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Conformation of Linear Chains and Their Mode of Packing in the Crystal State*

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The study of the crystal structure of a number of new crystalline polymers prepared for the first time in our Institute[1] allowed us to confirm some known general principles and to establish new ones concerning the shape and mode of packing of macromolecules in crystals.[2]

The importance of stereoisomerism as a determining factor of the ability of polymers to crystallize has long been recognized. Before the discovery of stereospecific polymerization processes, only a relatively small number of crystalline synthetic hydrocarbon polymers were known. Those obtained by polyaddition were generally derived from monomers such as ethylene or some vinylidene monomers, which contain at least two planes of symmetry in the molecule.

All previously known synthetic polymers of α-olefins and diolefins were amorphous. On the contrary, the structure of the molecules of most natural polymers corresponds to an architectural model showing a regular steric arrangement.

As the definition of crystal implies a three dimensional order, a linear polymer, in order to be crystallizable, must at least show a regularity in the succession of its monomeric units. In linear crystalline polymers, in fact, the axis of the macromolecule has to be parallel to a single crystallographic axis of the crystal.

It is possible (as a simplified hypothesis) to assume that all monomeric units in a crystal occupy geometrically equivalent positions with respect to each chain axis (as this has been observed hitherto in all known structures of crystalline homopolymers). We shall refer in what follows to this postulate as to the *equivalence postulate*. It will be shown how, from the equivalence postulate, it is possible to determine the conditions which the configurations of the chains of polyhydrocarbons (e.g., polymers of α-olefins and diolefins) must satisfy in order that the corresponding polymers be crystallizable.

Let us consider a monomeric unit and define its conformation with respect to a particular axis by the coordinates of the atoms along the chain plus those of the two atoms defining the direction of its terminal bonds. It is

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useful to refer the coordinates of the atoms to a cylindrical coordinate system (ρ, φ, z), with the z axis coincident with the chain axis and the origin so chosen that (say) $z_0 = 0$, $\varphi_0 = 0$. In this way, we may define intrinsic coordinates for all the monomeric units along the chain, choosing for each unit a particular coordinate system, always maintaining, however, z in the same position and direction (the position and direction of the chain axis), measuring the φ's always (say) clockwise and taking $z_0 = 0$ and $\varphi_0 = 0$ for each monomeric unit.

Monomeric units equivalent with respect to the axis are, then, uniquely those, the ith atoms of which have coordinates

$$(\rho_i, \varphi_i, z_i)_{i=0}^{i=n+1}, \; (\rho_i, \varphi_i, -z_i)_{i=0}^{i=n+1}, \; (\rho_i, -\varphi_i, -z_i)_{i=0}^{i=n+1},$$

$$\text{or } (\rho_i, -\varphi_i, z_i)_{i=0}^{i=n}$$

The equivalence postulate ensures us that these are the only possible building stones of a regular succession along the chain axis.

Equivalent monomeric units, differing only for the sign of *one* of their intrinsic coordinates φ_i and z_i may be brought to coincide only by reflection and are thence enantiomorphous. Equivalent monomeric units differing in the sign of *both* their intrinsic coordinate φ_i and z_i are isomorphous, as they may be made to coincide by rotation around a straight line perpendicular to the axis.

We shall define as "isoclined" those equivalent monomeric units having the same z_i coordinates and as "anticlined" those equivalent monomeric units having opposite z_i coordinates. Thence, if $(\rho_i, \varphi_i, z_i)_{i=0}^{i=n}$ are the coordinates of a monomeric unit, we shall refer to another monomeric unit with intrinsic coordinates $(\rho_i, \varphi_i, z_i)_{i=0}^{i=n}$ as an isomorphous isoclined unit, one with coordinates $(\rho_i, -\varphi_i, z_i)_{i=0}^{i=n}$, as an enantiomorphous isoclined unit; one with coordinates $(\rho_i, -\varphi_i, -z_i)_{i=0}^{i=n}$, as an isomorphous anticlined unit; one with coordinates $(\rho_i, \varphi_i, -z_i)_{i=0}^{i=n}$, as an enantiomorphous anticlined unit.

From the equivalence postulate, the following is readily seen to be true. (a) To permit repetition along the z axis of equivalent isoclined units (Fig. 1), the two terminal bonds must be equivalent with respect to this axis; then within the same monomeric unit,

$$\rho_0 = \rho_{0'} \tag{1}$$

$$\rho_1 = \rho_{1'} \tag{2}$$

$$z_1 - z_0 = z_{1'} - z_{0'} \tag{3}$$

and $$\varphi_1 - \varphi_0 = \pm(\varphi_{1'} - \varphi_{0'}) \tag{3'}$$

Clearly, when $\varphi_1 - \varphi_0 = \varphi_{1'} - \varphi_{0'}$, the monomeric unit involved may be bound only to an equivalent isomorphous isoclined unit, and when $\varphi_1 - \varphi_0 = \varphi_{0'} - \varphi_{1'}$, the monomer unit involved may be bound only to an enantiomorphous isoclined unit, if the monomeric units are to be equivalent with regard to the chosen axis.
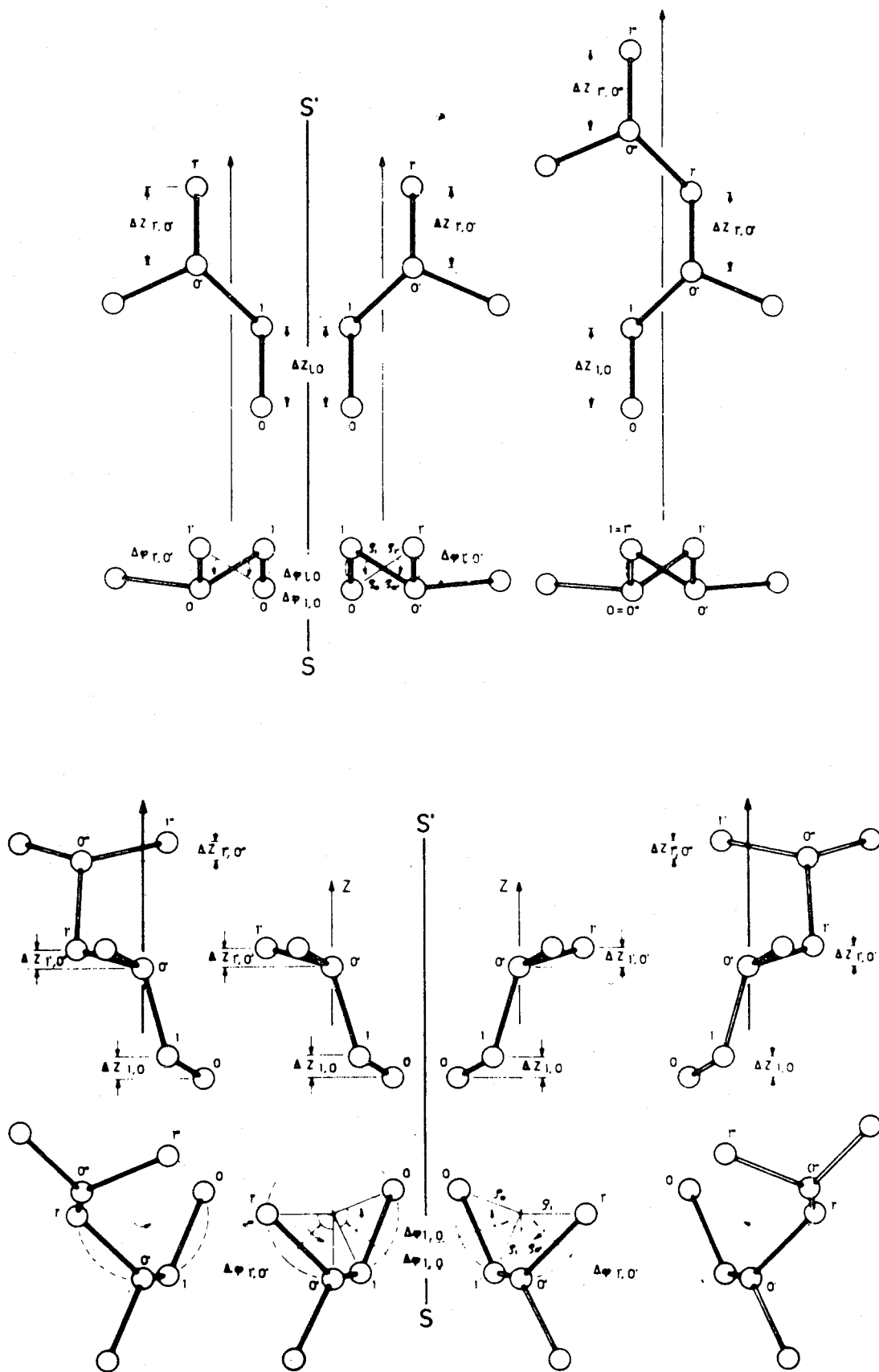
Fig. 1. Schematic diagram showing possible types of regular successions of iso-clined monomeric units along an axis: (above) glide-plane succession ($\Delta\varphi_{1,0} = -\Delta\varphi_1{'}_{,0}{'}$) (below) helix-type succession ($\Delta\varphi_{1,0} = \Delta\varphi_1{'}_{,0}{'}$).

