Å}$$

When, as it frequently occurs, both up and down molecules are represented in the unit cell, the space-group is such as to allow the presence in the lattice of anticlined chains in equivalent positions. When from a given monomeric unit equivalent right and left-handed helices are likely to be built up (for example from a monomer not containing asymmetric carbon atoms, like propylene) both are often represented in the crystal lattice, and the space-group is such as to allow the presence of enantiomorphous chains in equivalent positions; it may occur however that when bulky side groups are present along the chain, a suitably dense packing can be obtained only in space groups in which uniquely isoclined or uniquely isomorphous helices are accomodated.

For instance, whereas in the structure of polybutylene both up and down molecules may be accomodated, only isoclined molecules are present in the closely related structure of poly-o-fluoro-styrene [16]. There is increasing evidence that in some cases i.e. in the case of isotactic poly-t-butylacrylate only isomorphous helices can be accomodated in the same crystal [17] so that a separation of optical antipodes occurs on crystallization from the melt, when it contains both right and left-handed helices. In other cases, isomorphous helices provide a good filling of space only through a superspiralization, as in some proteins [18].

It frequently occurs that nearly isosteric (*e.g.* with a similar steric encumberment) equivalent chains (*e.g.* enantiomorphous isoclined, or isomorphous anticlined, or enantiomorphous anticlined) may vicariate themselves in the same lattice site. This phenomenon has been observed for the first time by NYBURG in natural rubber, in the crystal lattice of which, a statistical substitution mirrored chains is possible [19].

We have observed it in isotactic polymers [20], and found evidence for its existence also in guttapercha and polychloroprene [21].

Generally, in the packing, the polymer molecules tend to maintain, partially at least, the symmetry of the chain. For instance, in the structure of polymers whose chains are of the glide-plane type, the glide-plane is usually maintained in the lattice. This fact occurs in natural rubber, as well as in polyvinylchloride, syndiotactic 1,2 and cis 1,4 polybutadiene and rubber hydrochloride [22]. The threefold helical symmetry of the chain of poly-α-butene, polystyrene and poly-o-fluoro-styrene, so as the fourfold helical symmetry of the chain of polyvinylnaphtalene and poly-o-methylstyrene, are maintained in the respective crystal lattices [23].

In the parallel association of chains to provide polymer crystals, we often recognize ordered layers of macromolecules on planes by the parallel or antiparallel association of which we may imagine that the crystal is formed. These planes are defined by the chain axis and by one of the smallest crystallographic translations equatorial to the fiber axis. The value of both translations defining these planes are scarcely affected by thermal movements, so that thermal expansion occurs almost completely in a direction perpendicular to these planes [24].

We shall call them, whenever recognizable, «principal planes». They contain in general, as it was mentioned above, two crystallographic axes: the fiber axis and what we shall call « principal equatorial axis ». It is very likely that along this axis the polymer crystals may grow at their best, because generally we find it in the direction of growing of the spherulites, as we may conclude from the known structure of spherulites of polythene, polypropylene, and nylon [25].

With these background principles we shall now discuss in a more detailed way the structure of some crystalline polymers which have been studied by us.

3. – The structure of some crystalline polyhydrocarbons.

3˙1. *Polymethylene.* – Polymethylene, that is the polymer obtained by catalytic decomposition of diazomethane, is the simplest completely linear hydrocarbon polymer. Its structure is the same as that proposed by BUNN for the crystalline part of I.C.I. polyethylene [26]. The zig-zag structure of the chain
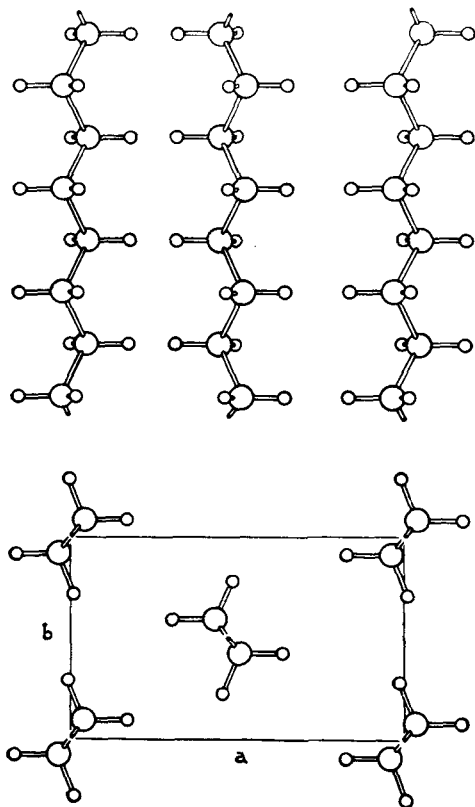
Fig. 11. – Model of the crystal structure of polymethylene.

has already been discussed in this paper, in connection with the equivalence postulate and minimum energy considerations: equivalent isomorphous —CH_2— groups repeat themselves along a two-fold helix. The nearly cylindrical molecules fit themselves in a quasi hexagonal array (Fig. 11).

3'2 *Isotactic polymers*. – Isotactic polymers are the cis stereoisomers of the vinyl head -to-tail polymers, as we have already quoted in Section 1. The bulky dimensions of lateral groups do not allow for these polymers a planar chain conformation. A planar structure is indeed impossible, because the distance of 2.5 Å (if we consider for example polypropylene), that should come out between the nuclei of two carbon atoms of successive methyl groups is such, that certain hydrogen atoms of the methyl groups would result too near to each other, in contrast with minimum energy requirements [26]. The nature of the strain may be easily understood when we consider that the large resonance energy of polyacetylene, which has a planar structure and is crystalline, is destroyed in polypropine, whose chain structure is non-planar, with a net loss, according to our calculations, of about 10 kcal per monomeric unit (something like happens with benzene and cyclooctatetraene) [27, 28].

A suitable accomodation of the methyl groups may be achieved in a helix type structure, imposed by the equivalence postulate, and in accordance with the principle of staggered bonds, only when the successive monomeric units are arranged on a three-fold helix.

