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# The crystal structure of stereoregular polymers<sup>(\*)</sup>

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Sur la base des résultats importants acquis dans les recherches structurales, sur les polymères stéréoréguliers, les auteurs considèrent successivement :

- 1) les isomérismes chimiques et stéréochimiques, c'est-à-dire la signification exacte de la stéréorégularité dans les polymères ;
- 2) la conformation des macromolécules au sein du cristal, c'est-à-dire les restrictions imposées par la stéréorégularité à la conformation moléculaire dans l'état cristallin ;
- 3) l'entassement, « packing », des macromolécules dans les cristaux, c'est-à-dire une description des différents types de structures observées.

A large number of new types of crystalline polymers has been synthesized since the discovery in 1954<sup>1)</sup>, of stereospecific catalysts for the polymerization of olefins and diolefins<sup>2)</sup>.

The large amount of study material available in the field has impelled an intensive activity of structural researches. Such researches have not only solved many problems, often quite complex, of Sterical and Chemical isomerism, but in many instances have given the appropriate suggestion for the synthesis of new macromolecules with pre-determined structural properties.

It is our purpose here to illustrate the most significant results obtained in these researches and indicate those developments which actually seem the most promising for the future.

One can safely state that a unitary picture of the structural behaviour of polymers has been already achieved ; perhaps in some particular fields our knowledge is even more advanced than in the classical structural organic chemistry of small molecules : as a matter of fact it is possible today to

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Steunende op de belangrijke uitslagen bekomen voor de strukturbepaling van stereoregelmattige hoogpolymeren, beschouwen de auteurs achtereenvolgens

- 1) de eigenlijke betekenis van de stereoregelmattigheid van hoogpolymeren van het standpunt uit van de chemische en stereochemische isomerie ;
- 2) de conformatie van de macromolekullen in het kristal, t.t.z. de beperkingen opgelegd door de stereoregelmattigheid aan de moleculaire conformatie in de kristallijne toestand ;
- 3) de « packing » van de macromolekullen in de kristallen, in het bijzonder de beschrijving van de verschillende types van vastgestelde structuren.

foresee the molecular conformation of a crystalline polymer as well as the packing in the crystal, much better than in the case of low molecular weight compounds.

Furthermore, because of the macromolecular nature of the compounds the microscopic interpretation of physical properties is often accessible just as it is in the case of very simple low molecular weight compounds.

For the sake of clarity, we shall in our exposition discuss :

*first* : the exact meaning of stereoregularity in polymers<sup>3)</sup> ;

*second* : the restrictions imposed by the stereoregularity on the molecular conformation in the crystalline state ;

*third* : the most common types of structures observed in the crystal state.

## CHEMICAL AND STEREO-ISOMERISM.

When we describe the crystal structure of a given compound we imply the existence of a regular three-dimensional order.

In the case of crystalline polymers, due to the periodicity of identical units within the same macro-

molecule, a disorder in the monomer sequence along the chain will in general hinder the possibility of crystallization. A short discussion on this point will be made at the end of the chapter.

The first necessary condition therefore, for the crystallization of a linear polymer, is that we must have the same type of configurational pattern along the chain for all macromolecules of the compound, at least for those portions of the macromolecules, which take part of the crystal<sup>3)</sup>.

This condition imposes narrow restrictions on the chemical and sterical structure of the polymer, that is on the type of sequence and on the possible stereoisomers.

If we are concerned with addition polymers, let us examine a few cases of chemical isomerism in the sequence of monomeric units.

Generally speaking an addition polymer can show two types of monomer unit sequences: head to head, tail to tail or head to tail sequences. In the following exposition we shall be concerned only with head to tail sequences because this type of sequence occurs always, at least for large sections of the chain, whatever the type of polymerization reaction (ionic or radical<sup>4)</sup>).

New different possibilities of chemical isomerism arise in dienic polymers.

In butadiene polymerization the addition of a new monomeric unit can take place in 1-2 (generally, as already reported, head to tail) or in 1-4 position<sup>5)</sup>.

In an isoprene polymer (head to tail) the addition takes place in 1-2, 3-4 or 1-4 position (fig. 1).

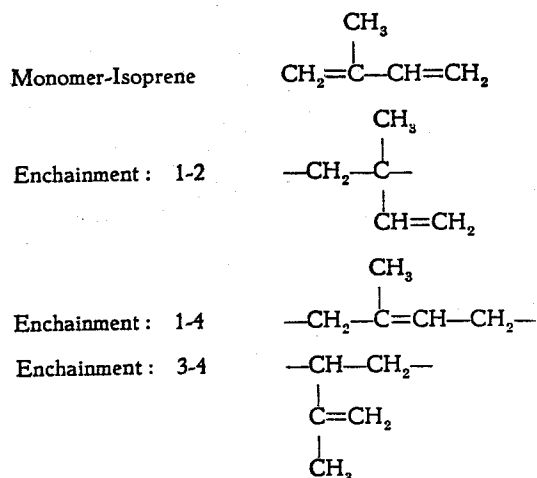


Fig. 1. — Various Types of enchainment for isoprene polymers

Of course, the chemical identity of monomer sequences, at least for large portions of each macromolecule, is a necessary although not sufficient

condition<sup>3)</sup> because, beside the chemical isomerism, the stereoisomerism of each monomeric unit plays an important role.

For instance in poly-1-3-diene with a 1-4 sequence, double bonds can be of both cis and trans type; however, in order to have a crystallizable polymer they need to be all of the same type.

In the same way, the two natural polymers of isoprene, natural rubber and gutta-percha, differ in the type of sequence, the first being of 1-4 cis and the second of 1-4 trans type (fig. 2).

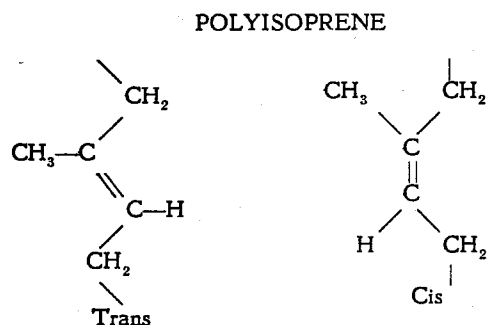


Fig. 2. — Structure of isoprene monomeric units in gutta-percha and in natural rubber

Even more complex is the study of the possible stereoisomerism which takes place in a polymer containing in the chain carbon atoms bonded to two different lateral substituents<sup>6)</sup>.

It is well known that in the case of vinyl polymers with head to tail sequences, two possible types of regular monomeric sequences can occur; for their description we have first used in 1954 and subsequently in 1956 the terms « isotactic » and « syndiotactic »<sup>7)</sup>.

We proposed the term *isotactic*, (from the greek *ισος*, equal, and *ταττω*, to bring in order) for those polymer chains whose tertiary carbon atoms have all the same sterical configuration, and the term *syndiotactic* (from the greek *συνδυω*, every two, and *ταττω*, to bring in order) for those chains whose tertiary carbon atoms have alternately opposite configuration.