From the statements under (a), several important conclusions follow.

(b) A regular succession of isomorphous isoclined units must necessarily follow a n/p-fold helix containing $n/p = 2\pi/(\varphi_{0'} - \varphi_0)$ monomeric units per pitch, n being the number of monomeric units and p the number of pitches contained within the identity period (helix-type succession). The ratio n/p is a rational number, and, for a particular case, it can assume the value 1 (e.g., simple repetition). An analogous hypothesis has been given by Pauling for proteins.

(c) A regular succession of alternatively enantiomorphous isoclined units must necessarily take place along a glide plane with translation parallel to the axis (glide-plane-type succession).

(d) A regular succession of isoclined equivalent units can assume only the forms of either a helix or a glide plane succession. All head-to-tail polymers in which the two possible chain directions are intrinsically nonequivalent (i.e., a polyamide) are subjected to this condition. In particular, a polyamide containing asymmetric carbon atoms must necessarily have a helix-type structure.

(e) Repetition of anticlined units (following arguments similar to those given above) may occur along helices associated with twofold axes perpendicular to z or through a translation along z associated with symmetry planes or centers.

A condition to be fulfilled by a polymer, in turn, in order to be crystallizable is that its monomeric units must have configurations which enable them to occupy equivalent positions along an axis.

On this basis we can now find which types of stereoisomers of vinyl and diene polymers may crystallize.

In the sense of what is stated above, only two types of regular sequences, intrinsically different, may be expected for vinyl head-to-tail crystallizable polymers. Isotactic vinyl polymers are those capable *per se* of assuming a helix-type crystalline structure. Syndiotactic vinyl polymers are those capable *per se* of assuming a glide-plane structure in the crystalline state. As the two possible chain directions are intrinsically equivalent in head-to-tail vinyl polymers, their chain may also be built up in the crystal state by a succession of anticlined units. For example, in theory a syndiotactic polymer may also achieve a helical chain structure associated with twofold axes perpendicular to z. Isotactic and syndiotactic polymers may be considered also as the *cis* and *trans* geometrical stereoisomers, respectively, of the same polyvinyl chain of infinite length. Analogous reasoning leads to various possibilities for regular, crystallizable, diene polymers. Figure 2 shows isotactic and syndiotactic main chains lying ideally in a plane.

We should like now to discuss briefly two more useful postulates related to the shape and mode of packing of macromolecules in crystals.

Provided the equivalence postulate is satisfied, the conformation of the chain in a crystal may be assumed to approach the conformation of minimum potential energy for an isolated chain oriented along an axis. We
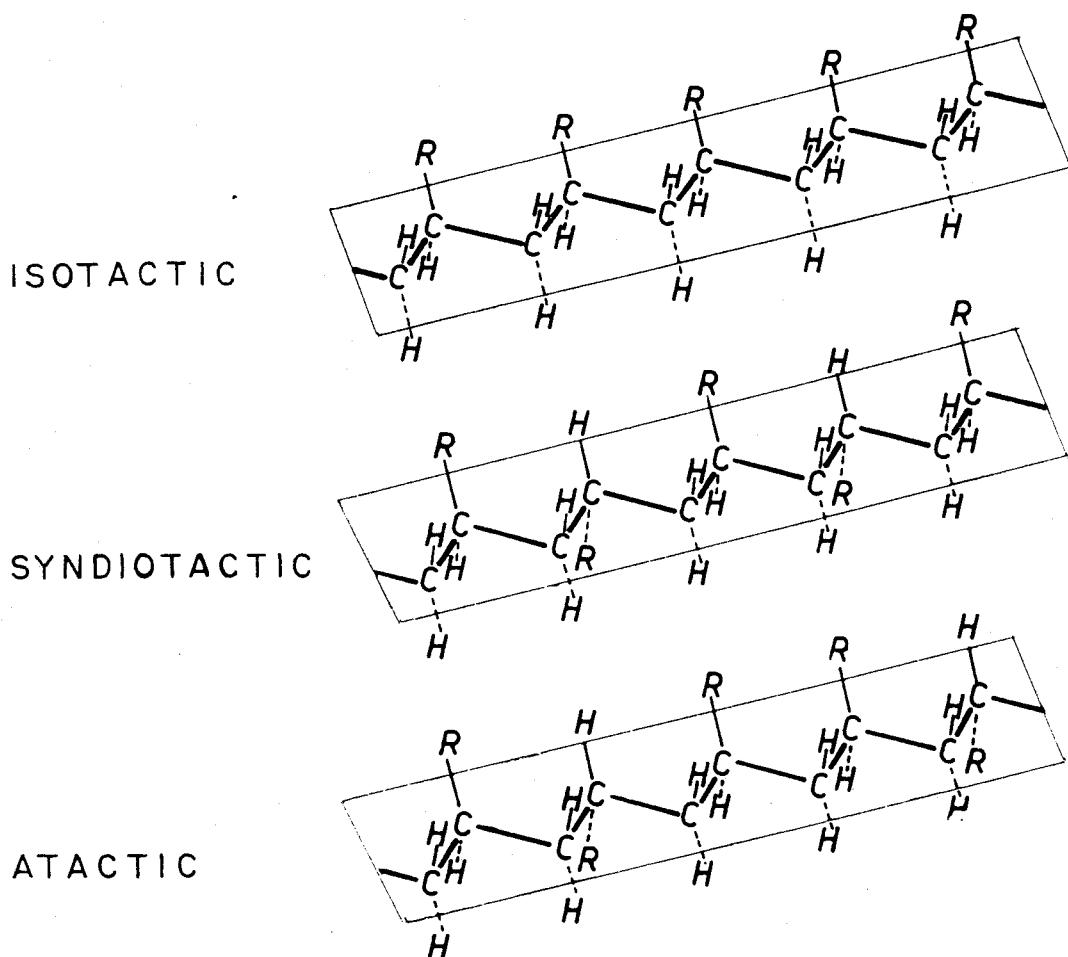
Fig. 2. Possible configurations of vinyl head-to-tail polymers. (Main chain arbitrarily stretched in a plane.)