This structure may be easily carried out from the planar one, sketched in Fig. 12-*a*), by effecting rotations of 120° around bonds L_1, L_2, L_3 or around bonds $L_{1'}$, $L_{2'}$, $L_{3'}$, respectively clock-wise or anticlock-wise; thus generating a left- *c*) or a right-handed *b*) helix. The methyl separation achieved in this way is comfortable (> 4 Å) and the staggered bonds principle is respected. As the planar configuration is strongly unfavoured from a thermodynamic

point of view, no interconversion of enantiomorphous helices appears to be likely at low temperatures, and we may consider left and right-handed helices as optical stereoisomers.
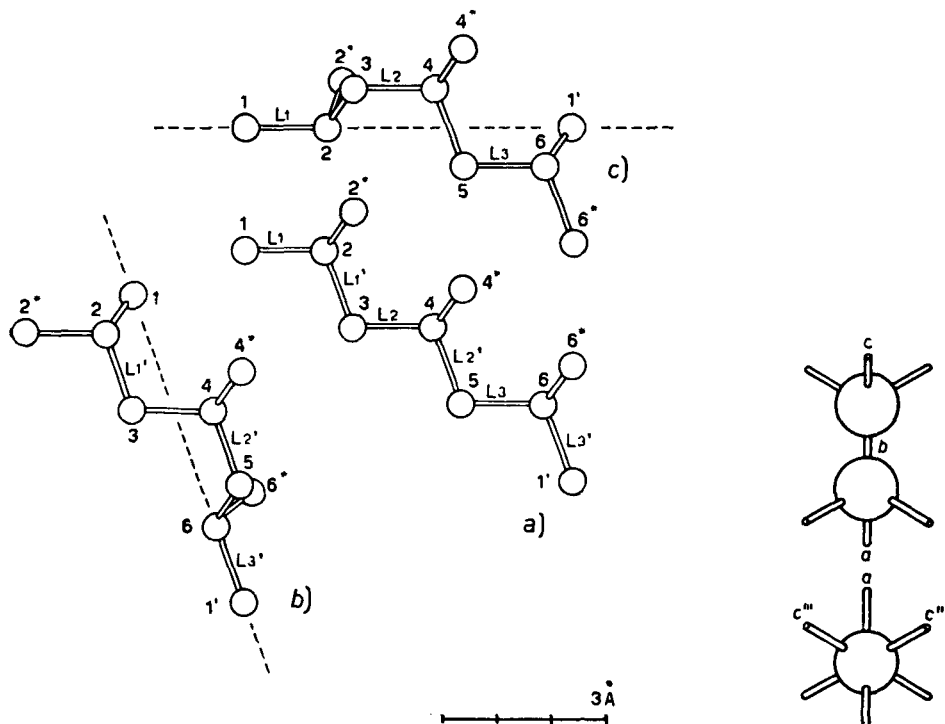

Fig. 12. – Actual conformation of isotactic polypropylene chain as derived from the planar chain structure.

Optical activity is prevented from the presence of an equal quantity of the two forms.

When built up with normal bond lengths (1.54 Å) and angles (109° 30′) the isotactic threefold helix should have an identity period of 6.2 Å; actually for polypropylene an identity period as large as 6.5 Å has been observed. A slight enlargement of C—C—C angles along the chain appears to be the reason of this fact, owing to a more confortable accomodation of Van der Waals contacts between the hydrogen atoms of the chain. The bulkiness of side groups, and more precisely, the steric encumberment of side groups in proximity of the chain is, on the contrary, the reason why 3-methyl substituted polyolefins have a four-fold helix structure in the crystalline state, and 4-methyl substituted ones a 3.5-fold helix structure. The staggered bonds principle is no more rigidly respected, but valence angles along the chain tend to approach the

normal ones again, so that very low differences in energy should be present
between a three-fold and a four-fold helix [29] (Fig. 13).

Thus, poly-α-butene, for instance, has been observed to be crystallizable
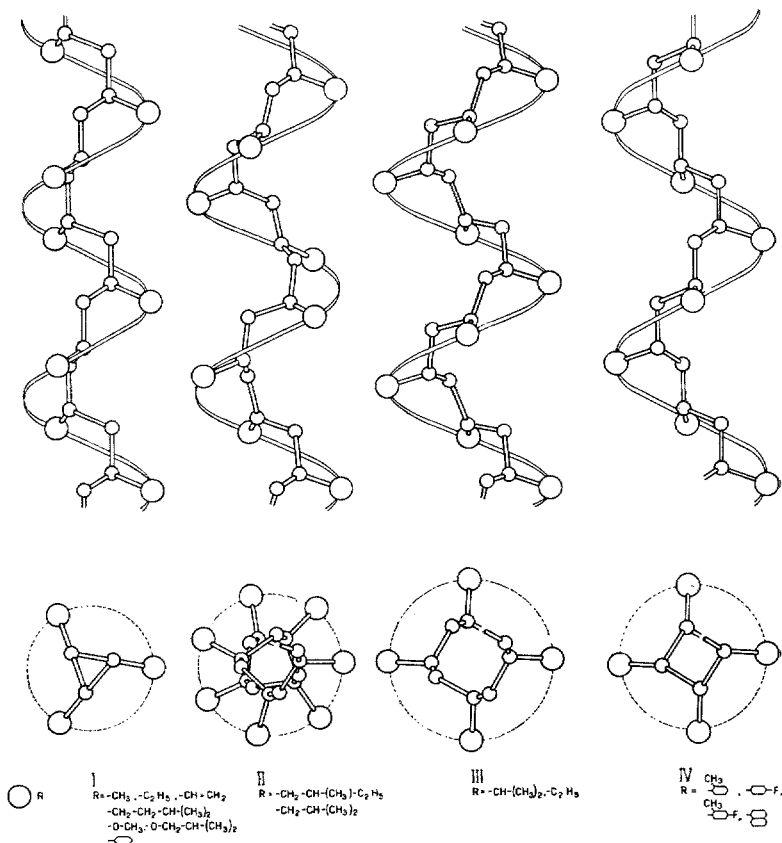in both forms, the four-fold one however being the least stable [30]. It has

Fig. 13. — Models of helicoidal chains found for different isotactic polymers.

been concluded, from the fact that this form is the first which appears on crys-
tallization both from the melt or from a solution, that in the liquid state there
is a certain degree of freedom with small energy intakes, to rotation around
single bonds in the chain, in the sense of a slight despiralization of the chain.

It is interesting to note that the four-fold helix poly-α-butene crystals are
suddenly transformed in the three-fold helix ones by drawing, or by pressing
and, more slowly, on standing at room temperature.