If we represent the polymer chain stretched in a plane and we use the concept of cis trans isomerism like in the cyclohexane substituted derivatives, we can also define as isotactic the cis stereoisomer of a vinyl polymer (all R substituents on the same side of the chain plane) and syndiotactic the trans isomer (R substituents alternatively above and below the chain plane) (fig. 3).

The success of the terms isotactic and syndiotactic has requested an extension of their meaning, originally restricted to vinyl polymers, to the general case of a polymer with carbon atoms

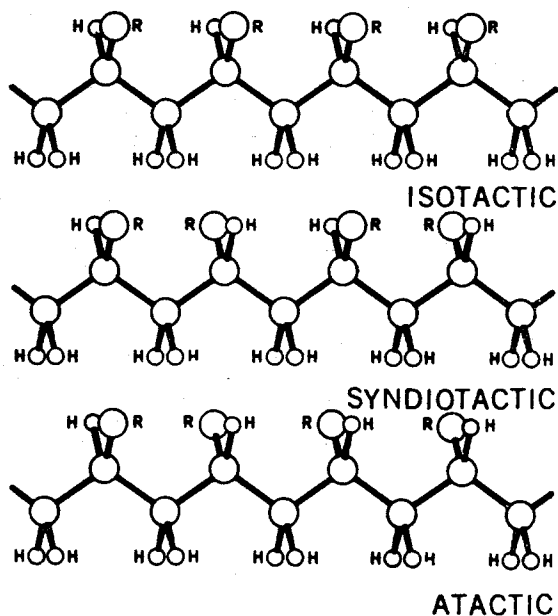


Fig. 3. — Various Types of possible head-to-tail succession of vinylic monomeric units: isotactic, syndiotactic, atactic (random); (main chain arbitrarily stretched on plane)

bonded to two different substituents like polypropylenoxide or 1-4 (cis or trans) poly-1-3-pentadiene<sup>9)</sup> (fig. 4).

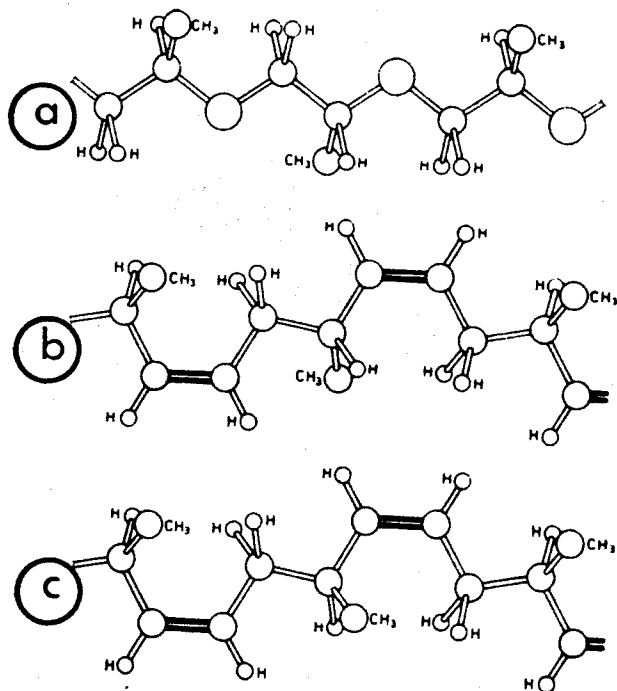
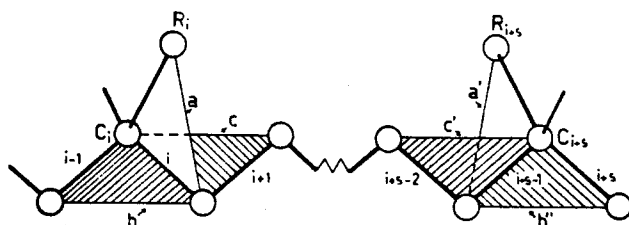


Fig. 4. — Other stereoregular polymers: a) isotactic polypropylenoxide; b) 1-4 cis isotactic poly-pentadiene; c) 1-4 trans syndiotactic poly-pentadiene

Today it seems definitely established for the terms isotactic and syndiotactic a definition like as follows.

Let us first remember that the chain *conformation* is completely defined (as we shall see better in a while) from the values of the internal rotation angles ( $\sigma$ ) around each single bond of the chain: in the same way differences between these angles define completely the chain absolute *configuration*, which is independent from the form actually assumed by the chain<sup>10)</sup>.

Let us consider a polymer chain with a regular spacing (with order  $s$ , that is every  $s$  bonds) of carbon atoms bonded to two different substituents (for instance R and H). Let us consider the bonds,  $i$  and  $i+s-1$ , adjacent to two successive R bonds, from the same side and the internal rotation angles defined in the figure 5.



$$\sigma_i = \hat{b}c ; \sigma_i^R = \hat{a}c ; \sigma_{i+s-1} = \hat{b}'c' ; \sigma_{i+s-1}^R = \hat{a}'c'$$

Fig. 5. — Reference of internal rotation planes for C-C polymeric chain bonds

Clearly the difference between the internal rotation angles  $\sigma_i - \sigma_i^R$  and  $\sigma_{i+s-1} - \sigma_{i+s-1}^R$  may be  $+$  or  $-120^\circ$ .

If  $\sigma_i - \sigma_i^R = \sigma_{i+s-1}^R - \sigma_{i+s-1}$  the polymer is isotactic

If  $\sigma_i - \sigma_i^R = \sigma_i - \sigma_{i+s-1}^R$  the polymer is syndiotactic

Generally speaking any kind of taxis can be defined from relations of the same type between internal rotation angles.

For instance the taxis relative to two substituents A and B on adjacent carbon atoms in the chain is called threo and erythro<sup>11)</sup> according to the conditions of fig. 6.

It may be of interest to discuss briefly the possibility of crystallization of copolymers.

When the copolymerized units are in a regular succession, both from the chemical and sterical point of view, the requirements for crystallizability are the same as those for homopolymers.

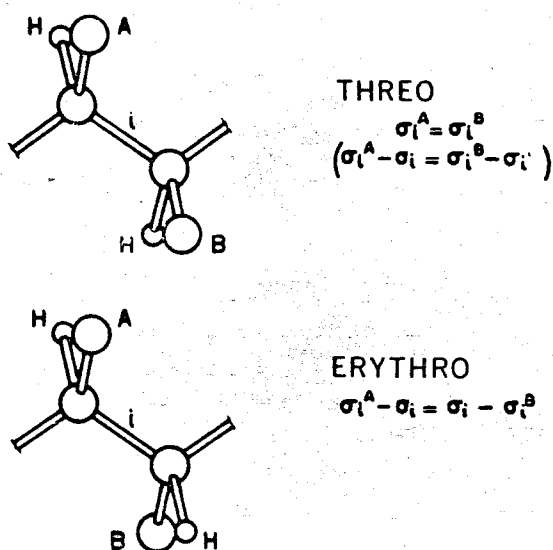


Fig. 6. — Internal rotation angles for threo and erythro-diisotactic configurations

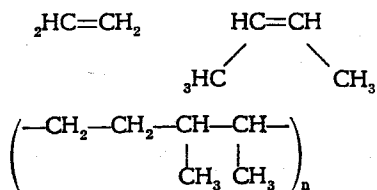
In the table I some characteristic examples of crystalline copolymers of different monomeric units are shown.