shall refer to this as the *minimum energy postulate*.[3] Lateral packing effects (between neighboring chains) are also important in determining the conformation of the chain, but these generally play a less important role compared to the packing effects inside the chain. The following rules should generally be satisfied in the conformation of the polymer chain.

1. Constancy of bond lengths.

2. Coplanarity of certain groups of atoms (for instance the amide group).

3. Constancy of bond angles.

4. Staggered single bonds.

5. Van der Waals distances between nonbonded atoms within the chain of such a magnitude as to permit unstrained packing.

When the rules outlined above cannot be satisfied simultaneously, we may, in general, expect:

1. Deformation of bond angles to values exceeding the normal values (e.g., more than 110° for the C—C—C angle).

2. Slight deviations from the principle of staggered bonds.

3. Distances between certain atoms of the chain which are slightly less than normal van der Waals distances.

All the above-mentioned deformations take place in general, but to dif-

ferent degrees for various types of chains, so that (according to the minimum energy postulate) a minimum potential energy for the isolated chain is approached. In actual structures, however, the necessity for filling space uniformly may slightly modify the form; for instance, in the case of a helix, the form corresponding to the minimum energy postulate for the free chain can be modified, giving smaller n and p values or slightly different n/p ratios. This follows from the fact that, in a crystal, the chains arrange themselves so that they are parallel to each other and spaced at an intermolecular distance so that they fill as much as possible any gap between them similar to that found in low molecular weight compounds. With this limitation, as many elements of symmetry of the isolated chain as possible are maintained in the lattice, and therefore, equivalent atoms of different monomeric units along an axis tend to assume equivalent positions with respect to the atoms of neighboring chains. The role of this postulate, which we call the *packing postulate*, will now be discussed.

Sometimes not all statements of the packing postulate can be satisfied simultaneously, in such a case, in a manner analogous to that discussed for the minimum energy postulate, a compromise is achieved in actual structures for filling space uniformly. In many cases both of the pair of anticlined molecules ("up" and "down" molecules) are present in the unit cell of the crystal of a head-to-tail polymer. Moreover, when a given monomeric unit may give rise to equivalent right- or left-hand helices (for example, in the case of a monomer containing no asymmetric carbon atoms, such as propylene), both are generally represented in the crystal lattice.

In isotactic polymers containing helices of the order of $n > 2$, each right-handed helix tends to face a left-handed helix. Whenever only one type of helix, either left-handed or right-handed, is possible, formation of a super helix of the chain may occur to provide a better filling of the space; this is the case with proteins.

Frequently, nearly isosteric equivalent chains, i.e., chains with a similar steric encumbrance (such as enantiomorphous isoclined chains, isomorphous anticlined chains, or enantiomorphous anticlined chains) may be substituted for each other in the same lattice site. This phenomenon was observed for the first time by Nyburg[4] in natural rubber and was observed by us in some isotactic polymers.[5]

In packing, the polymer molecules generally tend to maintain, at least partially, the symmetry of the chain. In the structure of polymers made up of chains of the glide-plane type, for instance, the glide plane is usually maintained in the lattice. This fact occurs in natural rubber, polyvinyl chloride, 1,2- (syndiotactic) and *cis*-1,4-polybutadiene, and in rubber hydrochloride.[6]

Another interesting feature of some crystalline polymers is that it is possible to recognize in their structure layers of molecules along planes, containing the fiber axis and generally the smallest equatorial translation, by the parallel or antiparallel association of which layers the crystal may be imagined to be formed. In many polymers which we have examined, it

was observed that the two translations determining such planes are only very slightly affected by thermal movements. From the results of the study of some types of spherulites, it appears likely that the polymer crystals grow best along the equatorial translation contained in the said above planes (principal planes) (which are parallel to the spherulite radius).[7]

Let us now see how these principles may justify the experimentally found structures of some new polymers.

ISOTACTIC POLYMERS[6]

Isotactic polymers are the *cis* stereoisomers of vinyl head-to-tail polymers as we have shown above. The bulky dimensions of lateral groups do not permit these polymers to assume a planar chain conformation. A planar structure is, indeed, impossible. For instance, in the case of polypropylene, a planar structure would result in a distance of only 2.5 A. between the nuclei of the two carbon atoms of successive methyl groups, which is very unlikely, because certain hydrogen atoms of the methyl groups would be, as a result, too near to each other, and this situation conflicts with the requirements of the minimum energy postulate. (The nature of the strain may be easily understood when we consider that the large resonance energy of linear crystalline polyacetylene, which, according to unpublished data, has a planar structure, is destroyed in polyhexyne, whose chain structure is nonplanar; the net loss, according to our calculation, is about 10 kcal. per monomeric unit, something like what happens in the case of benzene and cyclooctatetraene).

A suitable accommodation of the methyl groups according to the equivalence postulate and the principle of staggered bonds, may be achieved in a helical structure only when the successive monomeric units are arranged on a threefold helix.

This structure may be easily derived from the planar one shown in Figure 3, by clockwise or counterclockwise rotations of 120° around the 1–2, 3–4, 5–6 bonds or around the 2–3, 4–5, 6–1′ bonds, thus generating a left- or right-handed helix. The separation of the methyl groups achieved in this way (>4 A.), assumes a value comparable with the van der Waals distance, and there is no conflict with the principle of staggered bonds. As the planar configuration is very unlikely from the point of view of thermodynamics, no interchange of enantiomorphous helices appears to be possible, at least at low temperatures, and we believe that left- and right-hand helices can be considered to be true optical stereoisomers. Optical activity is not observed because of the presence of equal amounts of the two forms.