Other different forms of chains, slightly modified from the above mentioned
ones, may also appear in crystalline isotactic polymers. For example, poly-o-

methylstyrene has a four-fold helical chain structure different from the one described for aliphatic polyolefins (Fig. 13), whereas poly-m-methylstyrene has a 3.67-fold helical chain structure (11 monomeric units in three pitches
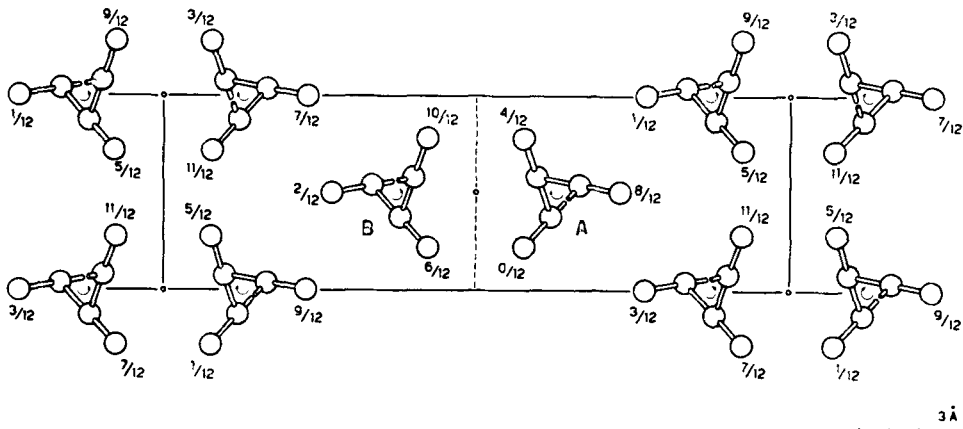

Fig. 14. – Mode of packing of polypropylene chains in the crystal.

along the identity period). Much complicated chain structures, which have not yet been completely examined, have been observed for other substituted polystyrenes. The reason of such a variety of different forms is to be found
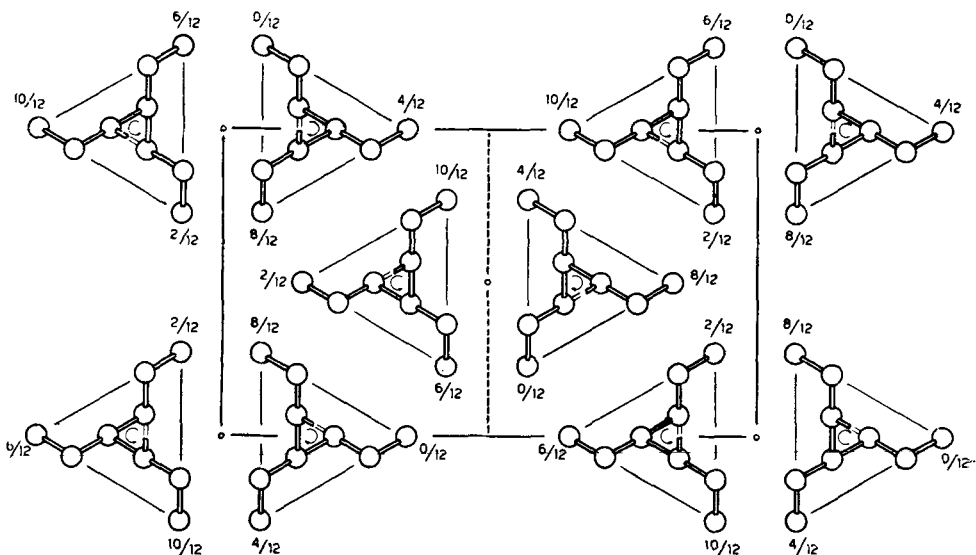

Fig. 15. – Mode of packing of poly-alpha-butene chains in the crystal.

in the packing requirements, both within the very chain and also among different chains, the side groups of substituted polystyrenes being very stiff and bulky indeed. The solution of the complete cry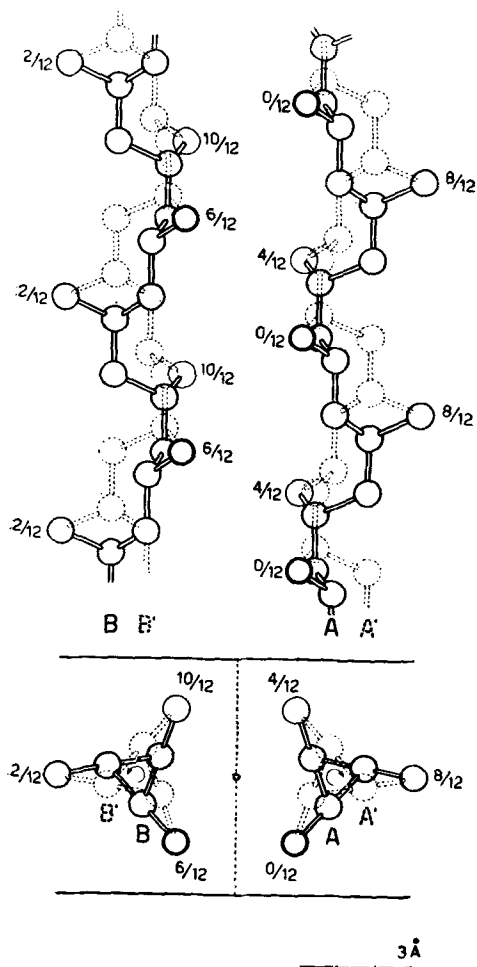stal structure of polypropylene and poly-α-butene effected by us [31] permits a discussion of the mode of packing of the chains of these isotactic polymers in crystals (Figs. 14, 15).

On considering the packing requirements explained in Sect. 1, the lattice of an isotactic polymer should possibly accomodate in equal quantity enantiomorphous chains, presumably through operations of symmetry of the space group.

According to the requirements just explained, it is actually found that, in all these polymers, enantiomorphous chains face each other in pairs, a close packing being realized through the operation of a glide-plane with translation parallel to the fiber axis. Moreover, anticlined isomorphous chains of the isotactic polymers of propylene and α-butene are nearly isosteric, when we refer to the encumberment of lateral groups (Fig. 16) and as long as intermolecular contacts are realized almost uniquely by these lateral groups, anticlined isomorphous chains may in principle vicariate in the same lattice site. In fact it is thought that each crystal of these polymers is composed of very small blocks of anticlined crystallites built up of isoclined chains, so that diffraction phenomena

Fig. 16. – Model showing isosterism of anticlined isomorphous chains of polypropylene in a crystal.

may be easier interpreted supposing that anticlined isomorphous chains may statistically vicariate in each site of the crystal.

Poly-α-butene (and the closely related isotactic poly-1,2-butadiene) are able to maintain the complete symmetry of the chain, so that three glide planes making angles of 120° among themselves and related by a three-fold screw axis are easily recognizable in the rhombohedral structure of these polymers.

A too loose mode of packing should result when a similar structure is supposed to be likely also for polypropylene.