In the case of the ethylene-butene-2 copolymer alternate copolymerization occurs between similar functional groups of different monomeric units (olefinic double bond).

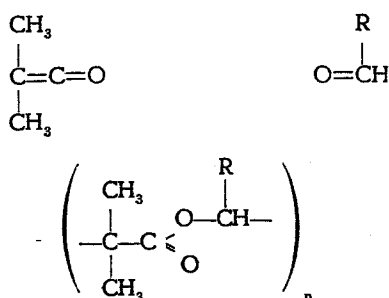
In the case of the copolymers between dimethylketene with aldehydes or ketones, having a polyester structure, alternate copolymerization occurs between different reactive functional groups.

TABLE I. — Some examples of crystalline copolymers of different monomeric units

Ethylene-butene-2-cis alternate copolymer



Dimethylketene-aldehyde alternate copolymer



However, in some cases, crystalline copolymers may be obtained from randomly copolymerized monomeric units.

For a tactic polymer, this occurs when the configurational structure is regular and the side groups do not differ very much in shape and encumbrance (isomorphism of monomeric units).

This type of isomorphism differs from the previously known types because it takes place among parts of molecules (monomeric units) linked by stable covalent bonds. Isomorphous monomeric units in the same chain cannot be separated one from another by physical means (for instance, by solution or by melting).

Three different cases of isomorphism of monomeric units may be observed.

These are as follows.

- a) Both monomers give crystalline homopolymers having the same type of crystalline structure and nearly the same lattice constants.
- b) Both homopolymers are crystalline, but with different crystalline structures.
- c) Just one of the two homopolymers has been observed in crystalline form.

The second case consist of a particular type of isomorphism which, in analogy with what is observed in solid solutions of low molecular weight substances of different structure, may be defined as isodimorphism.

In general, the melting temperature, of crystalline random copolymers, is intermediate between those of the corresponding homopolymers.

## MACROMOLECULAR CONFORMATION IN THE CRYSTALS.

The macromolecular conformation in the crystalline state obeys some fundamental principles first illustrated by *Pauling* for the proteins<sup>12)</sup> and subsequently extended, especially from our school, to linear synthetic polymers.

Small molecules are ordered in a crystal in a three dimensional periodic structure; in a linear crystalline polymer however, the periodic structure is already present in the chain. Therefore the chain axis must necessarily be parallel to one of the crystal axes. Thus in crystalline polymers a sequence of structural units, geometrically equivalent with respect to one axis, is required along each chain.

This principle gains a fundamental euristic importance if one realizes that these structural units coincide, in almost all known structures, with one single monomeric unit or even, with appropriate chain symmetry, with a fraction of it. The same happens in the case of small molecules, which gene-

rally occupy equivalent sites in the crystal, the equivalence occurring in some instances, even between parts of the molecules.

The necessary equivalence of structural units (in homopolymers we have seen that they coincide generally with monomeric units) with respect to one axis, allows an exact definition of the possible symmetry types in a linear crystalline polymer.

The symmetry groups defined in this way are thirteen, but the most important are only five <sup>13</sup>).

The most common group possesses as symmetry element, generating an equivalent unit, a rotation-translation axis (this gives rise to a helix, defined by the symbol *s*). A degenerate case is a simple translation when the rotation is an integer multiple of  $2\pi$ .

Examples of polymers with this symmetry are isotactic polypropylene <sup>14</sup>) (three monomeric units for each pitch) or the 3,5-helix of some polyolefins as shown in the figure and the Pauling's  $\alpha$ -elix <sup>12</sup>) (3.7 monomeric units for each pitch) (fig. 7).

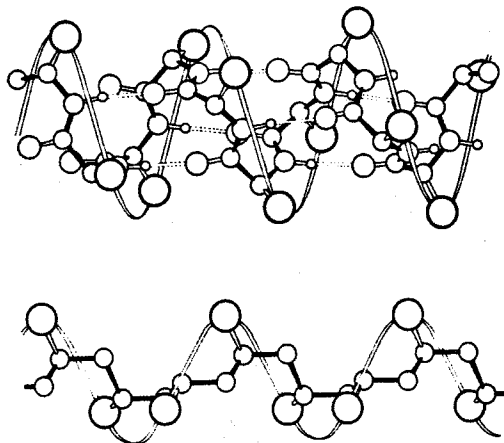


Fig. 7. — Model of the helicoidal structure of isotactic polypropylene (3,5 m. u. for a pitch) as compared with the helix found from Pauling for proteins (3,7 m. u. for each pitch)

If the structural unit possesses a local symmetry element by itself, the following possibilities occur :

1) The local symmetry element is a two-fold axis, perpendicular to the screw axis (symbol *s*<sub>2</sub>). This occurs in the case of syndiotactic polypropylene <sup>15</sup>), where each monomeric unit is repeated by a two-fold axis centered on a CH<sub>2</sub> group and perpendicular to the screw axis (fig. 8).

2) The local symmetry operation consist of a reflection followed by a translation parallel to the chain axis (that is a glide-plane) (symbol *tc*).

This type of symmetry occurs very often, for instance in the cases of syndiotactic 1-2 polybutadiene, of syndiotactic 1-4 cis polypentadiene <sup>16</sup>) (fig. 9), of natural rubber <sup>17</sup>) and polyvinylchloride <sup>18</sup>).

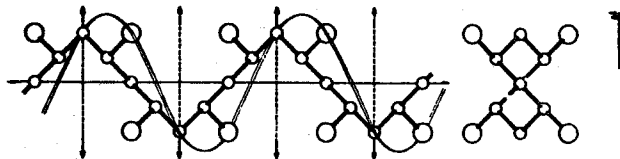


Fig. 8. — Model of the chain found for syndiotactic crystalline polypropylene

3) The local symmetry element is a center of symmetry (symbol *ti*), the screw operation being degenerate in a simple translation, as for instance in the case of the alternate copolymer ethylene-butene-2-cis <sup>19</sup>) (fig. 10).

4) The local symmetry element is a symmetry plane perpendicular to the chain axis (symbol *tm*) as for nylon 77 <sup>20</sup>) (fig. 11).