When built up with normal bond lengths (1.54 A.) and angles (109° 30′), the isotactic threefold helix should have an identity period of 6.2 A. Actually, the periods are 6.5–6.65 A. A slight increase in the C—C—C angles along the chain appears to be the reason for this, as this arrangement permits a better accommodation of the hydrogen atoms of the chain at sepa-
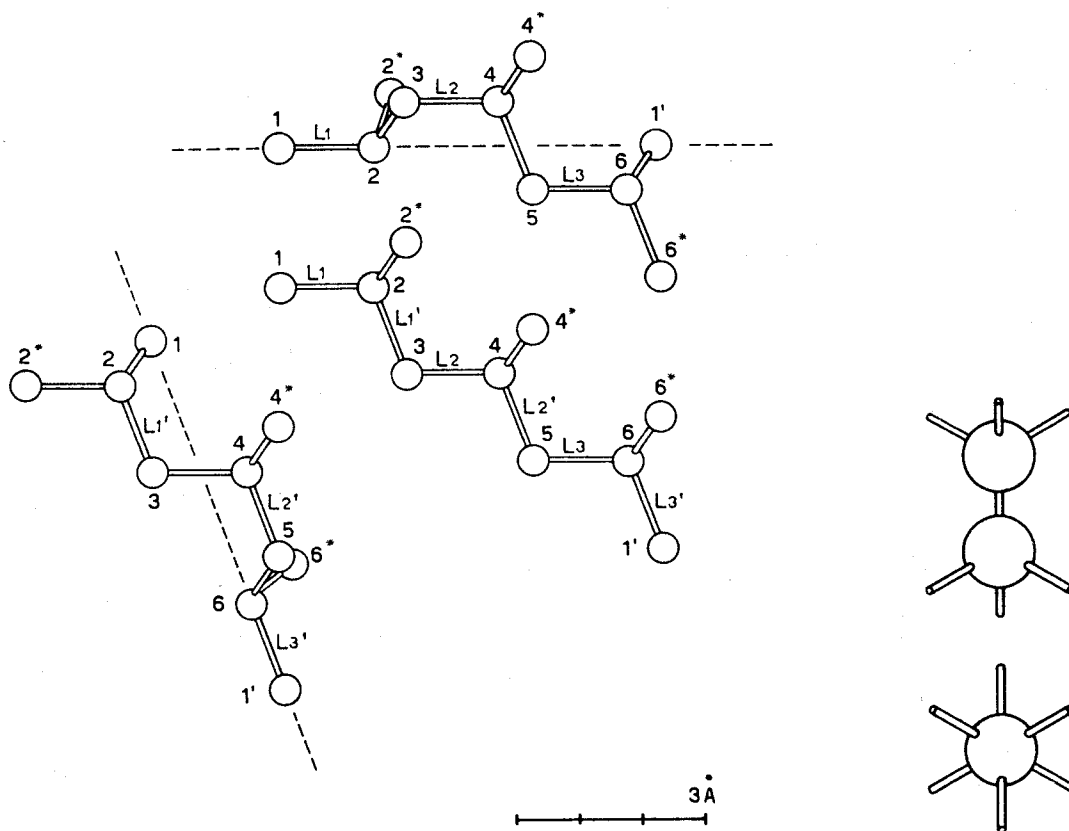
Fig. 3. Genesis of right- and left-handed isotactic helices from a planar chain.
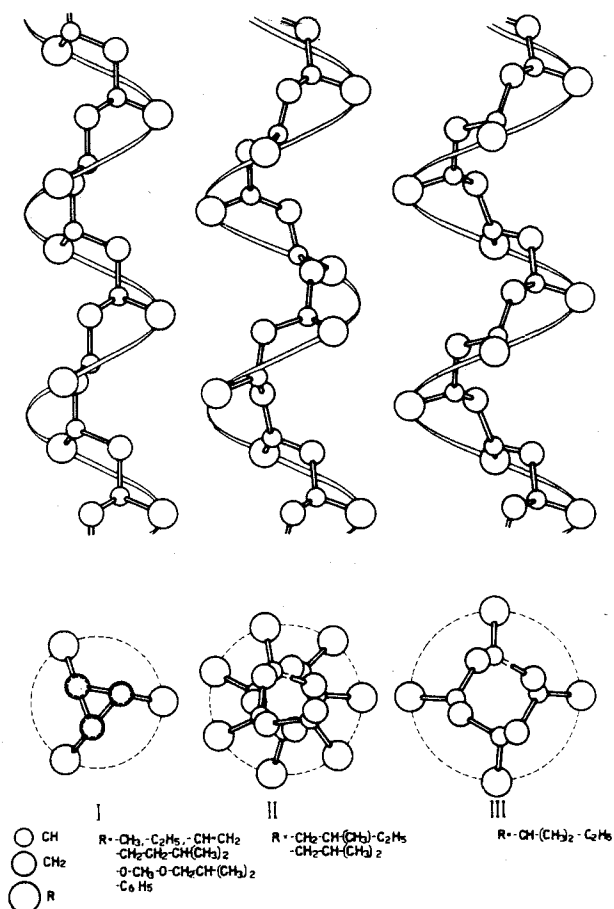

Fig. 4. Possible types of isotactic chains, according to the nature of the lateral group.
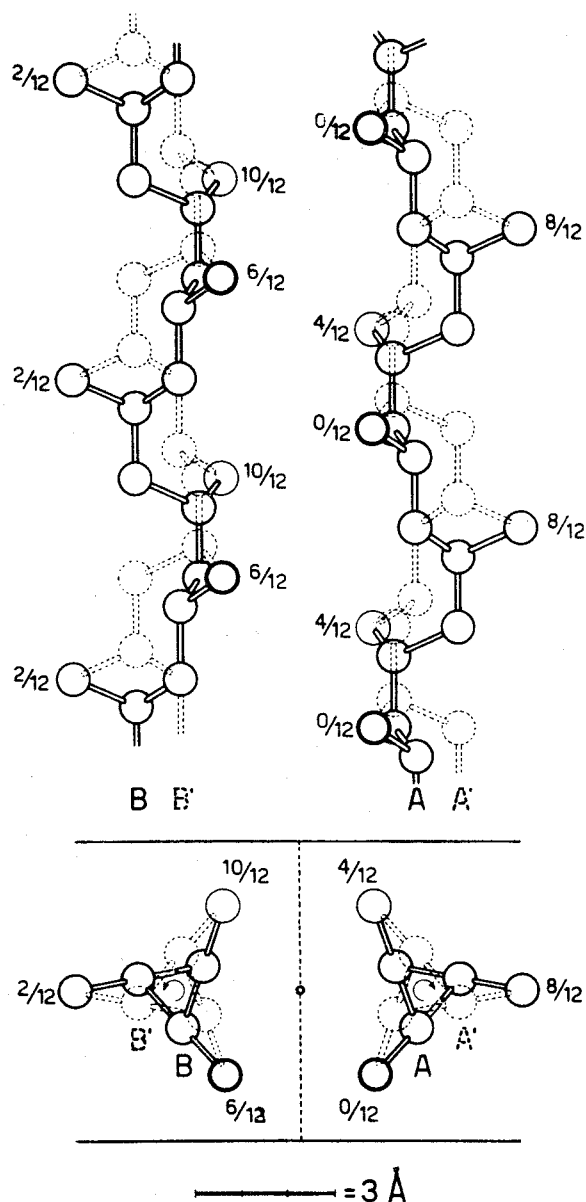
Fig. 5. Mode of packing of enantiomorphic chains in polypropylene.