The glide plane, through which two enantiomorphous facing chains are related, turns out to be, in this case, a principal plane. Evidence that the *a-c*
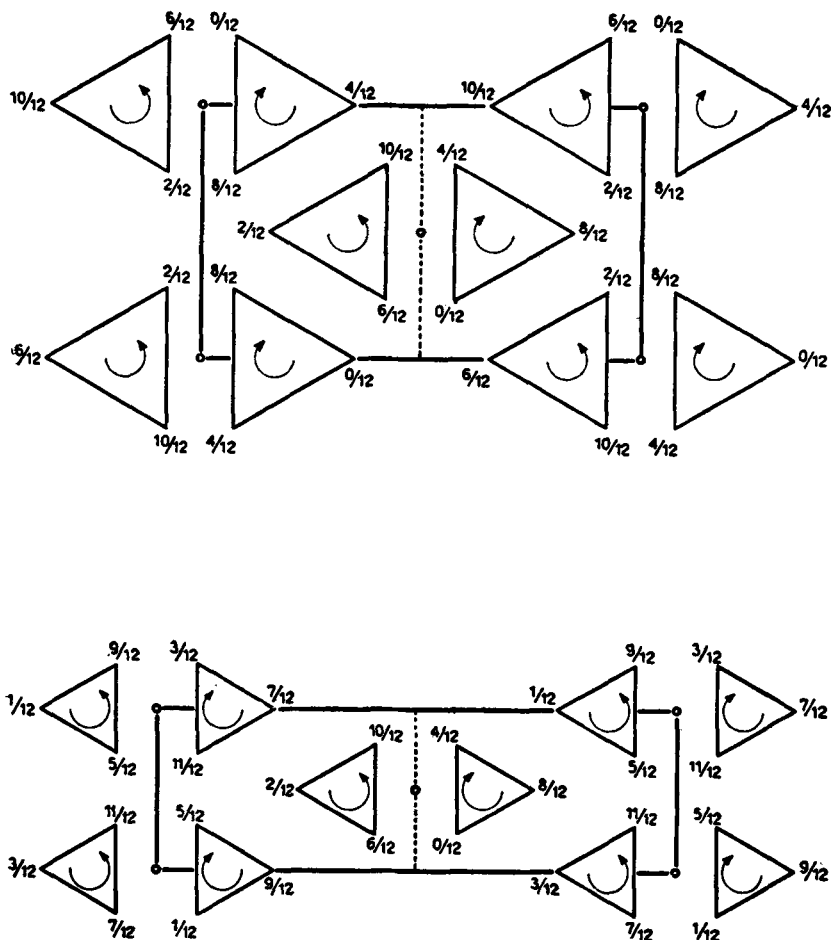

Fig. 17. – Comparison between the mode of packing of polypropylene and poly-alpha-butene in the crystal state.

plane is a principal plane in polypropylene is found in the close-packing realized along this plane of the side groups of two enantiomorphous symmetry related chains (Fig. 17) and hence in the shortness of the *a*-axis, in its parallel orientation along the radii of spherulites and in its very low thermal expansion, as compared to the one taking place along the *b*-axis.

The mode of packing of four-fold helix polyvinylnaphtalene and poly-o-

methylstyrene is also obtained through the operation of glide-planes between enantiomorphous chains, as it is possible to see in the Fig. 18.
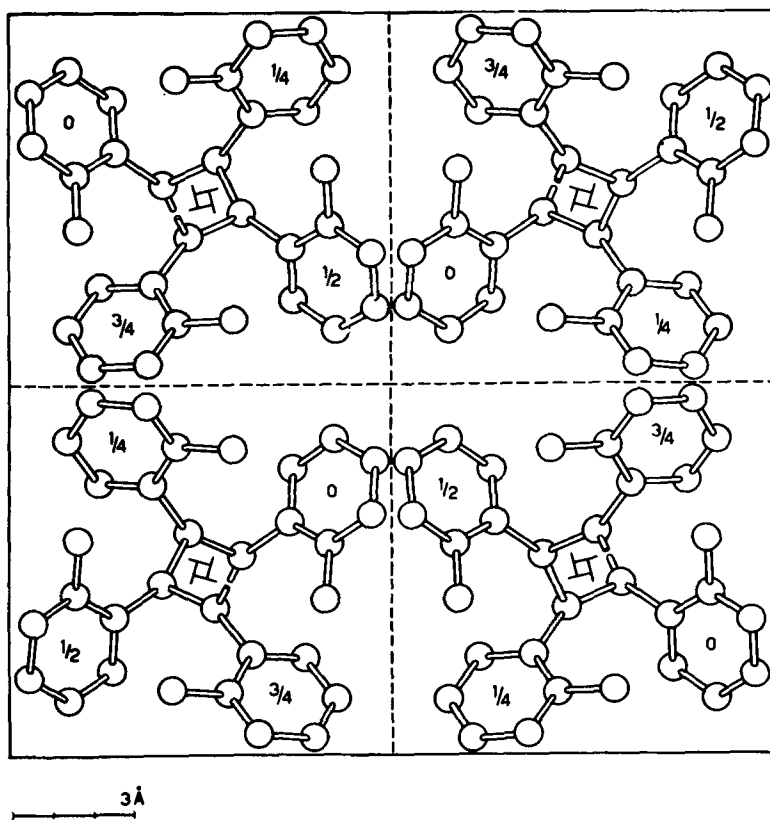

Fig. 18. – Model of packing of poly-ortho-methylstyrene chains in the crystal.

3·3. Syndiotactic polymers. – Syndiotactic polymers may be defined as trans stereoisomers of the vinyl head-to-tail polymers.

Their chain structure may be, according to the equivalence postulate, of the glide-plane type, hence repetition being achieved along the fiber axis every two (σὺν δύο) monomeric units, or their chain may follow a helix associated with perpendicular twofold axes (*).

Now it is known that two polymers possess a syndiotactic chain structure: polyvinylchloride and one of the two crystalline stereoisomers of 1-2 polybutadiene [32].

_____

(*) *Note added in proof.* – This is the type of chain recently found by the AA. for syndiotactic polypropylene. The model is shown in Fig. 1 of the introductory paper of this series.

The bulkiness of the side groups of these two polymers does not hinder, as was the case of isotactic polymers, a planar or nearly planar conformation of the chain. Only with regard to polybutadiene a slight deviation from a completely zig-zag planar structure of the chain has been supposed, but not thoroughly confirmed, owing to steric repulsions between successive lateral vinyl groups, the perpendicular orientation of which in regard to the chain axis obeys the principle of staggered bonds (Fig. 19, see also Fig. 9). In every case it is easy to see on inspection that no distinction is needed between up and down molecules, and in the lattice we have to accomodate only one type of chain.