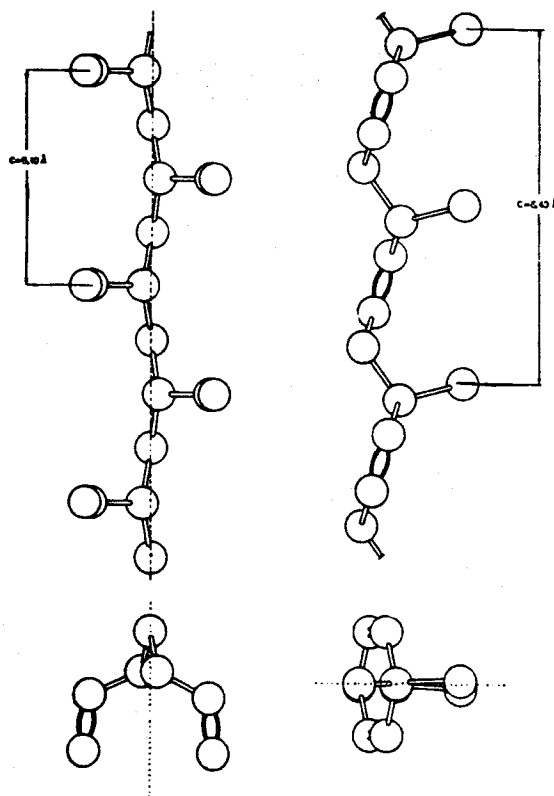


Fig. 9. — Chain conformations of 1,2 syndiotactic polybutadiene and 1,4 cis syndiotactic polypentadiene

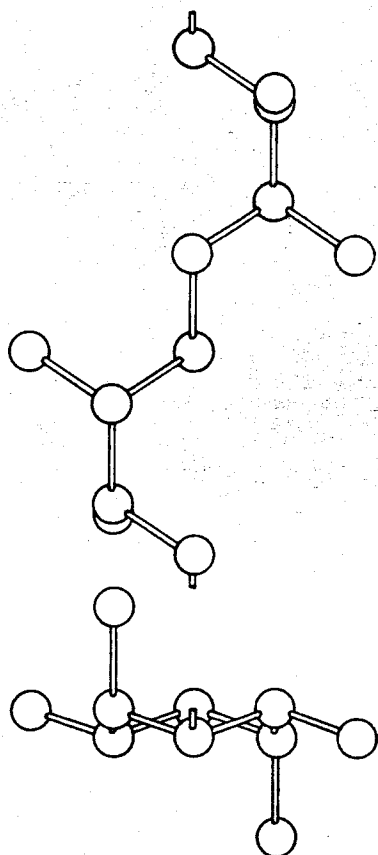


Fig. 10. — Model of the chain of alternate ethylene cis-2-butene copolymer with erythro-di-isotactic structure

The presence of the last three types of local symmetry imposes the degeneration of the screw symmetry operation which generates the helix, in a simple translation, because they would change the direction of the screw progression.

On the other hand it can be shown that other symmetry types within the structural unit different from a two-fold axis, symmetry center and symmetry planes are not allowed in general by a chain structure and therefore must not be considered in a systematic classification of the conformations of linear crystalline polymers<sup>13</sup>).

Of course the above shown symmetry groups are not all appropriate for a given steric and chemical structure of a polymer. For instance in head to tail polymers with two non-equivalent chain directions, as in polyamides or in polysoprene, the groups corresponding to center of symmetry and helix plus two fold axes of repetition are not allowed (In a polyamide a symmetry plane or a two-fold axis perpendicular to the chain axis, or a center of symmetry, would reverse the direction of the polar amide).

If, in addition to this, the polyamide contains asymmetric carbon atoms of the *l* type, the existence of the glide-plane group is ruled out and the only possible type of repetition, as shown by Pauling, is a screw axis. A reflection in a symmetry plane followed by a translation would in fact change a *l*-carbon atom in a *d*-carbon atom.

Once the chain symmetry of a crystalline polymer with a given regular configuration has been assigned using the equivalence principle, the problem arises how to decide the actual conformation.

Let us suppose to change all internal rotation angles, the only restriction being the equivalence principle, and to be able to calculate the difference in internal conformational energy between the resulting models, for one isolated chain<sup>10, 21</sup>). If the energy minima in the potential energy surface are deep enough and their values differ from one to the other, it seems reasonable to assume that crystal field forces (especially if only Van der Waals forces are involved) are unable to modify in a sensible manner those conformations corresponding to the energy minima.

We can therefore state the following principle of the « minimum internal energy »<sup>3</sup>).

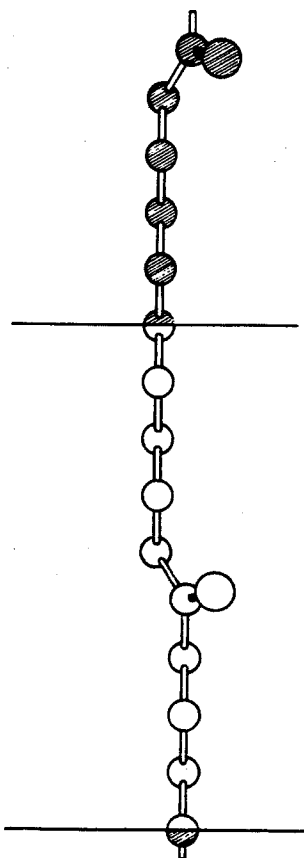


Fig. 11. — Model of the chain found for nylon 77

« The chain conformation in a crystal is close or equal to one of those conformations of minimum internal energy that an isolated chain would assume under the restrictions of the equivalence principle ».

Let us show how this principle works in the case of isotactic and syndiotactic polypropylene. First we need to analyze the restrictions imposed by the equivalence principle on the chain conformation of polypropylene (as for any other vinyl polymer).

In isotactic polypropylene the monomeric units have all the same sterical configuration ; it is therefore reasonable to expect for them also the same conformation : this implies that, for the chain conformation in the crystal (refer to fig. 12 A).

$$\sigma_1 = \sigma_3 = \sigma_5 \dots$$

$$\sigma_2 = \sigma_4 = \sigma_6 \dots$$

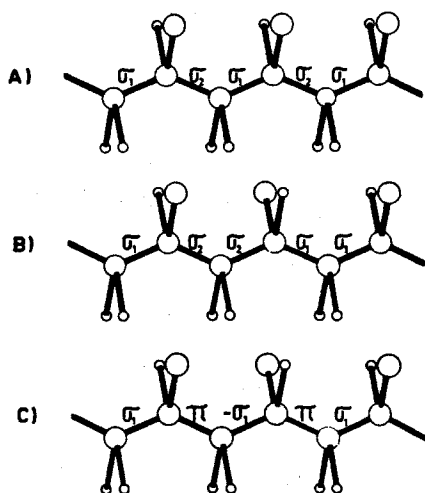


Fig. 12. — Internal rotation allowed from equivalence postulate angles in isotactic (A) and syndiotactic polypropylene (B) e (C)

Once we have fixed the values of the bond distances and angles, we need only to minimize the internal energy with respect to only two variables, the internal rotation angles  $\sigma_1$  and  $\sigma_2$ , in order to find the most probable conformation of isotactic crystalline polypropylene.

In syndiotactic polypropylene, monomeric units have alternatively opposite sterical configurations in the chain : from the analysis of the symmetry groups it is easily seen that there are only two possible ways to arrange geometrically equivalent subsequent units in the chain :

a) a reflection in a symmetry plane followed by a translation ; that is a glide-plane succession ; this will produce a succession of internal rotation angles of the type  $\sigma_1, \pi, -\sigma_1, \pi, \sigma_1 \dots$  (Fig. 12C).

b) a rotation around a two-fold axis perpendicular to the chain axis, centered on a  $\text{CH}_2$  group : this produces a succession of internal rotation angles of the type  $\sigma_1, \sigma_1, \sigma_2, \sigma_2, \sigma_1, \sigma_1 \dots$ , each pair  $(\sigma_1, \sigma_1)$  or  $(\sigma_2, \sigma_2)$  being adjacent to a  $\text{CH}_2$  group (Fig. 12B). Thus again for syndiotactic polypropylene, to find the most probable crystalline conformation, it is enough to minimize the internal energy with respect to only two variables.