rations of the order of van der Waals distances. The bulkiness of side groups, and more precisely, the steric hindrance of side groups near the chain axis, is the reason for the four-fold helix structure of 3-methyl-substituted polyolefins in the crystalline state and the 3,5-fold helix conformation of 4-methyl substituted polyolefins (Fig. 4). The principle of staggered bonds no longer holds strictly, but valence angles along the chain tend to approach normal values once again, so that there should be only very low differences in energy between a threefold or fourfold helix. Indeed, polybutene-1 has been observed to crystallize in both forms, the fourfold helix, however, being the more unstable. This form is the first to appear on crystallization from the melt or from a solution. Therefore, we can deduce that, in the liquid state, there is sufficient freedom to permit rotation around single bonds in the chain at a low energy level; this leads to a slight despiralization of the helix.
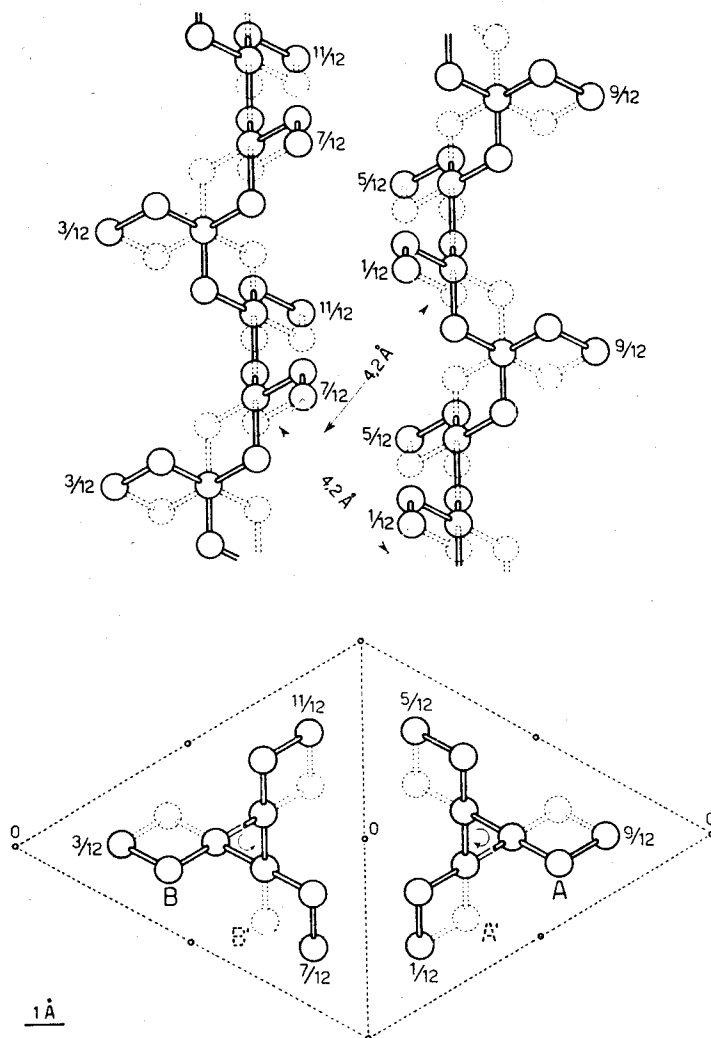
Fig. 6. Mode of packing of enantiomorphic chains in polybutene-1.

It is interesting to note that crystals with fourfold helix of polybutene-1 are transformed immediately to crystals with threefold helix by drawing, and that this transformation takes place much more slowly on standing.

Chains slightly different in form from those discussed above may also appear in other isotactic polymers and have been found, for example, in substituted polystyrenes; their stability is attributed to better packing of lateral groups within the chain and between different chains.

The complete determination of the crystal structure of polypropylene and polybutene-1 permits a discussion of the mode of packing of the chains of these polymers in crystals at this point.

According to the requirements just explained, we found that in all these polymers enantiomorphous chains face each other in pairs. Close packing is obtained through the operation of a glide plane with translation parallel to the fiber axis.

The anticlined isomorphous chains of these two polymers are nearly isosteric with respect to the encumbrance because of the lateral groups. As the intermolecular contacts, that is, the closest approaches of the chains
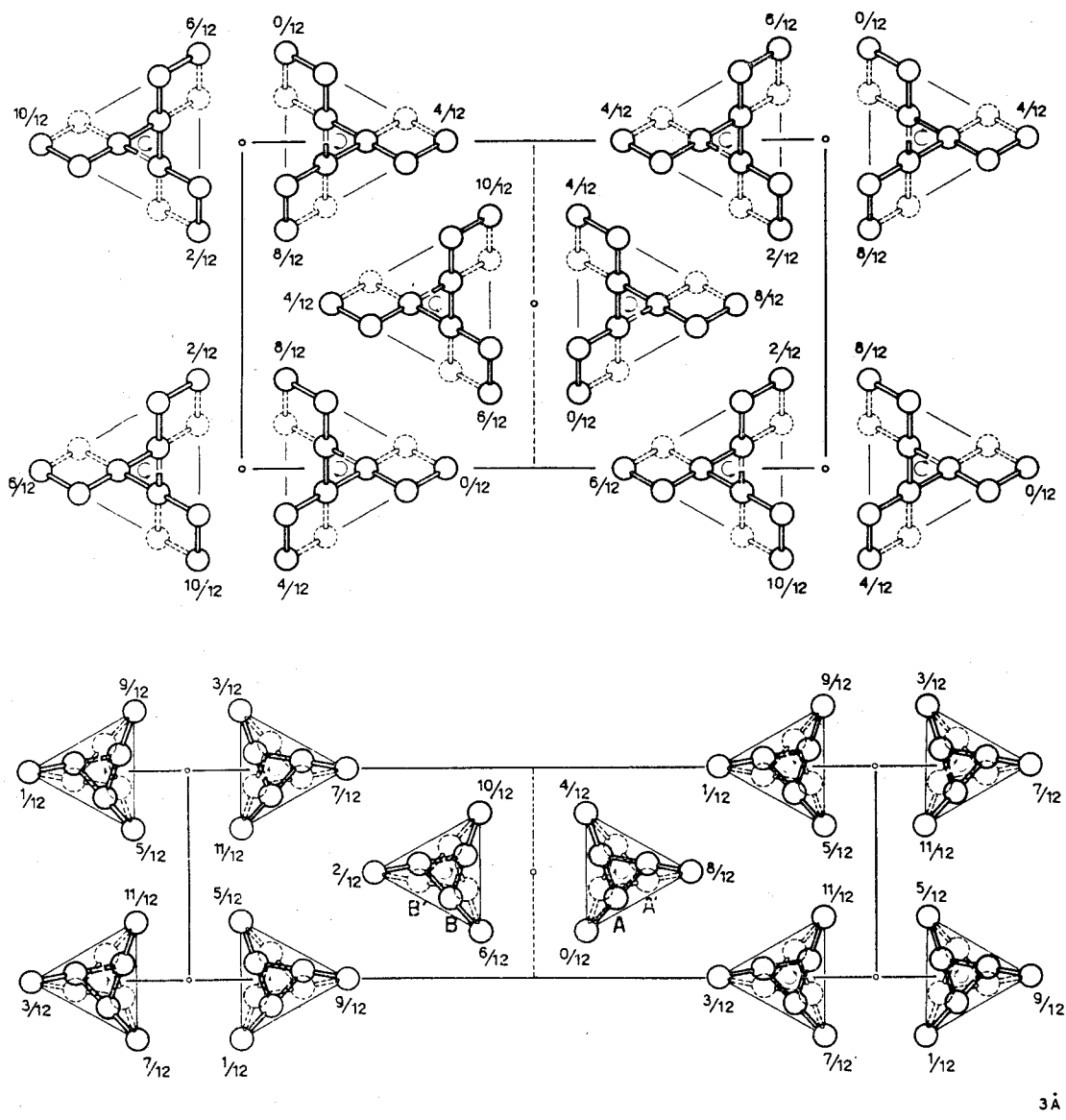
Fig. 7. Comparison between the crystal structures of polypropylene and polybutene-1 projected along the fiber axis.