The glide plane is maintained in the unit cell of these polymers. The molecules pack closely in layers along this plane. The crystal is built up of many antiparallel layers packing at their best between themselves.

The thermal expansion occurs almost completely in syndiotactic 1,2 polybutadiene in a direction perpendicular to the glide-plane, according to the phenomena connected with the supposed existence of a principal plane of packing.

3.4. Crystalline 1,4 polydienes. – Under the heading of isotactic and syndiotactic polymers we have dealt with the known structure of 1,2 stereoisomeric polydienes. In this chapter we shall deal with the known structures of crystalline 1-4 polydienes. The synthesis of all four crystalline stereoisomers of polybutadiene and the study of their structure

Fig. 19. – Model of packing of syndiotactic, 1-2 polybutadiene in the crystal.

effected in the Institute of Industrial Chemistry of the Polytechnic of Milan, permits now to have a clearer idea of stereoisomeric phenomena in the field of polydienes.

a) Cis 1,4 polydienes. – Natural rubber is the regular head-to-tail polymer built up of cis 1,4 isoprene units. Its chain structure may be expected uniquely
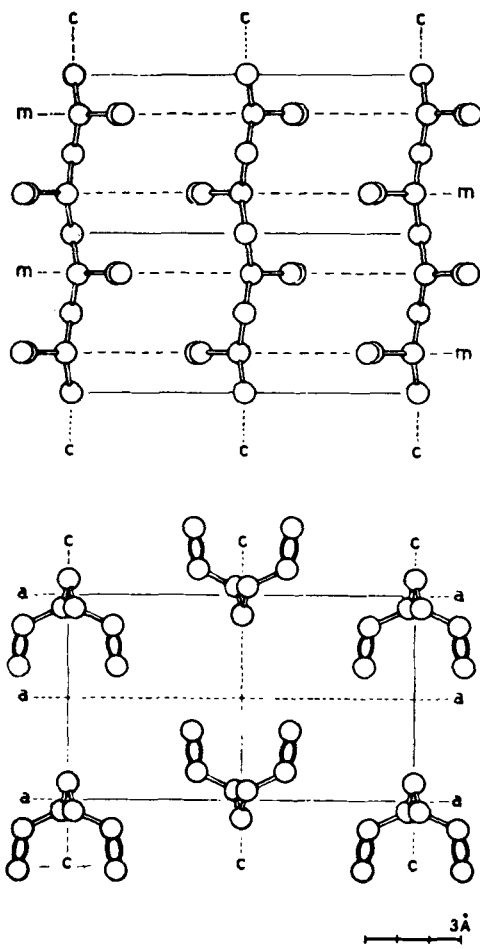
in one of two types of successions, the glide-plane and the helix-type succession. However it is impossible, on the basis of the equivalence postulate only, to establish which of the two forms will be actually chosen by the macromolecules on crystallization, as they would not correspond to intrinsical differences in the configuration of the chain.
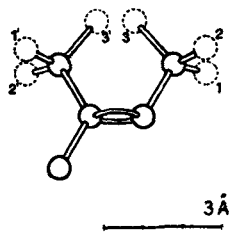
Actually a glide-plane non-planar structure is found for the chain of crystalline cis 1,4 polyisoprene [33]. Indeed on the basis of minimum energy considerations we should expect that:

1) the five atoms of each monomeric unit be in a plane;

2) the direction of the CH_2—CH_2 bond, should take, in accordance with the principle of the staggered bonds, any of the three positions outlined in Fig. 20. Positions 3 and 3′ must be discarded because of excessively short Van der Waals contacts between atoms of the same chain;

Fig. 20. – Possible conformations of 1-4 cis isoprene unit satisfying the principle of staggered bonds.

3) the directions of the two CH_2—CH_2 bonds on the two sides of the isoprene unit should be in opposite and parallel directions; i.e. the enantiomorphous conformations 1-1′ and 2-2′ are best likely to be realized;

4) repetition of a monomeric unit with such a conformation, may be achieved in a helix type or in a glide-plane type succession, the first possibility being discarded because of unsuitable contacts between the methyl group and some chain carbon atoms.

The glide-plane is maintained in the lattice, according to a common feature occurring in many studied polymers, so that a close packing of molecules is expected along this plane; also, alternatively up and down molecules should be represented along this plane.

As the contacts lateral to the principal plane thus realized are due only to methyl groups, we find that, in the
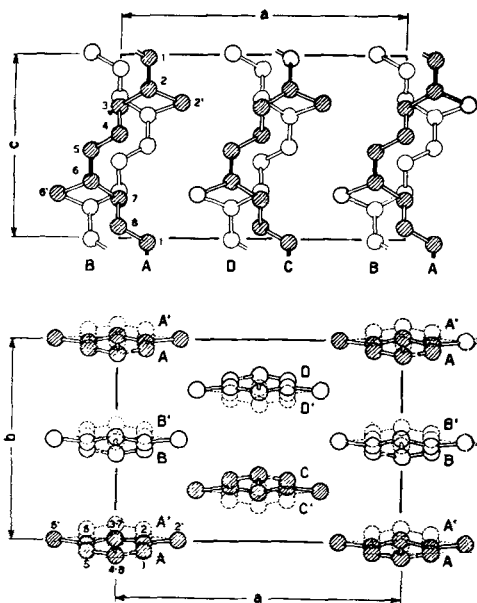

Fig. 21. – Model of the structure of 1-4 cis polyisoprene.

actual structure, successive parallel or antiparallel principal planes (*bc*) are able to pack themselves at random. It is possible to see from Fig. 21 that a layer of molecules such as A—B—A—B can be followed equally well by a layer such as C—D—C—D or C′—D′—C′—D′—.

Perhaps, we may explain the low melting entropy of rubber in comparison with the one of guttapercha, by supposing that, in the molten state, not only a certain degree of parallelism between the chains is maintained, but also that the flexible ribbon-shaped molecules tend to maintain some kind of parallel association of the ribbons.

A great similarity of structure is to be expected between [34] cis 1,4 polybutadiene and cis 1,4 polyisoprene: actually a similar conformation of the chain was found by us, in which enantiomorphous monomeric units repeat along a glide plane. No more distinction however, is needed in cis 1,4 polybutadiene as compared with cis 1,4 polyisoprene between up and down molecules; also, one finds an identity period slightly longer than the one foreseeable on the basis of the staggered bonds principle; this fact is probably due to repulsions between hydrogen atoms of two CH_2 groups, in opposite position relative to the double bond, which tend to lengthen the chain; repulsions which could not be eliminated in the case of polyisoprene because of the steric hindrance provided by the methyl group (Fig. 22).