An approximate calculation of the internal energy content of a isolated molecule, as a function of the internal rotation angles permitted by the equivalence principle, can be done transferring from known simple molecules the knowledge of the potential energy barrier to the internal rotation around carbon-carbon bonds (which depend on  $\sigma_1$  and  $\sigma_2$  alternatively) and the *Van der Waals* repulsion energy between non bonded atoms (which depend both on  $\sigma_1$  and  $\sigma_2$ )<sup>22</sup>.

A plot of the internal energy as a function of  $\sigma_1$ - $\sigma_2$  for isotactic polypropylene shows two minima corresponding respectively to a right handed ternary helix and to a left handed ternary helix, in perfect agreement with the results of the X-Ray structure (Fig. 13).

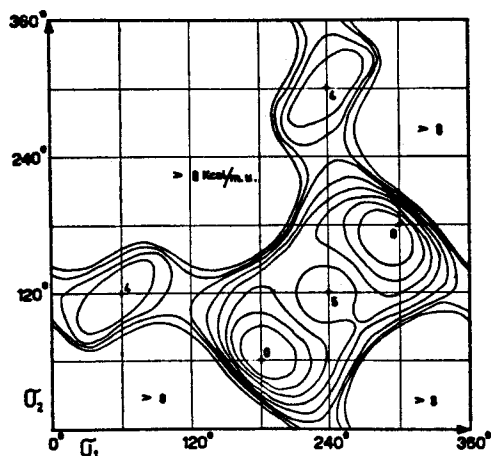


Fig. 13. — Calculated internal conformational energy of an isotactic polypropylene (chain for different helicoidal conformations  $(\sigma_1, \sigma_2 \dots)$ )

For the chain conformation of syndiotactic polypropylene (Fig. 14) three equivalent minima occur, corresponding to the values of

$$\sigma_1 = 180^\circ, \sigma_2 = 60^\circ; \quad \sigma_1 = 300^\circ, \sigma_2 = 180^\circ;$$

$$\sigma_1 = 180^\circ, \sigma_2 = 180^\circ$$

for pairs of subsequent internal rotation angles.

The first two conformations correspond to those found experimentally for the right handed and for the left handed helix of syndiotactic polypropylene, while the third corresponds to that found in the case of syndiotactic polybutadiene.

It is worth to observe that the chain conformation of syndiotactic polypropylene was first predicted in this way and after confirmed with the

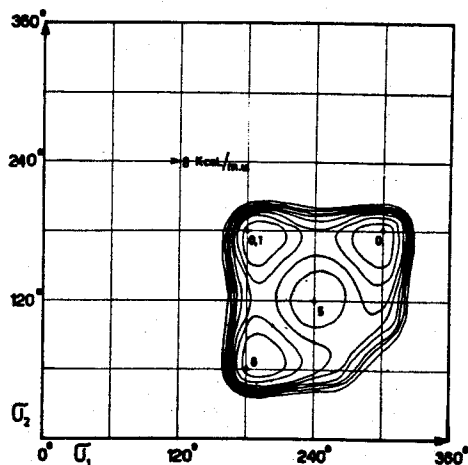


Fig. 14. — Calculated internal conformational energy of a syndiotactic polypropylene chain for different helicoidal conformations ( $\sigma_1, \sigma_1, \sigma_2, \sigma_2, \dots$ )

X-Ray analysis, a fact that undoubtedly proves the heuristic power of the principles shown above.

The deepness of the minima in the energy plot drives to the conclusion that for other isotactic and syndiotactic polymers, the chain conformation should not much deviate from the minima found for polypropylene.

The steric hindrance of side groups induces, in some studied 3-substituted polyolefins a fourfold helicoidal structure in the crystal and in 4-substituted polyolefins a helicoidal structure with 3,5 monomeric units for each pitch.

More complex helices occur in polymers of styrene substituted derivatives, even if the internal rotation angles do not deviate of more than  $30^\circ$  from those found in polypropylene.

In each practical case it is possible to furnish a quantitative explanation for these deviations.

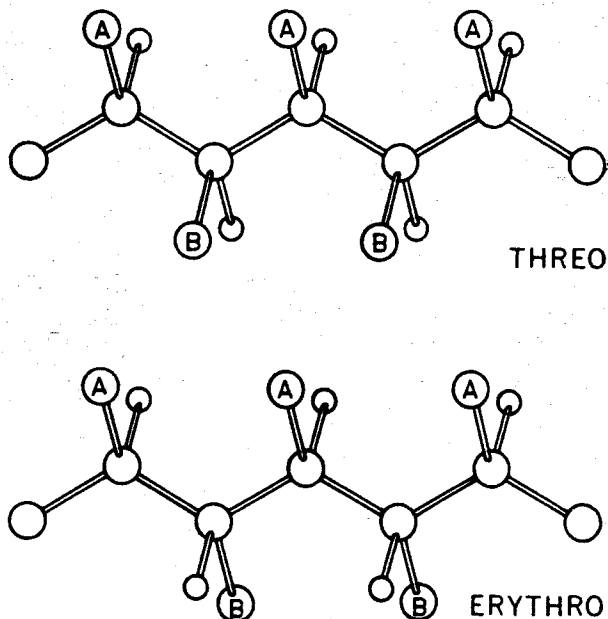


Fig. 15. — Chain of threo-di-isotactic and erythro-di-isotactic polymers of monomers  $CAH=CBH$  (main chain arbitrarily stretched on plane)

Fig. 16a. — Calculated internal conformational energy of the chain of a trans-alkenylether. (We left out the alkylic lateral group in our calculations) (voir fig. 13)

Likewise isotactic polymers of the aldehydes <sup>26)</sup> and diisotactic polymers of alkenylethers <sup>27)</sup> assume chain conformations extremely similar to those found by us for isotactic vinyl polymers.

Detailed calculations have been done by us of the internal conformational energy content of polymers of threo and erythro-diisotactic type <sup>28)</sup>.

In the case of polyalkenylethers, this type of calculations has allowed a definite assignment of the configuration, once the chain conformation was known from the X-Ray results (fig. 15, 16a, 16b).

These results were completely confirmed afterwards from the optical diffraction analysis of models.

Calculations of the internal energy content of a polymer chain with a given sequence of internal rotation angles have a great importance also in the study of the unperturbed mean square length of a stereoregular polymer in solution <sup>29, 30)</sup>.

For isotactic and syndiotactic polypropylene, the results being of course extendible to other isotactic and syndiotactic polymers, the following models result.