are between these lateral groups, anticlined isomorphous chains can, in theory, replace each other in the same lattice site, and, at least partly, they do it.

Polybutene-1 crystals are able to maintain the complete symmetry of the chain, so that three glide planes at angles of 120° to each other and related by a threefold helix are easily recognizable in the rhombohedral structure of this polymer.

Assumption of a similar structure for polypropylene also would yield too loose a mode of packing however. The glide plane through which two enantiomorphous facing chains are related is, in this case, a principal plane. Evidence that the a–c plane can be considered a principal plane in polypropylene is found in the close packing realized along this plane of the groups of two enantiomorphous symmetry-related chains (Fig. 7).

This is in accordance with the shortness of the a-axis, its orientation parallel to the spherulite radii and its very low thermal expansion in comparison with that one taking place along the b axis.

We believe that the main features of the structure of other isotactic polymers may be explained following these lines.

SYNDIOTACTIC POLYMERS[9]

Syndiotactic polymers may be defined as the *trans* stereoisomers of vinyl head-to-tail polymers. Their chain structure should be, according to the equivalence postulate, of the glide-plane type, and hence repetition
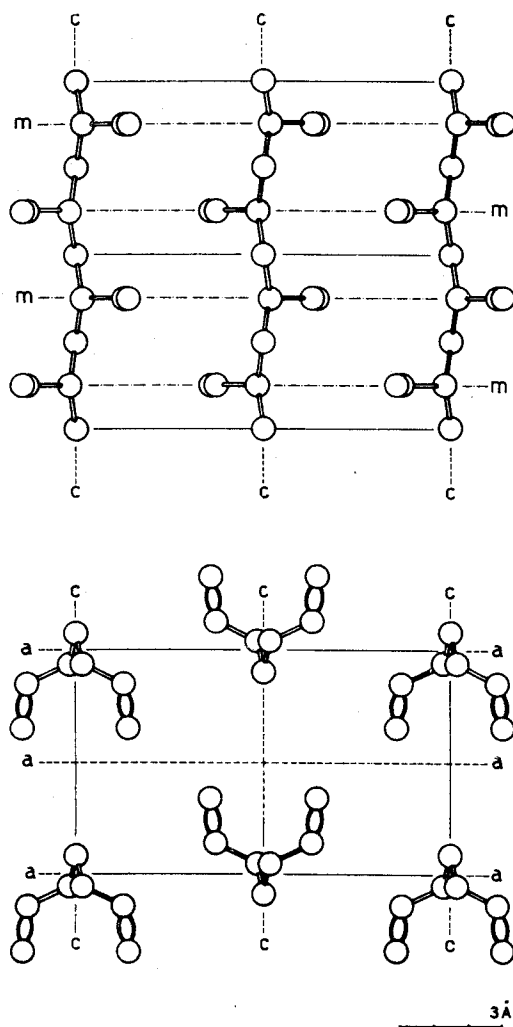

Fig. 8. Crystal structure of syndiotactic 1,2-polybutadiene.

should be achieved along the fiber axis every two (in Greek σύν δύο) monomeric units or of the helix type associated with twofold axes. Two polymers are now known to possess a syndiotactic chain structure, i.e., polyvinyl chloride and one of the two crystalline stereoisomers were found for 1,2-polybutadiene.

The bulkiness of the side groups does not hinder a planar or nearly planar conformation of the chain as was the case for isotactic polymers. A slight deviation from a completely zigzag planar structure of the chain has been supposed, but not proved, to exist in polybutadiene as a result of steric repulsion between successive lateral vinyl groups; the perpendicular orientation of these side groups with respect to the chain axis obeys the principle of staggered bonds (Fig. 8). In every case it is easy seen that no distinction is possible between "up" and "down" molecules, and therefore only one type of chain must be accommodated in the lattice.

The glide-plane is maintained in the three-dimensional structure of these polymers, so that the closest packing of these molecules occurs in layers along this plane; different layers pack among themselves in an anti-parallel way.

Thermal expansion in syndiotactic 1,2-polybutadiene is almost completely in a direction perpendicular to the glide plane c, a phenomenon which is believed to be associated with the existence of a principal plane of packing.

CRYSTALLINE 1,4-POLYDIENES[10]

Under the headings of isotactic and syndiotactic polymers we have dealt with the known structures of stereoisomeric 1,2-polydienes. In this section we shall deal with the known structures of crystalline 1,4-polydienes. The synthesis of all four stereoisomeric crystalline polybutadienes effected in the Institute of Industrial Chemistry of the Polytechnic of Milan, and the study of their structure have permitted to give us a full idea of stereoisomeric phenomena in the field of polydienes.

Natural rubber is a regular head-to-tail polymer built up of cis-1,4-isoprene units. Its chain structure may be expected to be a glide-plane or a helix-type succession only. However, on the basis of the equivalence postulate only, it is not possible to establish which of the two forms will actually be assumed by the macromolecule on crystallization, as neither can be correlated with intrinsic differences in the configuration of the chain. This may be easily seen on considering that, by permitted rotations around single bonds, the completely planar structure (I), corresponding to a set of equal units (which may be considered a onefold helix) may be transformed to the planar glide-plane type structure (II) (Fig. 9).