1 - 4 CIS POLYBUTADIENE

Fig. 22. – Model of the structure of 1-4 cis polybutadiene.

The glide-plane may be also considered a principal plane in polybutadiene, and determines a mode of packing of the macromolecules in the crystalline state, which is very similar to, but simpler than, that realized in the structure of polyisoprene. In fact, there is no more need for accomodation of up and down molecules, nor for statistical distribution of successive antiparallel or parallel layers of molecules developed on the principal plane, owing to the absence of lateral groups.

b) *Trans* 1,4 *polydienes*. – The structure of guttapercha, the trans 1,4 head-to-tail stereoisomer of polyisoprene, was thoroughly studied for the first
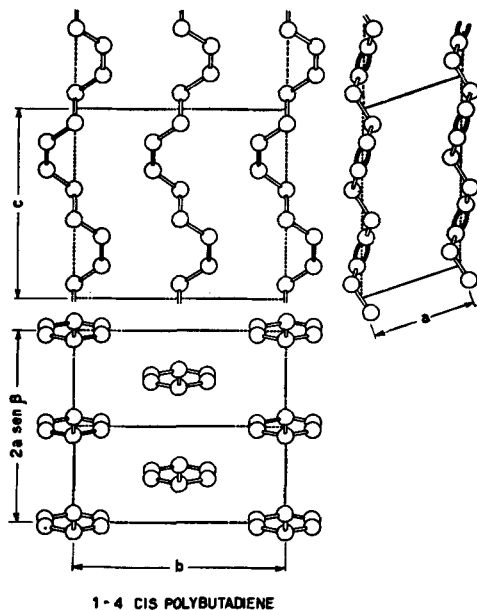
time by C. W. BUNN [35], who assessed the principal features of the structure of one of the three crystalline forms in which this polymer may occur (β form).

Some strangeness of the chain structure was eliminated by JEFFREY [36], supposing and proving that the five atoms of each isoprene unit must be in a plane.

As a matter of fact, successive trans isoprene units may repeat according to the principle of the staggered bonds in various ways without any great difference in regard to sterical hindrances and, according to this fact, different identity periods have been found for the three different crystalline forms in which guttapercha may occur; and yet, however, there is no complete agreement as to the form of the chains, reported from different authors.

In accordance with the equivalence and minimum energy postulate, we tentatively proposed, the three forms shown in Fig. 23, whose calculated identity periods are in accordance with literature data [37].
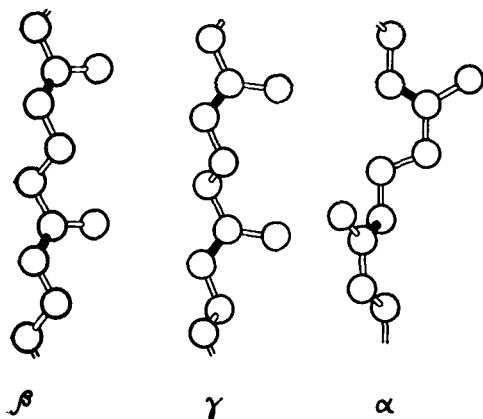

β   γ   α

Fig. 23. – Models of the chain of guttapercha (trans 1-4 polyisoprene) in different crystalline modifications.
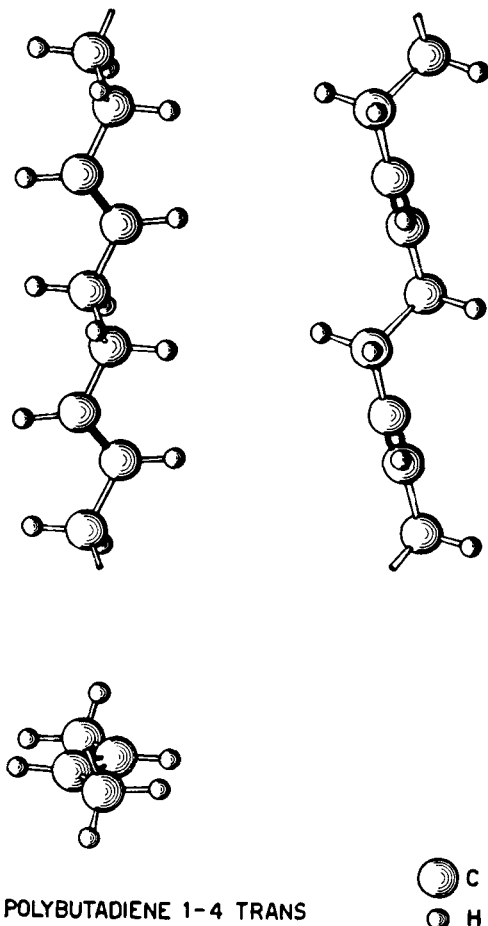
POLYBUTADIENE 1-4 TRANS   ⊚ C   ⊙ H

Fig. 24. – Model of the chain of 1-4 trans polybutadiene.

A structure of chain similar to the one of β-guttapercha is possessed by trans 1,4 polybutadiene, which according to our studies can also appear, in different crystal forms as guttapercha does [38].

This polymer shows in its crystal state at room temperature, a chain structure (with an identity period $c = 4.92$) very similar to that of β-gutta-percha (Fig. 24). The almost cylindrical shape of its molecules favours a mode of chain packing in a pseudo-hexagonal array with $a = 4.54$ Å. At about 65 °C a first order transition in the solid state takes place. The structure of the high temperature phase corresponds to a mode of packing in which the chains, always remaining parallel to each other, should be more free to move and rotate along the chain axes. The phase change is accompanied by a lowering of the density of more than 9%. The low density phase possesses a pseudohexagonal array with $a = 4.88$ Å, $c = 4.68$ Å. In a drawn fiber this transformation gives rise to a sudden reversible contractile process, which is obviously analogous to the one taking place in living muscles.

The dimensional change along the fiber axis corresponds to the change of the c dimension (about 5%). We believe this is the first time that a similar phenomenon has been observed in synthetic fibers, related to a first order crystal-crystal transition.

4. – Other notable structures.

The principles discussed in this work with regard to hydrocarbons may be also applied to other notable structures of non-hydrocarbon polymers; so we report some examples to demonstrate the general validity of the principles previously discussed.

Nylons. – The form of the chain of nylon is found to be nearly planar in accordance with the principle of staggered bonds [39]. Hydrogen bonds are formed among different molecules in the same plane in which the chain is contained; successively these planes pack themselves at their best. Along these planes the direction of accretion of spherulites is found.