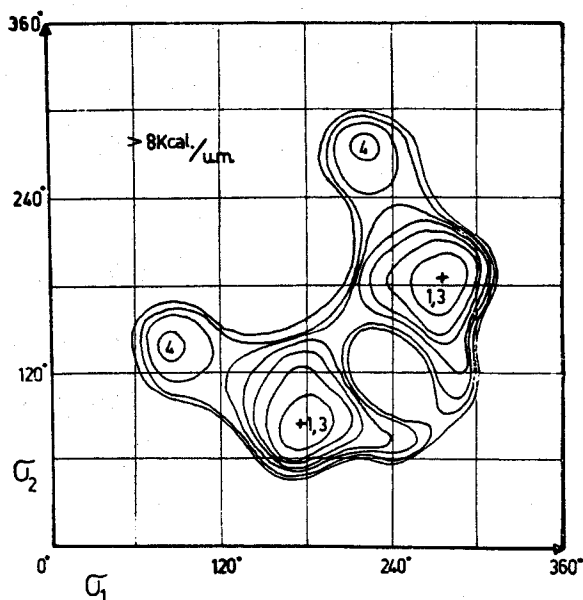


Fig. 16b. — Calculated conformational energy of the chain of a cis-alkenylether. (We left out the alkylic lateral group in our calculations)

The model for an isotactic polymer consists of a sequence in the chain of small right handed spirialized blocks followed by small left handed spirialized blocks; the mean square length depends from the temperature (in this computation it is necessary to minimize the free energy instead of the internal energy) and it is of the order of magnitude of four to eight monomeric units.

The model for a syndiotactic polymer consists of a chain sequence of small blocks (about three monomeric units) with a trans conformation, separated by a pair of gauche bounds.

Only the use of detailed structural models has allowed, in these last few years the introduction, in the calculations of the unperturbed mean square length, of the correlation between subsequent internal rotation angles, and has brought to light its importance, as done for instance by Lifson, by Russian people and also by us.

For instance the optical activity of isotactic polymers containing asymmetric carbon atoms in the side chain, near to the principal chain, is almost certainly connected with the conformational stabilization of one kind of gauche bonds, that is of one kind of spiralization, even in solution, with respect to the enantiomorphous spiralization<sup>31</sup>).

## THE PACKING OF MACROMOLECULES IN CRYSTALS.

We have seen, going through the exposition of the equivalence and of the minimum energy principles, how to foresee the conformation of a macro-

molecule in the crystal; we could ask ourselves the question if, and up to what point it is possible, to foresee the packing of the macromolecules in a crystal. It is soon evident that the polymer chains in a crystal will come close together at distances of the same order of magnitude of those occurring in crystals of small molecules, in order to fill the space in the best possible way.

Clearly, just in the case of polymers, a great simplification arises from the fact that the known chain conformation enables us to determine the structure at least along one of the identity periods of the crystal, namely the one corresponding to the chain axis.

The problem is further simplified if, in addition to that, as it happens in the great majority of the cases, the symmetry elements of an isolated chain (those allowed in a crystal) are preserved in the crystal, that is to say if atoms geometrically (but not crystallographically a priori) equivalent, belonging to different monomeric units of the same chain, can assume equivalent positions, with respect to the corresponding atoms of neighbouring chains.

In such a case it is almost possible to predict theoretically the space group and the unit cell parameters of the resulting lattice.

We shall first describe the packing of some isotactic polymers, that occurs when the chain symmetry is preserved in the crystal.

Thus we shall be concerned only with polymers with a ternary or quaternary helix conformation.

The simplest case to occur is that of a lattice in which the macromolecules are all isomorphous, that is to say they are all spirialized in the same direction, with same groups oriented all in the same direction with respect to the chain axis (i.e. all chains isocline each to the other).

The ternary helix type of chain leads always to the  $P3_1$  space group (for right handed helices) or to the  $P3_2$  space group (for left handed helices).

The only reasonable way of fitting for the side groups is a disposition of them near to the three hexagonal axes (a, b, a-b) perpendicular to the threefold axis.

Figure 17 shows the simple geometry of the form II of isotactic polypropylene lattice<sup>32</sup>) whose unit cell parameters are strictly regulated by: 1) the threefold helix conformation of the chain concerning the c axis. 2) the necessity to bring the methyl groups at Van der Waals distance of about 4.2 Å with hexagonal axes of the lowest possible

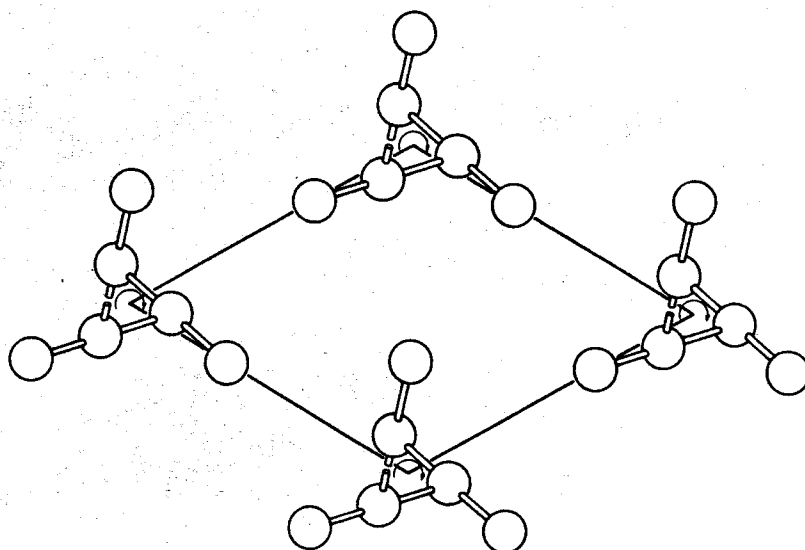


Fig. 17. — Model of packing of polypropylene chains (Form II) in the crystal

length for the a and b axes :

A lattice similar to that of the form II of polypropylene (obtainable at about 140° C in particular condition of spherulitization) occurs in the case of poly-*t*-butylacrylate as shown in fig. 18<sup>20</sup>).

Let us examine the type of lattices occurring when enantiomorphous macromolecules are present in each crystal. We shall distinguish between two cases depending upon the relative isocline or anticline orientation of the side groups of enantiomorphous molecules facing each other.

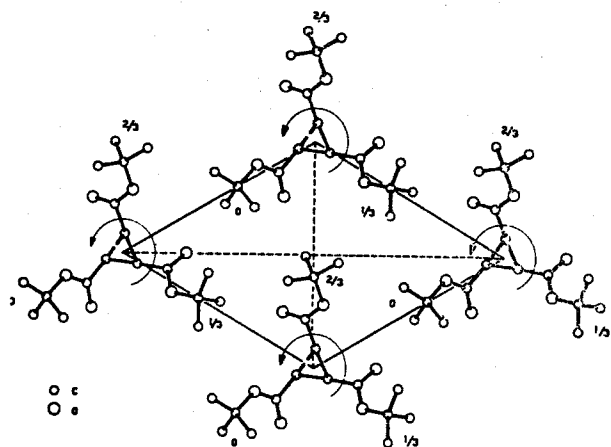


Fig. 18. — Model of packing of isotactic poly-*tert*-butylacrylate

In the first case (isocline orientation) the possible symmetry elements able to repeat neighbouring molecules are either a symmetry plane or a glide plane parallel to the chain axis.