Actually, a glide-plane, nonplanar structure is found for the chain of crystalline cis-1,4-polyisoprene. Indeed, we should expect on the basis of the minimum energy postulate that: (1) the five atoms of each monomeric unit should be in a plane; (2) in accordance with the principle of staggered bonds, the direction of the CH_2—CH_2 bond should take each of the three positions outlined in Figure 10, positions 3 and 3' having to be discarded because of too short van der Waals contacts; (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 the most likely to be realized; (4) repeti-
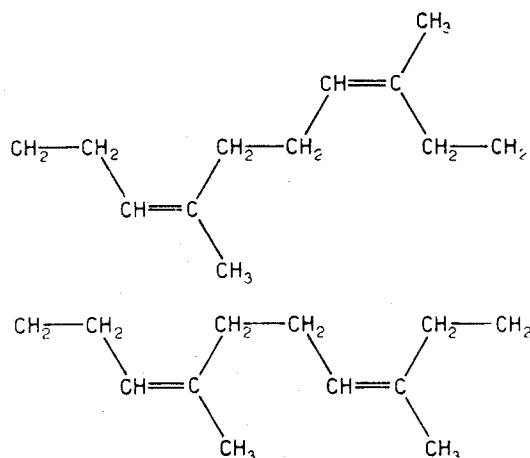
Fig. 9. Possible structures of a polyisoprene chain considered stretched in a plane:
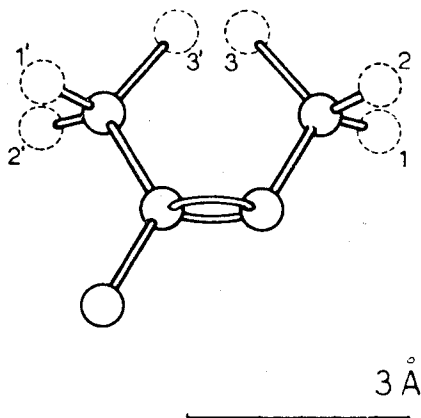(above) II; (below) I.

3 Å

Fig. 10. Possible conformations of an isoprene monomeric unit.

tion of a monomeric unit with such a conformation, owing to the fact that

$$\Delta\varphi_{1,0} = \pi = \Delta\varphi_{1',0'} = -\Delta\varphi_{1',0'}$$

may be achieved in a helix type or a glide-plane type succession. The first possibility may be discarded because of unlikely van der Waals contacts, and therefore only the glide plane type conformation may be admitted.

The glide plane is maintained in the lattice so that close packing of molecules is expected along this plane; also, alternatively anticlined molecules should be represented along this plane.

As contacts lateral to the so realized principal plane are due only to methyl groups, we find that, in the actual structure, successive parallel or antiparallel principal planes are able to pack themselves at random (Fig. 11). It is possible to see from Figure 11 that a layer of molecules such as ABAB can be followed statistically by a layer such as CDCD or C'D'C'D'.

A great similarity of structure is to be expected between cis-1,4-poly-butadiene and cis-1,4-polyisoprene, and actually a similar conformation of the chain is found; in both of these enantiomorphous monomeric units repeat along a glide-plane. No further distinction, however, is possible
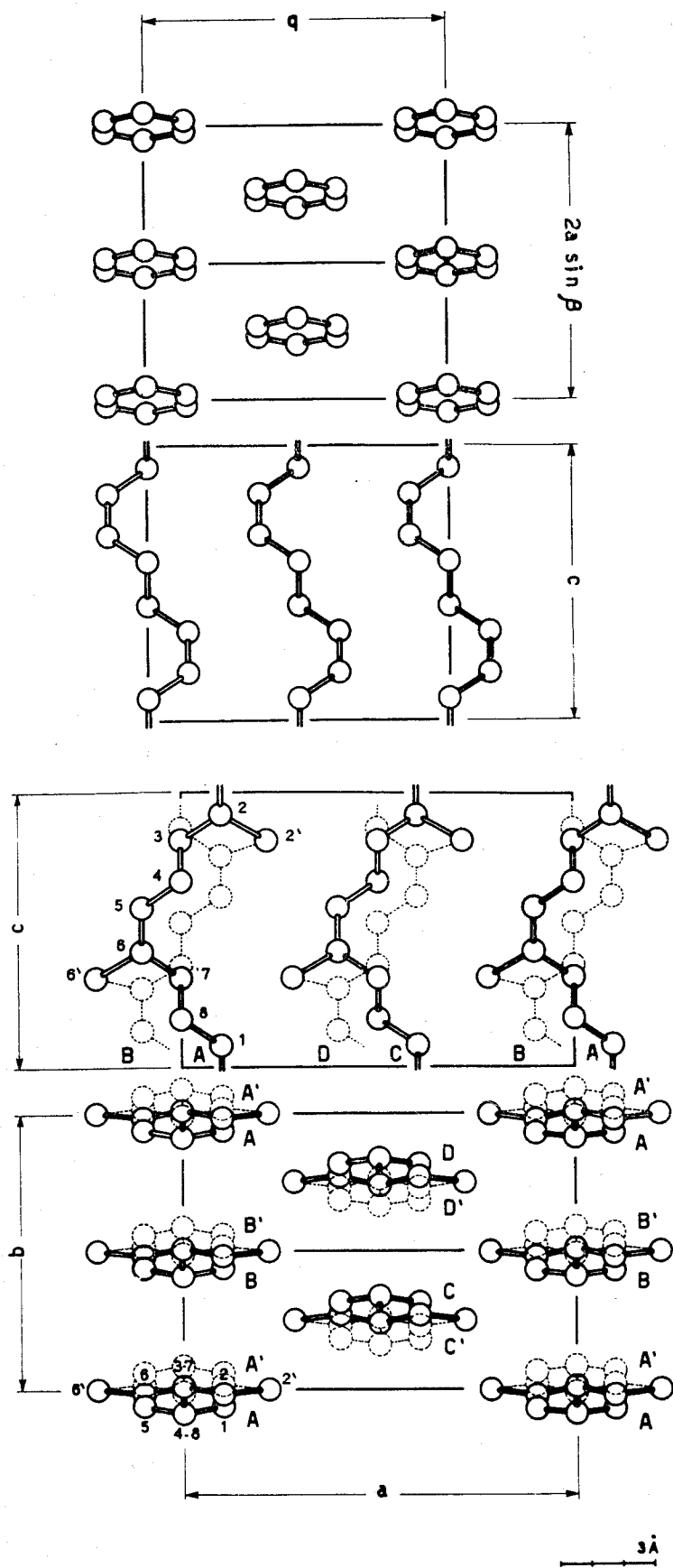
Fig. 11. Comparison between the crystal structures of *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene.
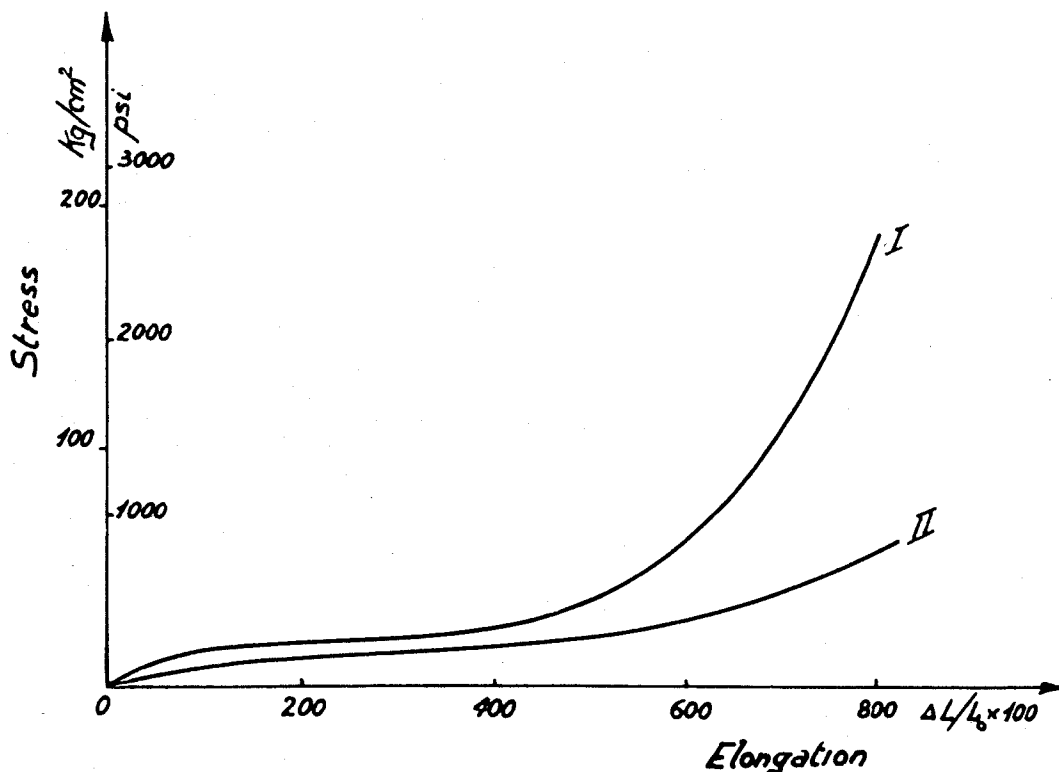
Fig. 12. Stress-elongation curves for cis-1,4-polybutadienes to different stereoisomeric purity: (I) > 95% cis; (II) 85–90% cis.