At the melting point [41] we should expect disruption of the lattice prevailingly in a direction normal to this plane. As long as thermal oscillations should occur at their best, owing to lower potential barriers, around CH_2—CO— and NH—CH_2 bonds, giving rise to typically different deviations from the planar form of the chain, a lower packing efficiency and then a lower melting point should be expected for nylon 6 in comparison with nylon 66 (Fig. 25) and, more generally, for nylons containing odd sequences of CH_2 groups in comparison with those containing even sequences of CH_2 groups.

There is some evidence that a slight deviation from the completely planar form is present in nylon 66 and nylon 6 even at room temperature. The fact

which has not yet been explained that nylons have a lower heat and entropy of fusion than polyolefins or polyethers supports our assumption that hydrogen bonds are statistically maintained on layers also in the melt.
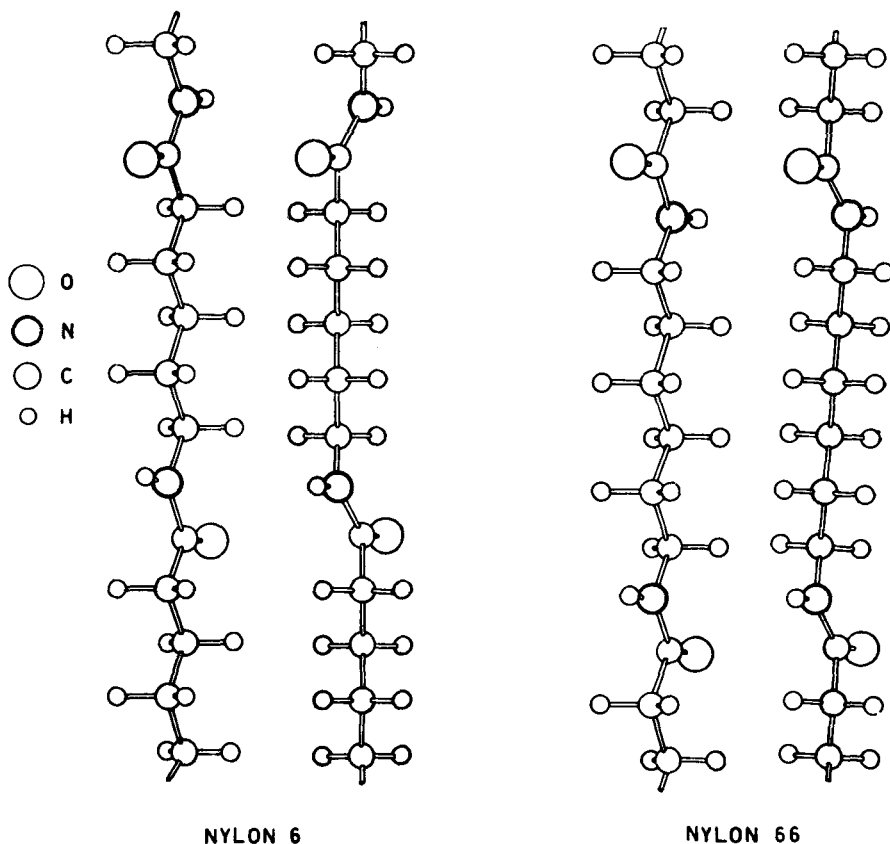

NYLON 6   NYLON 66

Fig. 25. – Possible models of the chains of nylon 6 and nylon 66 slightly deviating from planarity in a thermal vibration.

Teflon. – Teflon is the polymer of tetrafluoroethylene. According to the principle of staggered bonds the best form of the chain should be the planar one; but, owing to repulsions between fluorine atoms, a slight spiralization of the chain occurs, giving rise to a helix along a pitch of which 13 CF_2 units repeat themselves [41].

The chains have an almost cylindrical encumberment, so that they pack in a pseudo-hexagonal array.

Polyisobutene [42], *polyvinylidene chloride* [43]. – The complete crystal structures of these polymers are not known; but the form of their chains is supposed to be of the glide-plane type for polyvinylidene chloride, and, according to LIQUORI, of the helix-type for polyisobutene as may be deduced from the length of the fiber axis and the principal features of their X-ray spectra. The deviation from staggered structures of their chain is certainly due to the great steric encumberment of the lateral groups (see Fig. 4).

Poly-propylene-oxide [44]. – This polymer has been studied by us, and it is of some interest because the monomer contains asymmetric carbon atoms. In fact a helix structure has been found, in accordance with the equivalence postulate, satisfying the minimum energy requirements. When prepared from the racemic monomer, a crystalline polymer is obtained only with stereospecific catalysts, which permit the growing of chains only from isomorphous monomeric units (Fig. 26).

Polyvinylalcohol [45]. – This polymer, notwithstanding the irregular succession of hydroxyl groups, is able to crystallize. Actually, the chain form is similar to that of polyethylene, the OH groups being of a sufficiently small size (in comparison to the H atoms) to be accomodated also in a cis succession. In the crystal structure, the molecules face in pairs, realizing hydrogen bonds between themselves, whenever possible, *i.e.* at random, according to the distribution of the hydroxyl groups.
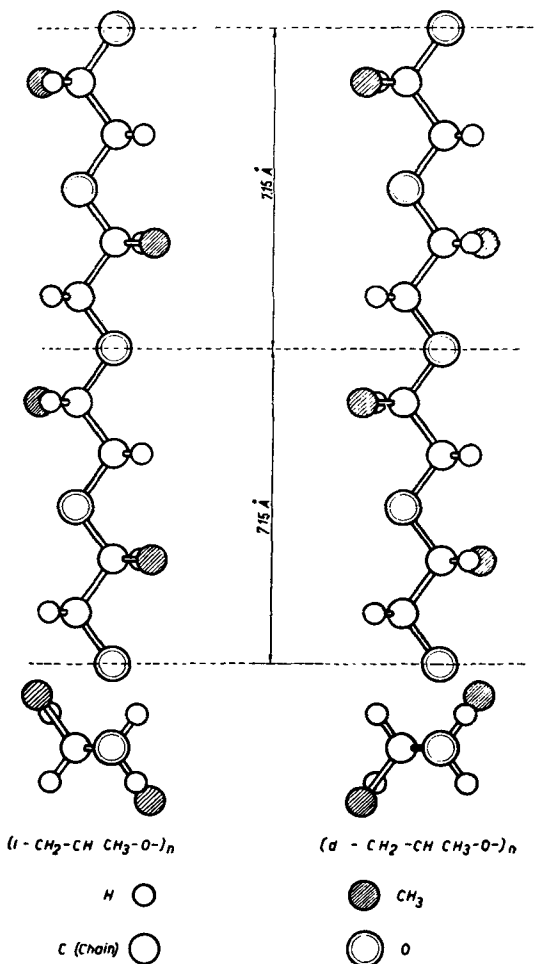

Fig. 26. – Model of the chain of d- and l- polypropyleneoxide.