It is well known that a good space filling is generally obtained much easier through a glide plane than through a symmetry plane, particularly with objects having a periodic in and out pattern as in the case of spiralized polymer chains<sup>3</sup>).

If the helix is of a ternary type, each right handed helix will be surrounded, through a glide plane operation, with three left handed helices and vice versa (Fig. 9). This type of crystal lattice occurs for isotactic polystyrene<sup>34</sup>), polybutene<sup>35</sup>), polybutadiene<sup>36</sup>), poly-*o*-fluorostyrene<sup>37</sup>). It does not occur for polypropylene since it would give rise to a low density lattice assuming Van der Waals contacts between carbon atoms of neighbouring chains of 4.2 Å<sup>3</sup>).

If a quaternary helix occurs, each right handed helix will be surrounded through the glide operation by four left handed isoclinic helices and vice versa: the only possible space group will therefore be 14 *c d* (Fig. 20).

This type of lattice occurs for isotactic poly-*o*-methylstyrene and poly- $\alpha$ -vinyl-naphtalene<sup>23</sup>).

If the relative orientation of the side groups is anticlined, the only symmetry element able to repeat one chain in the neighbouring is a symmetry center.

Again for a ternary helix, each right handed spiral will be surrounded, through three inversions

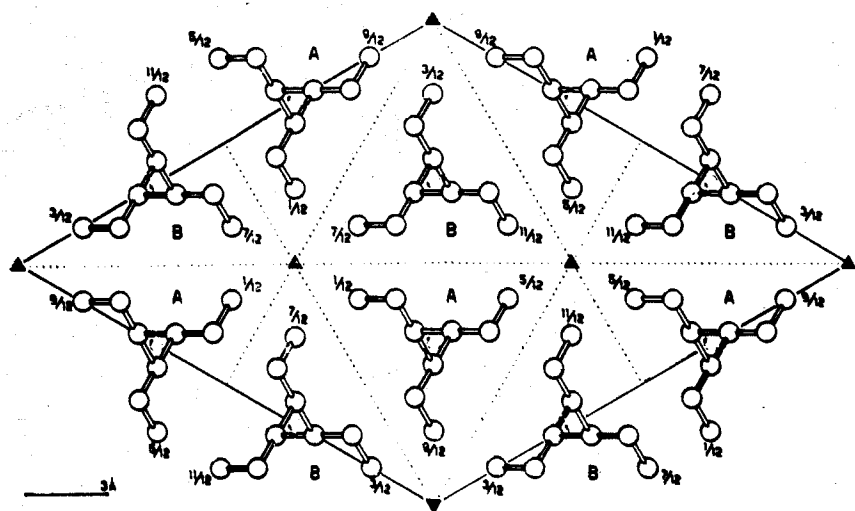


Fig. 19. — Model of packing of left and right handed isoclinal chains in poly- $\alpha$ -butene

at symmetry centers, at  $120^\circ$  each other, by three left handed helices and viceversa: the packed chains will thus be oriented in order to minimize the length of lattice constants perpendicular to the ternary axis, with the best possible Van der Waals

distances; the space group is therefore  $R\bar{3}$  and occurs for instance in polyvinylmethylether (Fig. 21).

With a quaternary helix, each right handed spiral will be surrounded through the use of four symmetry centers at  $90^\circ$ , by four left handed helices; the space group will be  $I4_1/a$  and occurs for

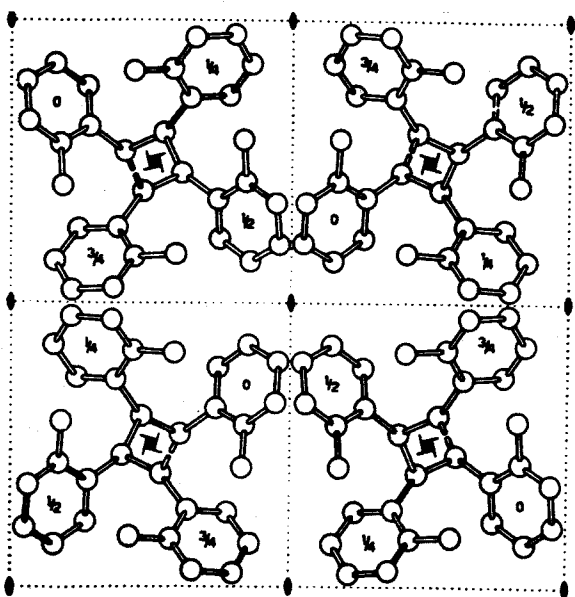


Fig. 20. — Model of packing of poly-ortho-methylstyrene chains in the crystal

almost all isotactic polyaldehydes (Fig. 22, <sup>26</sup>), and for polyvinylcyclohexane <sup>38</sup>). We have been able to show, from the knowledge of the chain conformation of acetic polyaldehyde, which defines the  $c$  axis, that both the  $a$  constant and the packing are defined by the simple condition that the contacts between side methyl groups be all greater than  $4.2 \text{ \AA}$ .

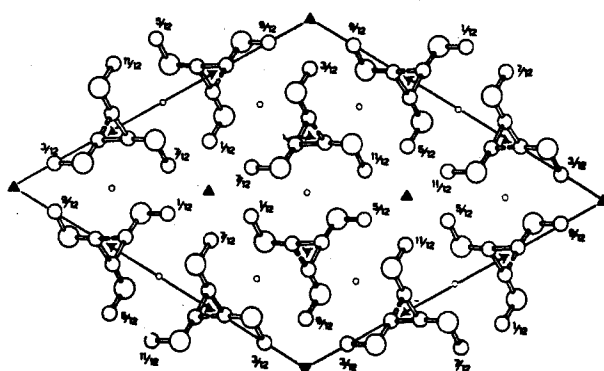


Fig. 21. — Model of packing of polyvinylmethylether chains in the crystal

These few examples show how in the case of polymers it is often possible, much better than in the case of molecular crystals of small organic molecules, to predict not only the chain conformation but even the packing of the macromolecules in the crystal.