in cis-1,4-polybutadiene, between "up" and "down" molecules as is the case with cis-1,4-polyisoprene; also, an identity period is found which is slightly longer than the one foreseeable on the basis of the principle of staggered bonds. This fact is probably due to repulsions between hydrogen atoms of two CH_2 groups in opposite positions with respect to the double bond, which tend to lengthen the chain. These repulsions cannot be eliminated in the case of polyisoprene because of steric hindrance due to the methyl groups.

The glide plane is also a principal plane in polybutadiene and determines a mode of packing of the macromolecules in the crystalline state which is very similar but simpler than the one realized in the structure of polyisoprene. In fact, because of the absence of side groups, there is no longer need for accommodation of "up" and "down" molecules, nor for a statistical distribution of successive antiparallel or parallel layers of molecules developed on the principal plane.

Along with the strong similarity of structure between cis-1,4-polybutadiene and cis-1,4-polyisoprene there is a correspondingly strong similarity between their physical and mechanical properties.

Only when we could prepare a 1,4-cis-polybutadiene with a high degree of stereoisomeric purity, i.e., equal to that of natural rubber, was it possible to compare in a quantitative way their physical properties.

Undrawn cis-1,4-polybutadiene has a melting point of about 0°C. The melting entropy should have a low value as in polyisoprene, because

melting points for drawn samples of polybutadiene were 80°C. higher than the melting point in the undrawn state.

The stress-strain curve shows very low initial modulus, which rises suddenly at elongation, depending on the sterical purity at which crystallization begins. This crystallization, which in cis-1,4-polybutadiene having a purity higher than 95% cis begins at 400–500% elongation, causes an elevation of the tensile strength in the polymers of high molecular weight cured with 0.5–1% S to values of about 3000 psi. Figure 12 shows a stress–strain curve of vulcanized samples of cis-1,4-polybutadienes of different steric composition.

In the crystal state at room temperature trans-1,4-polybutadiene[11] shows a chain structure (with an identity period c = 4.92) very similar to that of β gutta-percha. The nearly cylindrical shape of its molecules favors packing of the chains in a pseudohexagonal array with a = 4.54 A. At 67°C., a first-order transition takes place in the solid state. 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 relatively free to move and oscillate around the chain axes. The phase change is accompanied by a decrease in the density of more than 9%. The low-density phase possesses a pseudohexagonal array with a = 4.88 A. and c = 4.68 A. In a drawn fiber, this transformation gives rise to a sudden, reversible contractile process, which is analogous to that taking place in living muscle.

The dimensional change is of the same order as the change in the c dimension (∼5%). We believe this is the first time that a similar phenomenon, related to a first-order, crystal–crystal transition, has been observed in synthetic fibers.

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Synopsis

Some general rules regarding the conformation and mode of packing of macromolecular chains in crystals are illustrated. The monomeric units occupy equivalent positions in regard to the axis of the chain. It follows that crystallizable polymers must have a type of regularity which will enable them to assume the helix- or glide-plane conformation. Energy considerations lead to other rules regarding the conformation and the mode of packing of the chains. Isosterism phenomena leading to statistical substitution of chains in the lattice and to the existence of planes, along which the macromolecules pack preferentially are considered. The structures of isotactic and syndiotactic polymers, and of all four stereoisomeric polybutadienes are discussed.

Résumé

On explique quelques règles générales sur la conformation et le mode d'empaquettement des chaînes macromoléculaires. Les unités monomériques occupent des positions équivalentes par rapport à l'axe de la chaîne. Par conséquent les polymères cristallisables doivent avoir un type de régularité qui leur permettra de prendre une conformation en hélice ou en plan de symétrie avec glissement. Des considérations sur l'énergie entrainent d'autres règles regardant la conformation et le mode d'empaquettement des chaînes. On considère des phénomènes d'isostérie portant à la substitution statistique des chaînes dans le réseau et à l'existence de plans le long desquels s'empaquettent, de préférence, les macromolécules. On discute sur la structure des polymères isotactiques et syndiotactiques et sur les quatre polybutadiènes stéréospécifiques.

Zusammenfassung

Einige allgemeine Regeln betreffs der Konformation und der Art der Packung makromolekularer Ketten in Kristallen werden erläutert. Die Monomer-Einheiten nehmen äquivalente Stellungen bezüglich der Kettenachse ein. Daraus folgt, dass kristallisierbare Polymere eine besondere Art von Regelmässigkeit besitzen müssen, die sie in die Lage versetzt, eind Wendel- oder eine planare Struktur anzunehmen. Energetische Betrachtungen führen zu anderen Regeln betreffs der Konformation und der Art der Packung der Ketten. Phänomcne von Isosterismus, die zu statisticher Substitution des Ketten im Kristallgitter und zur Existenz von Gleitebenen, entlang denen sich die Makromoleküle bevorzugt packen, führen werden erörtert. Die Strukturen von isotaktischen und syndiotaktischen Polymeren und der vier stereoisomeren Polybutadiene werden diskutiert.