Proteins [46]. – According to whether hydrogen bonds are formed between different chains or in the same chain, two different kinds of helix type

structures are possible for the chain: 2-fold helix structures (Fig. 27) (the packing being determined by hydrogen bonds realized on opposite sides of the chain along a principal plane) or more-fold helix structures with the plane
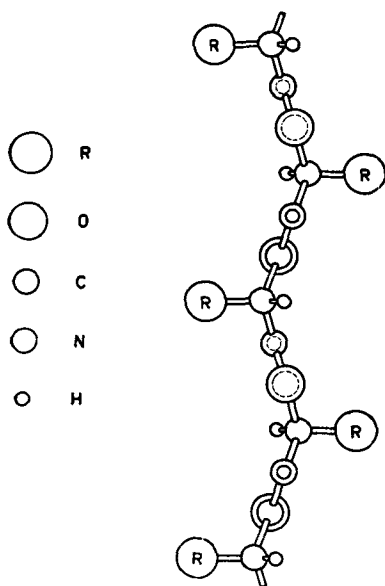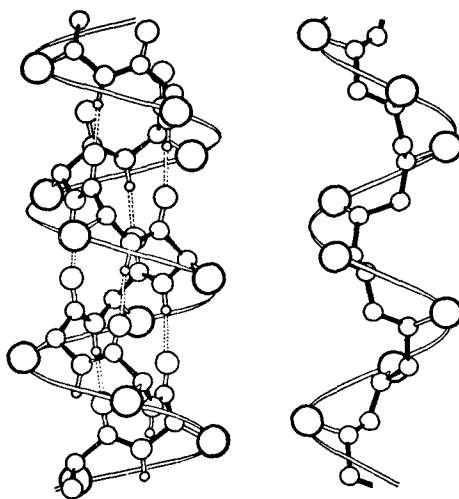
Fig. 27. – Model of the chain of β Keratin type proteins.

Fig. 28. – Model of the chain of α Keratin type proteins (left), compared with the chain of a 3,5 helix isotactic polymer (right).

of the amide group parallel to the chain axis so as to form intramolecular hydrogen bonds (Fig. 28) within the chain.

Polysaccharides [47, 48]. – Cellulose may be considered as the 1,4 connected polymer of α-glucose. Successive α-glucose residues are able to follow a 2-fold helicoidal path, without strain, satisfying the principle of staggered bonds.

A 2-fold helix path is no more possible for the chain of starch, which is built up of β-glucose residues, so that a three-fold helix results; close similarity may be found between the chain structures of these two polymers, respectively with the 2-fold helix structure of polyethylene (all « trans » bonds) and with the 3-fold helix structure of polypropylene (alternatively « trans » and « gauche » bonds) (Fig. 29).

The packing of the chains of polysaccharides appears mostly dependent on the formation of strong intermolecular hydrogen bonds.
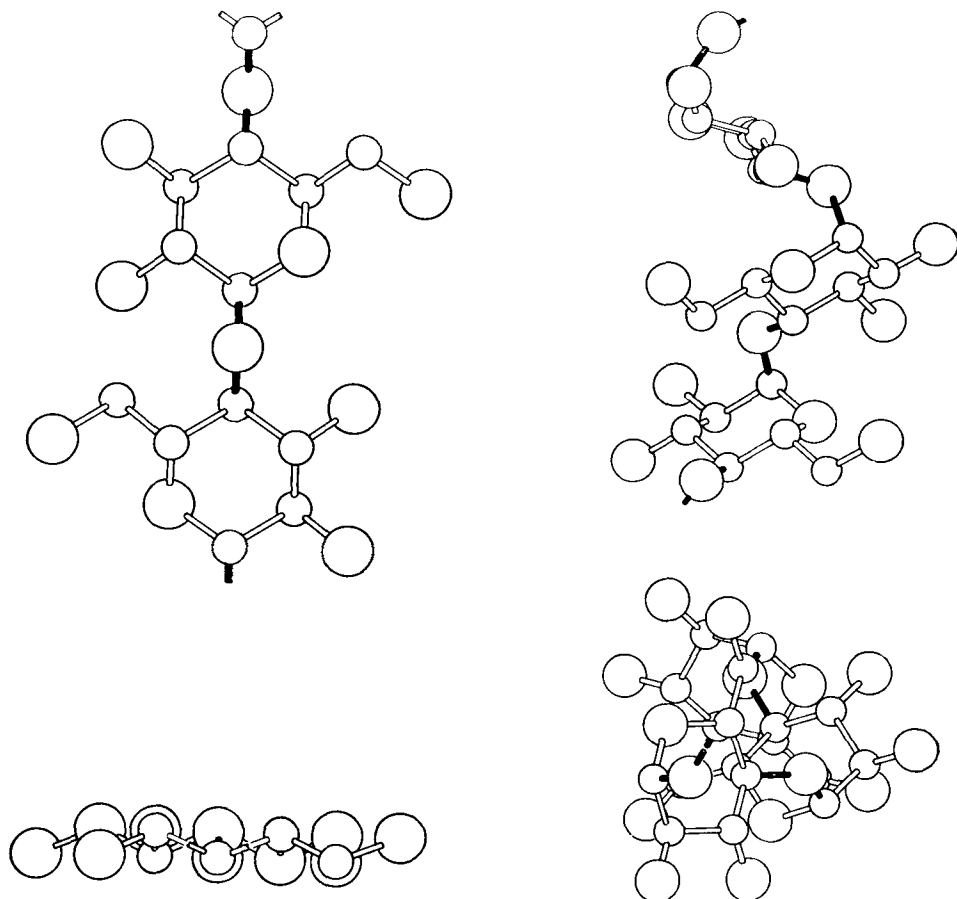
Fig. 29. – Comparison between the chain of cellulose (left) and that of starch (right). The piranic ring is rigid. The black drawn bonds, joining the rigid rings through an ethereal oxygen atom, follow one to another like polymethylene (cellulose) and poly-propylene (starch) bonds.

The uniqueness of helix-type structures for the chain of crystalline proteins and polysaccharides follows directly from the equivalence postulate, as the corresponding monomeric units contain asymmetric carbon atoms.

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