After this necessarily rapid and incomplete exposition of the crystal lattices of isotactic polymers with ternary and quaternary helices, it is probably worth mentioning polymers with a different chain symmetry. If this symmetry is permitted in a crystal, it will in many instances be preserved. This

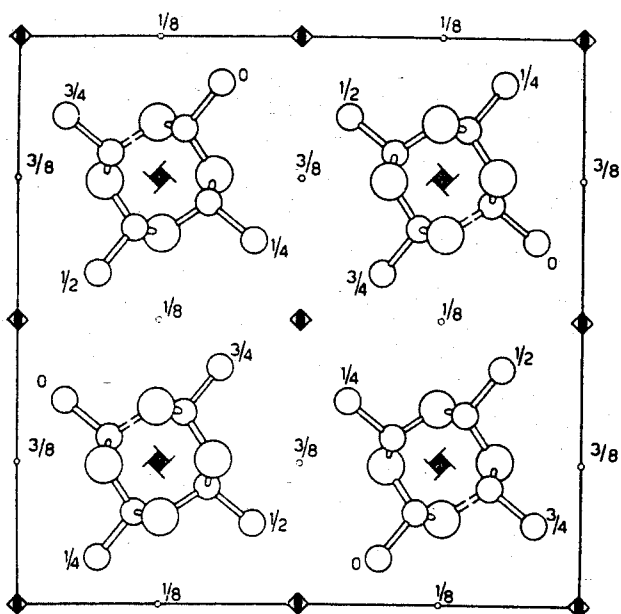


Fig. 22. — Model of packing of isotactic polyaldehyde

happens especially for symmetry elements of the glide type, since they permit a good distribution of the bulky substituents of different chains between themselves.

In almost all known structures of polymers showing a chain conformation with a glide plane, this symmetry element is preserved in the crystal lattice. This occurs for 1-4 cis polybutadiene<sup>17)</sup>, for natural rubber and for its hydrochloride<sup>49)</sup>, for 1-2 syndiotactic polybutadiene<sup>7)</sup>, for polyvinylchlori-

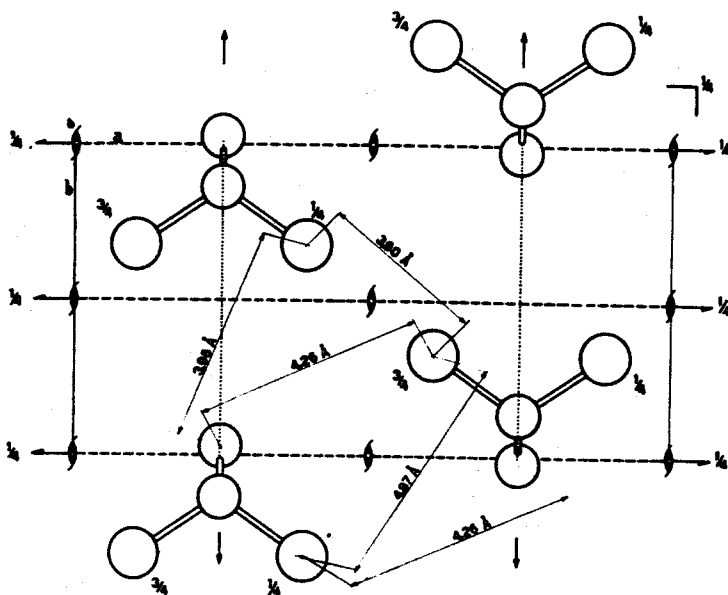


Fig. 23. — Model of packing of syndiotactic polyvinylchloride chains

de<sup>18)</sup>, while syndiotactic 1-4 cis polypentadiene builds an exception<sup>9)</sup> (fig. 23).

In some of the above shown examples the complete chain symmetry is preserved in the crystal lattice: for instance in 1-4 cis polybutadiene the binary axes perpendicular to the chain axis and going through the double bonds, as well as the symmetry centers located on the  $\text{CH}_2\text{-CH}_2$  bonds are maintained in the crystal lattice; in 1-2 syndiotactic polybutadiene the binary axes centered on the  $\text{CH}_2$  group and the symmetry planes perpendicular to the chain axis are also preserved; under such restrictions the lattice geometry depends upon one parameter only, which characterized the distance between layers containing the glide plane at Van der Waals contact distances.

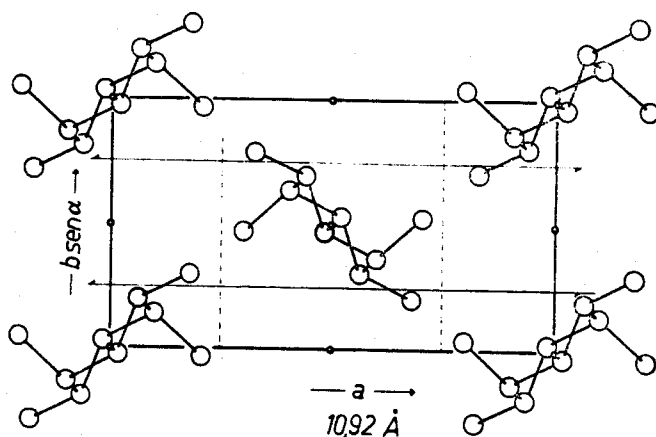


Fig. 24. — Model of packing of ethylene-butene-2 cis copolymer chains

After the discussion of the packing of polymers with the most common two types of conformations, we are left with the discussion of the packing of polymers having the other three less common types of conformation, namely those with a symmetry plane perpendicular to the chain axis, with symmetry centers and with binary axes perpendicular to the helix axis.

For the first type, we can quote nylon 77 in which the symmetry plane of the chain is preserved in the lattice; for the second type, nylon 66, polyethylterephthalate and ethylene-butene-2 copolymer, that we have studied recently, in which is retained the center of symmetry in the lattice as shown in the fig. 24: for the third type, syndiotactic polypropylene and the II crystalline form of polyformaldehyde, which retain the complete  $2_1 22$  symmetry.

Of course it is easily explained in this way the occurrence of a monoclinic lattice for nylon 77<sup>20)</sup>, of a triclinic lattice for nylon 66<sup>41)</sup> and of an ortho

rhombic lattice for syndiotactic polypropylene<sup>51</sup>). In these cases too, the lattice geometry is a simple function of Van der Waals conditions.

The final goal is of course, the prediction, for every actual case, of the type of macromolecular conformation and of the type of crystal lattice. The general aspects of this fascinating question, seem to become more and more accessible, at least in their simplest form.

The present development in the field of polymer structural researches tends to accumulate an always greater number of structures to feed the theoretician with experimental results.

We have the feeling that the a priori prediction of the packing and of the molecular conformation, will be probably soon systematically resolved just for macromolecular compounds, as it is for ionic crystals.

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*On the basis of the intensive structural researches carried out on stereoregular polymers, the authors consider and discuss successively :*

- 1) *the chemical and stereo-isomerisms, i.e. the exact meaning of stereoregularity in polymers ;*
- 2) *the macromolecular conformation in the crystals, i.e. the restrictions imposed by the stereoregularity on the molecular conformation in the crystalline state ;*
- 3) *the packing of macromolecules in crystals, i.e. a description of the most common types observed structures.*

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*Auf Grund der wichtigen Ergebnisse, welche bei den Forschungen zur Struktur der stereoregularen Polymere auftraten, betrachten die Verfasser nacheinander :*

- 1) *die chemischen und stereochemischen Isomerismen ; d.h. den genauen Begriff der Stereoregularität bei Polymeren.*
- 2) *die Ausbildung der Makromoleküle im Innern des Kristalls ; d.h. die Beschränkungen, welche die Stereoregularität der molekularen Ausbildung im Kristallzustand auflegt.*
- 3) *die Häufung, « packing », der Makromoleküle in den Kristallen ; d.h. Beschreibung der verschieden beobachteten Strukturtypen.*